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A novel application of Hβ-zeolite in catalytic dehalogenation of halophenols

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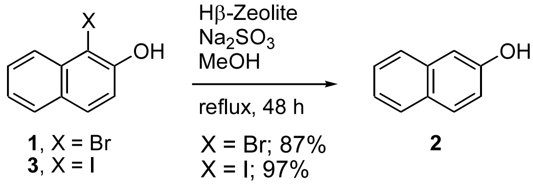
Abstract—A new application of Hβ-zeolite for debromination of bromophenols and deiodination of iodophenols is presented in this note. The heterogeneous catalyst can be recovered and recycled effectively for subsequent reactions. The catalyst was found ineffective for similar action on chlorophenols.

Recently there has been significant interest in exploring the possibility of using aromatic bromine as a protecting group in synthetic organic chemistry.[1,2] This concept is supported by the accessibility of aromatic bromo compounds as well as the conceptually simple debromination reaction. Generally this electrophilic debromination reaction is brought about with aqueous hydrobromic acid (HBr) in the presence of a suitable bromine scavenger such as aromatic amines like aniline or sodium sulfite.[1,3] There are a few elegant applications of utilizing bromine as a protecting group for the preparation of synthetically useful molecules.[1]

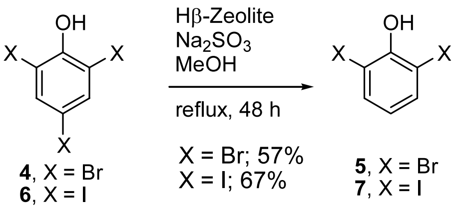
The use of hydrobromic acid is cumbersome due to its hazardous and corrosive nature. Therefore, this may cause practical difficulties in extending the scope of utilizing bromine as a protecting group for large scale preparations. Also in recent years there has been a trend to explore various solid acid catalysts for processes traditionally involving mineral acids. In this account, we wish to present our preliminary findings on using Hβ-zeolite as a heterogeneous catalyst acting as a source of protons to initiate electrophilic debromination.

The strategy was tested by carrying out debromination of 1-bromo-2-naphthol **1** with a catalytic quantity of Hβ-zeolite (50% w/w) and an excess of sodium sulfite (5 mol. equivalents) as a bromine scavenger, in dry methanol, at reflux temperature (Eq. (1)). The course of the reaction was followed by checking the formation of 2-naphthol **2** by TLC comparison with an authentic sample. The reaction needed about 48 h for completion and the debrominated product was isolated in 87% yield. The analogous deiodination of 1-iodo-2-naphthol **3** under identical conditions gave a higher yield of 97%, in accordance with the expectation that the iodonium species is a better leaving group than the bromonium ion species. The dechlorination reaction of 1-chloro-2-naphthol was not found to be feasible under the reaction conditions as the material remained unchanged even after prolonged reaction.



(1)

2,4,6-Tribromophenol **4** and 2,4,6-triiodophenol **6** were subjected to similar reaction conditions to give 2,6-dibromophenol **5** and 2,6-diiodophenol **7** in moderate yields (Eq. (2)).



(2)

Keywords: debromination; deiodination; heterogeneous catalysis.

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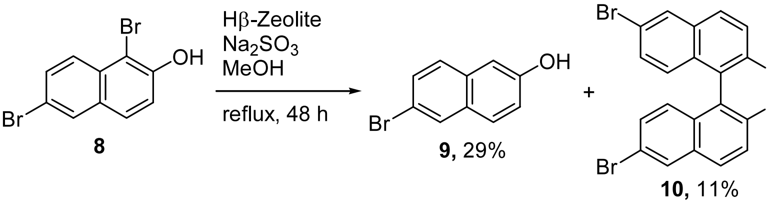
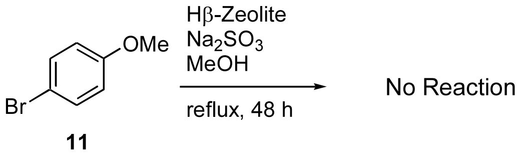
6-Bromo-2-naphthol **9** is an important industrial material and is prepared by selective debromination of 1,6-dibromo-2-naphthol **8**.[4] Although we succeeded in a selective debromination at the 1 position and isolated 6-bromo-2-naphthol **9**, we also obtained a considerable amount of 2,2′-dihydroxy-6,6′-dibromo-1,1′-binaphthol **10**, probably formed by the oxidative coupling of **9**,[5] see Eq. (3).



(3)

Debromination of 4-bromoanisole **11** under identical conditions was not successful even after prolonged exposure to the catalyst in refluxing methanol (Eq. (4)). This is probably indicative of the role of the hydroxy group in stabilizing the intermediate benzonium ion.[3]



(4)

The catalyst recovered after the deiodination reaction of **3** (Eq. (1)) was carefully washed with dilute mineral acid, water, methanol, acetone and dried. A powder X-ray diffraction analysis (XRD) and FT-IR spectra of this material were found to be comparable with fresh catalyst indicating retention of the physical properties of the material. The recovered catalyst was used in another set of deiodination reactions of **3** giving comparable results to the first cycle (ca. 94% yield in the second cycle). This clearly indicates the ability to recover and reuse the catalyst for repetitive use in dehalogenation reactions.

Standard reaction conditions

Deiodination of 1-iodo-2-naphthol: A mixture of **3** (0.27 g; 1.0 mmol), Hβ-zeolite (0.135 g; 50% w/w) and sodium sulfite (0.63 g; 5.0 mmol) was refluxed in dry methanol (10 mL) while the progress of the reaction was monitored by TLC. After 48 h the reaction mixture was cooled and filtered through a suitable device; the catalyst was washed several times with methanol and diethyl ether to recover the product completely. The organic solution was concentrated and the pure product **2** was isolated by column chromatography over silica gel (10% ethyl acetate in hexane) to give a colorless material (0.14 g; 97%), which showed satisfactory spectral data; mp 122°C (lit.[6] 122–3°C).

Thus we present our preliminary results on using Hβ-zeolite as a new heterogeneous catalyst for the debromination and deiodination of halophenols.

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