Beckmann rearrangement of E,E-cinnamaldoxime on rare earth exchanged (Ce^{3+}, La^{3+}, and RE^{3+}) HFAU-Y zeolites: An efficient green process for the synthesis of isoquinoline

Bejoy Thomas [1], S. Prathapan, S. Sugunan *

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

Abstract

In this paper, a novel application of solid acid catalysts in the Beckmann rearrangement of E,E-cinnamaldoxime in the synthesis of an important heterocyclic compound; isoquinoline is reported. E,E-Cinnamaldoxime under ambient reaction conditions on zeolite catalysts underwent Beckmann rearrangement to produce isoquinoline in yields of ca. 86–95%. Cinnamonitrile and cinnamaldehyde were formed as by-products. LaH-Y zeolite produces maximum amount of the desired product (yield 95.6%). However, the catalysts are susceptible for deactivation due to the basic nature of the reactants and products, which neutralize the active sites. H-Y zeolite is more susceptible (22% deactivation in 10 h) for deactivation compared to the cerium-exchanged counterpart (18% deactivation in 10 h). Thus, the optimal protocol allows isoquinoline to be synthesised in excellent yields through the Beckmann rearrangement of cinnamaldoxime. The reaction is simple, effective, does not involve any other additives, and environmentally benign.
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1. Introduction

Isoquinoline derivatives such as 5-substituted iso-quinoline-1-ones and 3,4-dihydro-5-[4-(1-piperidinyl)-butoxy]-1(2H)-isoquinolinone (DPQ) are potent inhibitors of poly(ADP-ribose) polymerase (PARP—an enzyme that plays a role in polymerizing ADP-ribose in DNA backbone synthesis) [1,2]. The former has potential therapeutic applications in several diseases, including cancer, myocardial infarction, diabetics, stroke, rheumatoid arthritics, hemorrhagic shock, and retro-viral inflections [1–6]. Isoquinoline is the main het-erocyclic ring for a class of alkaloids, which have medicinal and toxic properties. Some examples are: scotch broom used for relaxation and sedative–hypnotic effects, Prinkly poppy which is smoked as a euphoriant, Mescal bean which is a hallucinogenic, used in Native American rituals and for medicinal purposes. These alkaloids are potential anti-tumor agents. Alexandrova et al. studied the effect of isoquinoline alkaloids such as hanandezine, thalfoetidine and protopine on tumor cell lines [7]. Dihy-droquinolinium salts are widely used as potential catalysts for the synthesis of optically active epoxides in asymmetric synthesis [8].
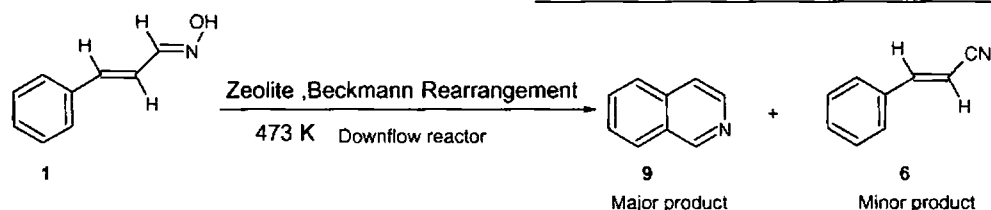
Bischler–Napieralski cyclization is one of the best routes for the synthesis of isoquinoline. In this reaction, the amide derived from a substituted phenyl ethylamine is cyclized under dehydrative acidic conditions. Commercially used dehydrating agents involve; P_2O_5, PCl_5

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* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 577595.
E-mail address: ssg@cusat.ac.in (S. Sugunan).
[1] Present address: NMR Research Center, Indian Institute of Science, Bangalore 560 012, Karnataka, India. Tel.: +91 080 22932920.

