Microwave-assisted zeolite catalyzed Claisen rearrangement of allyl aryl ethers under solvent-free conditions

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Claisen rearrangement of allyl aryl ethers has been studied extensively over various zeolites under microwave activation and solvent free conditions at 80°C. Hβ-zeolite is found to be an efficient catalyst for the rearrangement. The reaction gives o-rearranged product selectively instead of expected further cyclized dihydrobenzofuran derivative.

Keywords: Claisen rearrangement, allyl aryl ethers, zeolites, solid acids

Since the discovery of the Claisen rearrangement in 1912 (Ref 1), the rearrangement and its variations have been used extensively for the synthesis of natural products as it is an excellent tool for the selective formation of a new carbon–carbon bond and predictability of stereochemical outcome. Although the reaction is traditionally performed under thermal conditions without any catalyst, there is considerable current interest in the catalysis of the Claisen rearrangement.

Claisen rearrangement is generally performed by heating the substrate at an elevated temperature (>473K), and is reported to be susceptible to catalysis by Bronsted and Lewis acids such as BF₃, HOAc (Ref 8), BCl₃ (Ref 9), AlCl₃ (Ref 10), ZnCl₂ (Ref 11), TiCl₄ (Ref 12) Yb(OTf)₃ (Ref 13), Sc(OTf)₃ in ionic liquid (Ref 14), IrCl₃ (Ref 15) and Mo(CO) (Ref 16). However, in spite of having potential utilities, many of these methods involve the use of toxic and expensive reagents, longer reaction time and high temperatures. On the other side, solid acids which are inexpensive, heterogeneous and greener catalysts have also been used. Kotha used silica gel as support in the synthesis of bis-allyl ketones via Claisen rearrangement (Ref 6f). Sheldon et al. have studied the use of H-FAU and H-MOR in the rearrangement of allyl phenyl ethers (Ref 18).

Zeolites have been commonly used as catalysts in the petroleum refining and chemical industries as well as in the preparation of fine chemicals due to their properties such as highly acidic and basic nature, high thermal stability and specific shape selectivity. Pitchumani has observed shape selectivity in zeolites in photo-assisted Claisen rearrangement (Ref 21).

In recent years, solvent-free reactions over organic or inorganic solid supports for the above rearrangement have received increasing attention. The advantages in performing the reactions in dry media are shorter reaction time, economic advantage due to absence of the solvent and increased safety. Use of microwave activation in organic synthesis has become a standard tool for organic chemists because of enhancement in rate of reaction, higher yields and improved selectivity in comparison to conventional reactions (Ref 24). Further, in addition, microwave-assisted solvent-free reactions are clean and efficient.

Herein is reported an efficient methodology for selective Claisen rearrangement of allyl aryl ethers using zeolites as mild, inexpensive and green catalysts under microwave-activation and in the absence of solvent (Scheme I).

Results and Discussion

Allyl aryl ether on Claisen rearrangement gives 2-allylphenol and in some cases 4-allylated product (Ref 7b). Sheldon has reported the formation of 2-allylphenol and 2-methylidihydrobenzofuran, both as major products when the reaction is carried out in the presence of zeolites in refluxing benzene whereas 2-methylidihydrobenzofuran is obtained as a selective product when Al-MCM-41 is used in tetrachloroethylene (Ref 6a) and IrCl₃ in dichloroethane (Ref 6b).

Microwave-assisted Claisen rearrangement of allyl-4-methoxyphenyl ether 1f was carried out in the presence of different zeolites (preactivated at 120°C)

Note

Scheme I — Microwave-assisted Claisen rearrangement in presence of zeolites
overnight) and in the absence of solvent at 80°C (Table I).

If was mixed with the activated catalyst and irradiated with microwaves in Biotage initiator at 80°C. Recently, very active acidic catalysts prepared by supporting FeCl₃ and SnCl₄ on Hβ zeolite have been reported. Modification of Hβ catalyst with FeCl₃ and SnCl₄ in acetonitrile and water solutions gave ‘O’ and ‘A’ type of catalysts.

The reaction was possible with all catalysts, however, the yield varied considerably. In all the reactions, 2-allyl-4-methoxyphenol 2f was obtained as a sole product; however the starting allyl aryl ether was not consumed completely. There was no significant change in the yield of the product even after the reaction was carried out for more than the required time period.

