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H-β-zeolite catalyzed synthesis of β-bromostyrenes from styrene bromohydrins

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ABSTRACT

Synthesis of β-bromostyrenes from styrene bromohydrins using H-β-zeolite as catalyst under moderate conditions is reported. The catalyst could be regenerated and reused up to three consecutive cycles.

β-Aryl vinyl halides are key intermediates in the synthesis of fine chemicals and numerous biologically active compounds.[1] They have traditionally been prepared through the classical Hunsdiecker reaction involving the halo decarboxylation of cinnamic acid derivatives,[2] olefination of aromatic aldehydes,[3] homologation of benzyl bromides with dihalomethanes,[4] and reduction of 1,1-dihaloalkenes.[5] A powerful alternative strategy involves the intermediates of vinylboranes,[6] vinylsilanes,[7] vinylstannanes,[8] and vinylzirconates[9] with halogen analogues. However, with few exceptions, these methods require expensive and/or rare metal catalysts (Scheme 1). Therefore, improvements to achieve environmentally benign and cost-effective approaches would be highly desirable. Due to an appealing application of β-aryl vinyl bromides in the synthesis and our interest on environment-friendly brominations since a decade,[10] we intended to obtain these vinyl intermediates via selective dehydration of corresponding bromohydrins. Our previous efforts on selective intramolecular dehydration of styrene bromohydrin with various Brønsted acid catalysts led to the undesired condensation product ether instead of the desired β-bromostyrene.[11] This precedent enforced us to further investigate the selective catalytic system to access β-bromostyrenes.[12] Herein, we describe a strategy for the selective dehydration of bromohydrins that enable us to access β-aryl vinyl bromides using H-β-zeolite as heterogeneous catalyst. H-β-zeolite possesses Bronsted acid sites in the micropores and Lewis active acid sites on the external surface.[13] Because of these properties of H-β-zeolite, it has been used as heterogeneous catalyst in organic transformations.[14,15]

First, the selective dehydration was performed by choosing styrene bromohydrin (**1a**) as model substrate and H-β-zeolite as heterogeneous acid catalyst and the results are illustrated in Table 1. After the reaction of **1a** in toluene with 5% (w/w) of H-β-zeolite at 100 °C for 12 h, the desired product **2a** was detected in 11% GC yield (Table 1, entry 1). When the catalyst loading was increased to 10% and 20% (w/w), the yield of **2a** was increased to 20% and 30%, respectively (Table 1, entries 2 and 3). A clear improvement was observed when the reaction temperature was raised from 100 to 120 °C, and **2a** was obtained in 55% isolated yield (Table 1, entry 4). Furthermore, when chlorobenzene was utilized as solvent at 120 °C, **2a** was obtained in 72% isolated yield (Table 1, entry 5). Decrease of the catalyst loading and temperature decreased the yield (Table 1, entries 6–8). Other solvents and neat conditions were not favorable for this transformation (Table 1, entries 9–14). When the reaction time was decreased to 9 and 6 h, the same (72%) yield of **2a** was obtained (Table 1, entries 15 and 16). Based on the above screening results, the optimal conditions can be determined (Table 1, entry 15). To the best of our knowledge the selective catalytic dehydration of bromohydrins to access β-bromostyrenes has never been reported.

With the optimized conditions in hand, the substrate scope of the reaction was investigated (Table 2). All substrates examined

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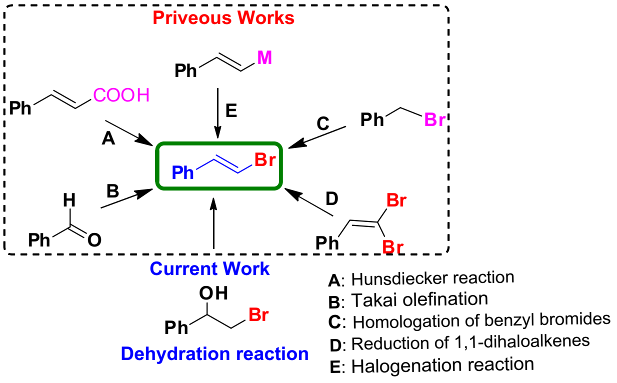
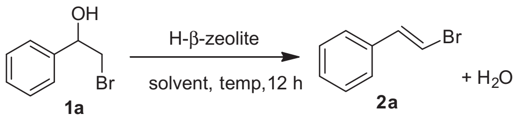


Scheme 1.