and $POCl_3$ in boiling xylene or decaline [9,10]. There is a pressing need for industrial processes that minimize consumption of energy, production of waste or the use of corrosive, explosive, volatile and non-biodegradable materials. Nevertheless, the above reagents possess extreme affinity for water, which makes their handling very difficult. Also, the normal work-up procedure for reactions employing them involves a water quench process, which prevents the acid being used again and on subsequent neutralization leads to an aqueous waste stream. Hence under the reaction conditions, these reagents are converted to materials that are toxic and non-environmental friendly. Since the reagents are irreversibly lost, these reagents are associated with low atom efficiency [11–13]. All these needs and other desiderata, such as the in situ production and containment of aggressive and hazardous reagents, and the avoidance of the use of ecologically harmful elements, may be achieved by designing the appropriate heterogeneous inorganic catalyst, which ideally should be cheap, readily preparable, and fully characterizable, preferably under in situ reaction conditions.

As part of our ongoing research in the development of environmentally benign chemical process for fine chemical synthesis, we required a fixed-bed solid-state protocol for the synthesis of isoquinoline. We have recently reported the dehydration/Beckmann rearrangement of benzaldoxime and 4-methoxy benzaldoxime for the synthesis of the corresponding nitriles and acetalization of ketones on various solid acid catalysts [14,15]. In the present paper, we report vapor phase Beckmann rearrangement of cinnamaldoxime to isoquinoline over rare earth exchanged H-Y zeolites and our attempt to rationalize the results on the basis of physico-chemical properties. Other reactions observed by us include dehydration of cinnamaldoxime to give cinnammonitrile and hydrolysis to give cinnammaldehyde. Since there is no waste formation in the reaction, the E-factor must be low and atom efficiency high. In conclusion, a simple, efficient, and environmental friendly protocol is described for the production of isoquinoline in quantitative yields. The reaction scheme can be represented as:

to the formation of isoquinoline (9) as the major product. Dehydration of cinnamaldoxime producing cinnamonitrile (6) is a minor pathway.

2. Experimental section

2.1. Catalyst preparation

Pure HFAU-Y zeolite (Si/Al ratio 1.5) was supplied by Sud-Chemie (India) Ltd. Rare earth zeolites were obtained by contacting H-Y zeolite with a 0.5 M nitrate solution (0.025 mol of nitrate/g of zeolite, obtained from Indian Rare Earths Ltd. Udyogamandal, Kerala) at 353 K for 24 h. H-Mordenite was supplied by Zeolyst International, USA (Si/Al ratio = 19, BET surface area 552 m^2 g^{-1}, pore volume 0.266 cm^3 g^{-1} and average crystallite size 0.92 μm). SiO_2 was prepared by the acidification of an aqueous solution of sodium silicate (supplied by S-D Fine Chemicals, India). The gelatinous precipitate obtained was washed free of electrolytes using de-ionized water. It was dried at 383 K overnight in an air oven and dehydrated by calcining to 773 K at a heating rate of 20 K/min under a constant flow of air over the sample (60 mL/min) [16].

2.2. Catalysts characterization

The chemical compositions and framework Si/Al ratio of rare earth exchanged zeolites were determined by Energy Dispersive X-ray analysis using a JEOL JSM-840 A (Oxford make model 16211 with a resolution of 1.3 eV). The crystalline nature of the materials was established by X-ray diffraction studies performed using a Rigaku D-max C X-ray diffractometer with Ni-filtered Cu Kα radiation. Infrared induced vibrations were studied using a Nicolet Impact 400FT IR spectrometer. Acid structural properties were estimated using temperature programmed desorption (TPD) of ammonia with a conventional equipment. Pelletized catalyst (500 mg) was activated at 773 K in a muffle furnace and loaded in a steel reactor of 15 cm length and 0.5 cm internal dia-

Zeolite ,Beckmann Rearrangement
473 K   Downflow reactor

1   9   6
                    Major product   Minor product

E,E-Cinnamaldoxime (1) under ambient reaction conditions on zeolites and alumina undergo E–Z isomerization followed by Beckmann rearrangement leading

meter. The catalyst was then activated at 573 K under constant nitrogen flow for half an hour. After cooling to room temperature, the sample was saturated with

ammonia in the absence of a carrier gas (N_2) and the system was allowed to attain equilibrium. Nitrogen flow was restarted to flush out excess and physisorbed ammonia. The temperature was then raised in a stepwise manner at a linear heating rate 20 K/min to 873 K. The ammonia desorbed from 373 to 873 K was monitored using a conventional TPD analyzer. BET surface area and pore volume measurements were performed using a *Macromeritics Gemini* surface area analyzer using N_2 adsorption technique at liquid nitrogen temperature.

2.3. Catalytic reaction procedure

Catalytic reactions were carried out in an ordinary fixed-bed, down-flow reactor made of a cylindrical quartz tube with 0.6 cm internal diameter and 30 cm height with a setup to carryout the reaction under a gaseous atmosphere. The catalyst particles were filled between ceramic beads. During the operation, the gaseous reactants flow through the reactor tube and over the catalysts bed, and reaction takes place. Catalysts (700 mg) were activated at 773 K for 12 h in the presence of oxygen, allowed to cool to room temperature in dry nitrogen and then heated to reaction temperature (473 K) where they were kept for 1 h. The reaction mixture (5% solution of 1 in 1:1 benzene acetonitrile mixture) was fed into the reactor (at a feed rate of 4 mL/h or WHSV, $0.29 \ h^{-1}$) using an infusion pump in the presence of dry N_2 (10 mL/h) and products were collected after 3 h and were identified using a gas chromatograph (GC1000, *Chemito* with an SE-30 capillary column), High Performance Liquid Chromatography (HPLC; *Shimadzu CLASS-VP* $V_{5.032}$), gas chromatography–mass spectrometer (*Shimadzu-5050* spectrometer having a 30 m HP-30 capillary column) and infrared (*Nicolet Impact 4000*) spectroscopic techniques. Finally, the product was characterized by ^1H NMR experiment (400 MHz *Bruker AMX 400* NMR spectrometer). The presence of aluminium in the reaction mixture was determined by EDX using a JEOL JSM-840 A (Oxford make model 16211 with a resolution of 1.3 eV).

3. Results and discussion

3.1. Physicochemical characterization

Chemical composition of the parent and different as-exchanged zeolites are shown in Table 1. X-ray diffraction and infrared spectral studies confirm that the zeolite framework remains intact after an exchange with rare earth cations at 353 K and activation at 773 K. All the as-exchanged zeolites crystallize into a cubic crystal system with F3dm space group as confirmed by Powder X-ray Diffraction (PXRD) studies. Fourier Transform infrared spectroscopy shows uniform transmittance patterns for the parent and rare earth exchanged zeolites. H-Y and various rare earth exchanged zeolites show bands characteristic of faujasite type of zeolites in the framework region. However, these framework vibrational bands shift to a higher wave number region on exchange with rare earth cations (see Table 1). Major shift in the framework vibrational band position is due to the strain in the framework induced by the presence of charged and bulky rare earth cations in the extra-framework cation locations. IR spectra and X-ray diffraction measurements showed that rare earth exchanged H-Y zeolites are crystalline and present well-defined structures.

The important physicochemical characteristics of different zeolites employed in the present study are summarized in Table 2. The table describes the distribution of acid sites strength in three temperature regions of 373–473 K (week acid sites), 473–673 K (medium acid strength) and 673–873 K (strong acid sites). Hence, NH_3-TPD presents the acid site distribution in zeolites rather than the total acidity. Amount of ammonia desorbed by each sample varies with the nature of the rare earth cation. All the rare earth exchanged samples invariably show high value of acidity in the weak and medium acid regions. Brönsted acidity in rare earth exchanged zeolites are generated by the hydrolysis of rare earth cations at SI' in the sodalite and super cages [17].