Table 1
Optimization of reaction conditions[a]



Entry	H-β-zeolite (wt%)	Solvent	Temp (°C)	Yield (%)	*E*/*Z*[b]
1	5	Toluene	100	11[b]	81:19
2	10	Toluene	100	20[b]	90:10
3	20	Toluene	100	30[b]	73:27
4	20	Toluene	120	55	90:10
5	20	Chloro benzene	120	72	85:15
6	10	Chloro benzene	120	66	84:16
7	20	Chloro benzene	80	17	76:24
8	20	Chloro benzene	100	57	82:18
9	10	Benzene	90	36[b]	78:22
10	10	Xylene	110	47[b]	80:20
11	20	Cyclo hexane	90	24[b]	79:21
12	10	Cyclo hexane	80	10[b]	80:20
13	10	CCl_4	75	12[b]	79:21
14	10	Neat	100	14[b]	78:22
15[c]	**20**	**Chloro benzene**	**120**	**72**	**85:15**
16[c]	20	Chloro benzene	120	72	85:15

The bold values represent the optimized conditions.

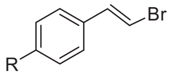
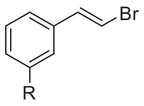
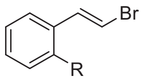
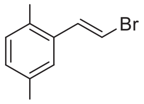
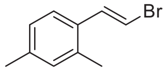
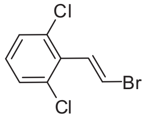
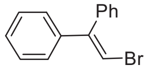
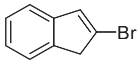
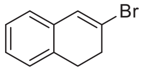
[a] Conditions: **1a** (1.25 mmol), solvent (1.0 mL), isolated yield unless otherwise stated.

[b] Yield and *E*/*Z* ratio were determined based on GC–MS (area%).

[c] Reaction time 6 and 9 h in entries 15 and 16, respectively.

under optimized conditions afford the corresponding products in moderate to good yield. The selective dehydration of *para*-substituted styrene bromohydrins with both electron-efficient and electron-deficient appears to be invariant to the electronic properties as the reaction proceeded smoothly to give the corresponding products (**2b**–**2f**) in moderate to good yield 60–77%. However, the strong electron withdrawing nitro group at *para*-position gave low yield (11%) of product **2g**. The electron rich substituents either at *ortho* or *meta* position of styrene bromohydrin provided moderate to good yields of β-bromostyrenes (**2h**–**2k**) and (**2m**–**2o**) respectively. Electron withdrawing groups at both *ortho*/*meta* substituents also gave products **2l** and **2p** in low yield 17% and 38%, respectively. Disubstituents at 2,5- and 2,4- and sterically demanding disubstituents at 2,6 positions of styrene bromohydrins were readily transformed into corresponding products (**2q**–**2s**). Alpha-substituted β-bromostyrene (**2t**) can also be obtained in good yield (78%). Interestingly, the cyclic vinyl bromides such as 2-bromo-1*H*-indene (**2u**) and 3-bromo-1,2-dihydronaphthalene (**2v**) also resulted in 77% and 32% yield, respectively.

Table 2
Scope for the synthesis of β-bromostyrenes[a]

Entry	Product			Isolated yield (%)	*E*/*Z*[b]
1		R = H;	**2a**	72	85:15
2		–CH3	**2b**	64	87:13
3		–^{t}Bu	**2c**	77	84:16
4		–Ph	**2d**	60	88:12
5		–Br	**2e**	66	84:16
6		–CI	**2f**	72	85:15
7[c]		–NO_2	**2g**	11	71:29
8		R = –Br	**2h**	70	84:16
9		–CI	**2i**	67	84:16
10		–F	**2j**	52	76:24
11		–CH_3	**2k**	55	88:12
12[c]		–NO_2	**21**	17	74:26
13		R = –Br	**2m**	63	80:20
14		–Cl	**2n**	62	83:17
15		–CH_3	**2o**	66	83:17
16		–F	**2p**	38	99:01
17			**2q**	65	83:17
18			**2r**	57	81:19
19			**2s**	70	100:–
20			**2t**	78	–
21			**2u**	77	–
22			**2v**	61[d]	–

[a] Conditions: See Table 1 entry 15.

[b] *E*/*Z* ratio determined by ^{1}H NMR.

[c] Reaction time 12 h.

[d] 29% yield of naphthalene was observed along with **2v** by ^{1}H NMR.