Table 1
Chemical composition and framework vibrational band shifts (400–1300 cm^{-1}) as observed by infrared spectral studies on pure H-Y and different ion exchanged rare earth zeolites such as CeH-Y, LaH-Y, and REH-Y

Zeolite	Chemical composition[a]	Asymmetric stretch (cm^{-1}) EL or IT[b]	Symmetric stretch (cm^{-1}) EL or IT	Double ring[c] (cm^{-1})	T–O bend[d] (cm^{-1})
H-Y	$H_{76.5}Al_{76.5}Si_{115.5}O_{384}$	1050	771	570	457
CeH-Y	$Ce_{14.06}H_{34.07}Al_{76.25}Si_{115.57}O_{384}$	1083	790	574	480
LaH-Y	$La_{15.44}H_{29.23}Al_{76.25}Si_{115.75}O_{384}$	1061	771	572	463
REH-Y[e]	$La_{9.01}Ce_{1.68}Pr_{3.91}Nd_{4.28}H_{18.78}Al_{75.42}Si_{116.58}O_{384}$	1072	772	573	469

[a] As determined by Energy Dispersive X-ray analysis.
[b] EL, external linkage; IT, internal tetrahedra.
[c] D_6R double ring units.
[d] T = Si, Al.
[e] REH-Y is a mixed rare earth exchanged zeolite with La^{3+} as the main counter cation and small amounts of Ce^{3+}, Pr^{3+} and Nd^{3+} etc.

Table 2
Textural and acid structural properties of different zeolites

Catalyst	Amount of ammonia (mmol/g^{-1}) desorbed within certain temperature range, K				Textural properties		
	W^{a,b}	M^a	S^a	Total	BET surface area, m^2/g	Langmuir surface area, m^2/g	Pore volume,^{c} cc/g
H-Y	0.69	0.41	0.33	1.43	398	593	0.266
CeH-Y	1.10	0.60	0.31	2.02	511	731	0.340
LaH-Y	0.51	0.71	0.46	1.68	464	679	0.288
REH-Y	0.68	0.86	0.49	2.03	483	699	0.301

[a] The ammonia desorbed in the temperature range 373–473 K might contain small amounts of physisorbed ammonia too.

[b] W, M, and S stand for weak (373–473 K), medium (474–673 K), and strong (674–873 K) acidic sites.

[c] Total pore volume measured at $0.9976P/P_0$.

Comparative low acid sites strength of LaH-Y could be due to the presence of a large number of La^{3+} ions in the small cages than Ce^{3+} in the case of CeH-Y zeolite [18,19]. The formation of inaccessible Brönsted acid sites (BAS) in the small cages is due to the migration of La^{3+} from super cages to small cages in the electrostatic repulsive field of residual cations upon heat treatment [18–20]. BAS are formed in zeolites containing multivalent cations upon thermal removal of the water initially present in the pores. In the local electrostatic fields, a water molecule dissociates and the proton formed with the negatively charged oxygen framework gives the so-called bridging hydroxyl group which is the catalytically active BAS. BAS that are formed in the small cages are non-accessible acid centers. According to Hirschler–Plank mechanism, cation migration influences the number of cations that are available for the formation of accessible BAS during the thermal treatment [20]. In the local repulsive interaction, rare earth cations migrate from super cages to small cages and is maximum in the case of lanthanum cations (as evidenced by the ^{29}Si NMR).

The repulsive interactions, which influence the cation distribution in the small cages of zeolite Y was discussed earlier by Van Dum and Mortier [21]. Migration of cations and probable influence on the acid sites distribution in rare earth exchanged zeolites is described in detail elsewhere [22]. The low temperature N$_2$ adsorption–desorption and BET surface area measurements gave surface area and pore volume (Table 2). Surface area and pore volume increase invariably on exchange with rare earth cations. The increase of surface area might be due to the decrease in the crystallite size and improvement in the microporous nature on exchange of hydrogen in H-Y zeolite with rare earth cations.

3.2. Beckmann rearrangement of E,E-cinnamaldoxime

We have used four classes of solid acid catalysts for the synthesis of isoquinoline by the Beckmann rearrangement of E,E-cinnamaldoxime. They include: (1) HFAU-Y zeolite, (2) rare earth exchanged H-Y zeolites, (3) H-mordenite zeolite, and (4) silica.

The results of Beckmann rearrangement of E,E-cinnamaldoxime over a series of solid acid catalysts are shown in Table 3. All materials show very high activity and selectivity for the formation of the desired product; isoquinoline (1, Fig. 2). Cinnamonitrile (6) and cinnamaldehyde (8) were the main by-products of the reaction. Isonitrile formation was not detected by careful analysis of the product mixture. Analysis of the product mixture using GC and GC–MS confirms the formation of small amounts of cinnamic acid and styrene. All catalytic systems invariably exhibit good activity towards Beckmann rearrangement of cinnamaldoxime to isoquinoline. However, zeolites show better results compared to SiO$_2$. Pure H-Y zeolite and its rare earth counterparts are highly selective for the production of isoquinoline (conversion > 97.5% and yield of isoquinoline > 86%). Lanthanum exchanged H-Y zeolite produces maximum amount of the desired product (yield 95.6%). Optimum number of acid sites on H-Y and

Table 3
Synthesis of isoquinoline, variation of catalyst

Catalyst	Oxime conversion (%)	Yield (%)			
		Isoquinoline	Cinnamonitrile	Cinnamaldehyde	Other^a
H-Y	97.9	89.8	4.3	5.3	0.6
CeH-Y	99.1	85.7	6.0	4.8	3.5
LaH-Y	98.5	95.6	2.4	1.1	0.9
REH-Y	99.7	85.0	8.4	3.9	2.7
H-MOR^b	100	92.3	4.6	3.0	0.1
SiO$_2$^{c}	55.0	73.9	2.3	8.2	15.6

Experimental conditions: catalyst amount, 700 mg; reaction temperature, 473 K; time on stream, 3 h; reactant, 5% oxime solution in 1:1 benzene acetonitrile mixture; feed rate, 4 mL/h; or weight hourly space velocity, 0.29 h^{-1}; nitrogen flow, 10 mL/h.

[a] Include cinnamic acid and small amounts of styrene.

[b] H-Mordenite is a product from Zeolyst International USA.

[c] SiO$_2$ was prepared by the acidification of an aqueous solution of sodium silicate.

other zeolite catalysts seems to work well in effecting the intramolecular cyclization of the intermediate (7, see Fig. 2) eventually producing isoquinoline.

We have compared the Beckmann rearrangement ability of different zeolite Y derivatives with some standard catalysts; namely H-mordenite and silica. Mordenite zeolite is active like any other zeolite (yield 92.3%)
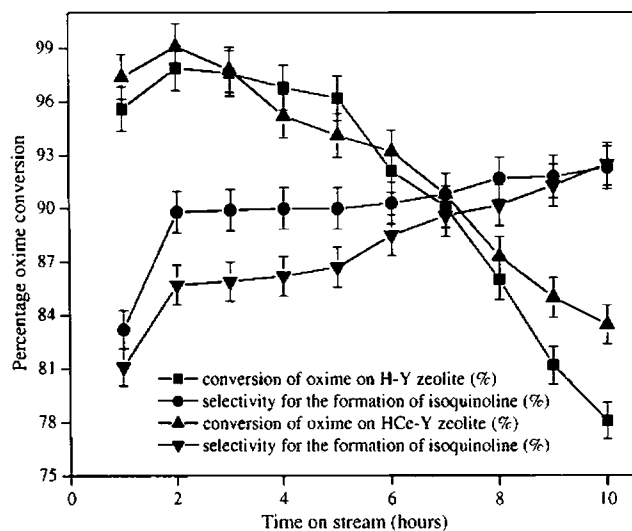

Fig. 1. Effect of time on stream on the percentage conversion of *E,E*-cinnamaldoxime and formation of isoquinoline on H-Y and HCe-Y zeolites. Experimental conditions: catalysts, H-Y and HCe-Y zeolites; catalyst amount, 700 mg; reaction temperature, 473 K; reactant, 5% cinnamaldoxime solution in 1:1 benzene acetonitrile mixture; feed rate, 4 mL/h; or weight hourly space velocity (WHSV), 0.29 h⁻¹; nitrogen flow, 10 mL/h.

for the reaction. However, SiO_2 produces only 73.9% of the desired product with a conversion of 55%. Silica with its weak acidic nature seems to be inefficient in effecting the *E–Z* isomerization of *E,E*-cinnamaldoxime (see reaction mechanism), which is the most crucial step in the production of the desired product. This results in the production of comparatively large amounts of side products such as cinnamaldehyde, cinnamic acid, and styrene. Perhaps, silica produces the least amount of nitrile also due to its weak acidic nature.