The stability and reusability of H-β-zeolite catalyst for the selective dehydration of styrene bromohydrin under optimized conditions have been examined at gram scale (10 mmol). After each cycle, the catalyst was separated from the reaction mixture by filtration, reactivated by simple treatment with mineral acid,[16] and subsequently reused under identical reaction conditions.[17] The recyclability data indicates that there is no considerable loss of catalytic activity for at least three repeated cycles (Fig. 1). However, in each recycle the *E*/*Z* ratio of the product remains the same (85/15). When the catalyst is reused without activation, the reaction was incomplete even after long reaction time compared to activated catalyst. Probably, it may be due to the acidic character of the catalyst. As the number of recyclability increases its acidic property slightly decreases, presumably due to leaching of H^+ ions. Hence, a slight decrease in the catalytic activity was observed. However, the catalytic activity can be restored by simple treatment of the catalyst with mineral acids at room temperature. The H-β-zeolite catalyst utilized in the present study is commercially available. The fresh and reused catalysts have been characterized by XRD (Fig. 2) and FT-IR analysis (see Fig. S1 in the Supporting information). The XRD analysis of the reused catalyst well matched with the fresh catalyst, this study also suggests that crystallinity and phase purity of the reused catalyst are comparable.

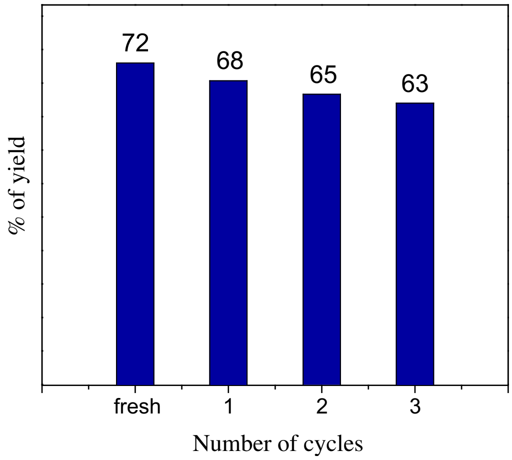


Figure 1. Recyclability study of catalyst.

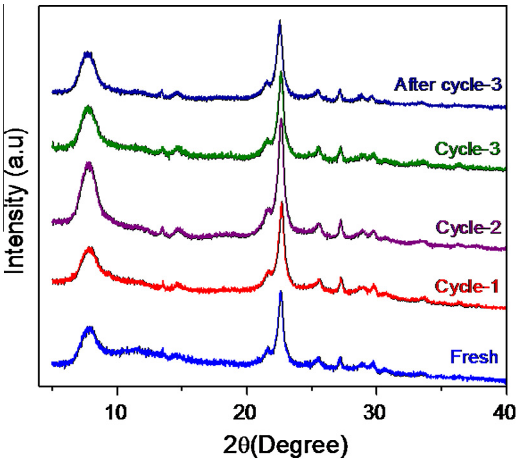


Figure 2. XRD Analysis of catalyst.

The present catalytic system has the following significant advantages over previously reported procedures for the synthesis of β-bromostyrenes: (i) atom efficiency and no by-product formation [only water is eliminated in the process], (ii) applicable for a variety of substituted styrenes (including alpha substituted derivatives), (iii) H-β-zeolite catalyst is inexpensive and commercially available, and (iv) easy separation of the catalyst and it can be reused up to three consecutive cycles without appreciable loss of catalytic activity.

In conclusion we have developed a green catalytic method for the synthesis of β-bromostyrenes through intramolecular dehydration of bromohydrins using H-β zeolite as heterogeneous and recyclable catalyst. The present method is applicable to a variety of substituted styrene derivatives under moderate conditions. The present approach highlights a useful alternative to the traditional Hunsdiecker reaction involving the halo decarboxylation of cinnamic acid derivatives. Notably, water is the only by-product generated, making this transformation more atom-economical and greener, than the traditional methods.

Acknowledgments

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Supplementary data

Supplementary data (detailed experimental procedure and spectroscopic data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.01.118.

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16. The recovered catalyst was activated with mineral acid, which showed same selectivities as with fresh catalyst than the unactivated catalyst.
17. *Synthesis of β-bromostyrene* ***2a:*** In a 25 mL round bottomed flask, 250 mg (1.2 mmol) of 2-bromo 1-phenyl ethanol (**1a**), 50 mg (20 W/W%) H-β-zeolite, and 1.0 mL of chlorobenzene were placed. The reaction flask was placed in an oil bath at120 °C for 6 h; the progress of the reaction was monitored by TLC. After completion of the reaction, the flask was allowed to attain room temperature, and filtered through Whatman filter paper and washed with 10 mL of diethyl ether. Upon removal of the solvent under reduced pressure, the left out residue was purified by column chromatography on silica gel (200–400 mesh) and hexane as eluent to obtain **2a** in (0.16 g) 72% yield.