3.3. Deactivation, reusability, and heterogeneity studies

Dehydration/Beckmann rearrangement reaction of *E,E*-cinnamaldoxime was performed over H-Y and CeH-Y zeolites for 10 h. The results of the deactivation studies are presented in Fig. 1. The error bar of the data in the figure is found to be 1.3%. For carefully dehydrated reagents, the conversion decreases quickly with reaction time. Periodic checks by GC and GC–MS showed this decrease in conversion. However, H-Y zeolite undergoes fast deactivation compared to the cerium-exchanged counterpart (22% and 18% deactivation in 10 h, respectively, for H-Y and CeH-Y zeolites). Generally, deactivation of the zeolites is due to coke formation [23,24]. In the present case, the deactivation of the catalyst is due to the neutralization of acid sites by the basic reactant and product molecules. The increase in the isoquinoline formation with time can be explained by considering the fact that the dehydration reaction needs strong acid centers, while mild or weak acid sites can
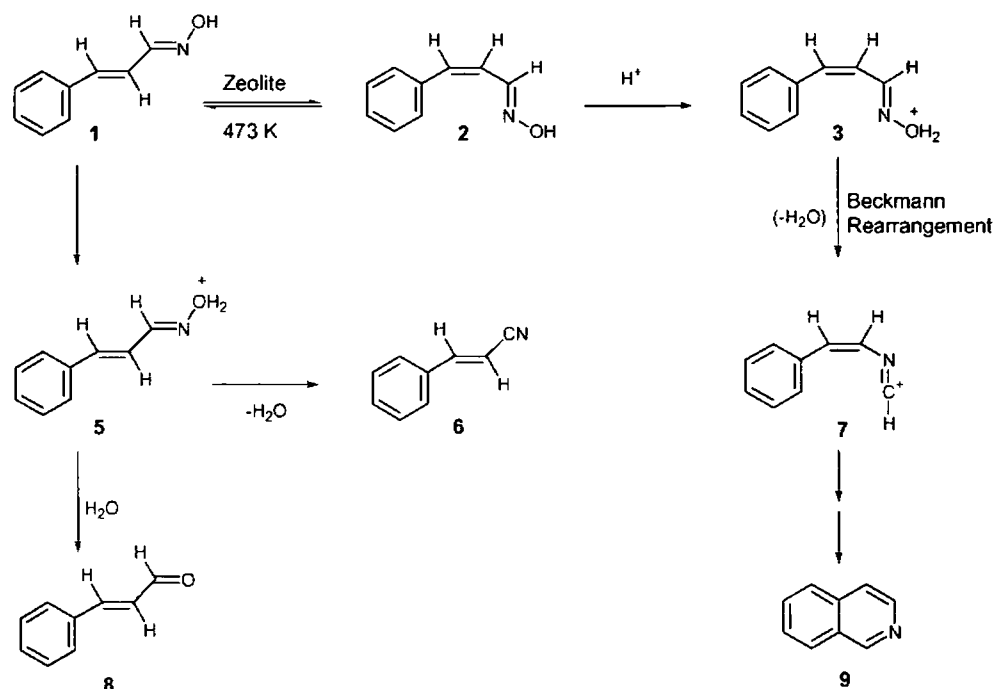

Fig. 2. Scheme showing the plausible mechanism of the reaction.

effect Beckmann rearrangement. As most of the strong acid sites are getting deactivated during the progress of the reaction by basic reactants and products, the dehydration becomes nominal and at the same time increases the probability of Beckmann rearrangement.

The deactivated zeolites (in fact other solid acids too) can be partially regenerated by solvent extraction followed by oxidative treatment. The deactivated zeolites (we studied H-Y and HCe-Y zeolites) were extracted with benzene to remove the reaction products from the catalyst surface. Further, they were washed with de-ionized water, dried at 383 K overnight and regenerated by activating to 773 K at a heating rate of 12 K/min. The catalysts were kept for 5 h at 773 K. Regenerated H-Y zeolite converted 96.8% oxime, while HCe-Y 97.5%, under similar reaction conditions. As the waste formation is a small extent, the reaction must have low E-factor and high atom efficiency. In conclusion, a simple, efficient, and highly environmental friendly protocol is described for the production of isoquinoline.

We also conducted experiments to obtain clear evidence for the stability and true heterogeneity of the catalysts for the reaction. The reaction mixture (E,E-cinnamaldoxime; **1**) was passed through H-Y and HCe-Y zeolites under standard reaction conditions for 10 h. No aluminium was detected in the reaction mixture by the energy dispersive X-ray analysis. Also, no aluminium was detected during qualitative analysis of the mixture. These results strongly suggest against possible aluminium leaching during the reaction.

3.4. Mechanism of isoquinoline formation

E,E-Cinnammaldoxime (**1**, mp 72–74 °C) [25] was prepared by a well-known procedure from cinnamaldehyde (99% trans available from *Aldrich Chemical Company*). Cinnamaldehyde is coupled with hydroxylamine hydrochloride (99%, *S-D fine chemicals*, India) in the presence of a mild base such as NaHCO$_3$ (also from *S-D fine chemicals*, India) at refluxing temperatures. The formation of various products may be understood in terms of the pathways described in Fig. 2. Since E,E-cinnammalodxime lacks the geometrical requirements to undergo isoquinoline formation; we propose that E–Z isomerization of cinnamaldoxime is a major reaction pathway. Reports on similar E–Z isomerizations of aldoximes can be found in the literature [25–29]. Thus, E,E-cinnamaldoxime (**1**) undergoes facile isomerization to give the Z,E-isomer **2** in the presence of acidic zeolites under the given reaction conditions. In a mechanism analogous to that suggested for Beckmann rearrangement of aldoximes, migration of the *anti* styryl moiety to electron deficient nitrogen in **3** leads to intermediate **7**. Intramolecular cyclization of **7** will eventually lead to isoquinoline (**9**). Amide formation is not observed under our reaction conditions. Two reasons

may be suggested for this observation: (1) intramolecular cyclization in **7** is a very facile pathway; (2) our reactions are carried out in the absence of water. It appears that protonation of **1** results in the loss of a molecule of water to give *trans*-cinnamonitrile (**6**). Acid-catalyzed hydrolysis of **1** will lead to the formation of *trans*-cinnamaldehyde (**8**). This is a minor pathway since the reactions are carried out under moisture-free conditions.

4. Conclusion

Isoquinoline is synthesized in quantitative yields over eco-friendly solid acid catalysts under well-optimized reaction conditions. Since E,E-cinnamaldoxime lacks the geometrical requirements to undergo isoquinoline formation via Beckmann rearrangement; undergoes a E–Z isomerization over the catalysts to produce isoquinoline in yields of ca. 86–95%. All zeolites used exhibit comparable selectivity for isoquinoline. However, the catalysts are susceptible for fast decline in the catalytic activity due to the basic nature of the reactants and products which neutralize the active sites. H-Y zeolite is more susceptible (22% deactivation in 10 h) for deactivation compared to cerium-exchanged counterpart (18% deactivation in 10 h). In conclusion, a simple, efficient, and environmentally benign protocol is described for the synthesis of isoquinolines from E,Z-cinnamaldoxime using rare earth exchanged zeolite-H-Y catalysts. The process does not produce any waste and catalysts can be recycled without loss of activity. They could be easily regenerated through oxidative treatment at 773 K.

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