Among the various catalysts, Hβ-zeolite was found to be the most active for the reaction, giving maximum yield of the product in the least time period. HY and NaY catalysts have been reported earlier for tandem Claisen rearrangement-cyclization of methylated allyl ethers producing 2,2-dimethyl-2,3-dihydrobenzofurans in good yields but when these catalysts were employed in the present reaction, poor yields of the product were obtained. Both ZSM-5 catalysts showed mild activity towards selective formation of 2f. Among the modified catalysts, Hβ-Fe-O and Hβ-Sn-O showed comparable activity with Hβ whereas Hβ-Fe-A and, Hβ-Sn-A gave moderate yields but the time required was more.

The Hβ catalyst was found to be recyclable up to three times without any loss in catalytic activity and selectivity (Table II).

In order to explore the scope of the methodology, a wide range of allyl aryl ethers were subjected to Claisen rearrangement. Electron donating groups on the phenyl ring did not have any influence on the course of the reaction since the yield remained unchanged in absence of these groups (Table III).

One of the major advantages of this methodology is that the 1,4-bis(allyloxy)benzene 1i underwent reaction smoothly to produce selectively the mono rearranged product 2-allyl-4-(allyloxy)phenol 2i in excellent yield without undergoing further rearrangement or cyclization reaction. The methodology has several advantages like use of inexpensive, recyclable, mild and green catalyst and lesser reaction time (4-10 min) compared to many reported procedures (>2 hr), considerably low temperature unlike reported procedures.

Experimental Section

Materials

All zeolites were procured from M/s Sud-Chemie (India). The chemical composition (wt. %) of the Hβ zeolite was: Al₂O₃/SiO₂ = 15, BET surface area 510 ± 20 m²/g, and micropore volume 0.11 m³/g. Prior to any further treatment, the zeolite was activated overnight at 120°C.

Catalyst preparation

Hβ-Fe-A catalyst: To anhydrous FeCl₃ (15 g), dissolved in demineralized water (60 mL), Hβ zeolite (10 g) was added over a period of 10 min and the resulting slurry was stirred at RT for 5 hr. The zeolite was filtered and washed with demineralised water until free from chloride ions.

Hβ-Fe-O catalyst: To anhydrous FeCl₃ dissolved in dry acetonitrile (60 mL), Hβ zeolite (10 g) was added over a period of 10 min and the resulting slurry was stirred at RT for 5 hr. The zeolite was filtered, washed with acetonitrile (10 mL), and then with benzene (60 mL).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Yield of 2f (%)</th>
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<tbody>
<tr>
<td>H-ZSM-5</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>12</td>
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<tr>
<td>NaY</td>
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<tr>
<td>Hβ</td>
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<td>64</td>
</tr>
<tr>
<td>Hβ-Fe-O</td>
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<tr>
<td>Hβ-Fe-A</td>
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<td>56</td>
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<tr>
<td>Hβ-Sn-O</td>
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<tr>
<td>Hβ-Sn-A</td>
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<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
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<tbody>
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<td>64</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>62</td>
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<tr>
<td>3</td>
<td>6</td>
<td>55</td>
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</tbody>
</table>

[a] If: 2.5 mmole, Zeolite: 0.3 g (activated overnight at 120°C), Temperature: 80°C
The same procedure was followed to prepare Hβ-Sn-A and Hβ-Sn-O using SnCl₄. The characterization of these catalysts is already reported²⁴.

**Claisen rearrangement of allyl aryl ethers**

Typical experimental procedure: Various allyl phenyl ethers were prepared by known procedures³². In a 5 mL Biotage initiator reaction tube, allyl aryl ether (2.5 mmole) was mixed thoroughly with the zeolite catalyst (0.3 g, activated overnight at 120°C). The mixture was subjected to microwave irradiation in Biotage initiator with the time interval of 2 min. The reaction was monitored by TLC. After the completion of the reaction, reaction mixture was filtered through a sintered glass funnel (G4), and the catalyst was washed with ethyl acetate (3 × 5 mL). The combined organic layer was concentrated in vacuo to afford the crude product which was purified by column chromatography over silica gel (60-120 mesh) using petroleum ether (60-80°C):ethyl acetate (95:5, v/v) solvent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allyl aryl ether</th>
<th>Zeolite</th>
<th>Temperature</th>
<th>Time (min)</th>
<th>Yield of 2 (%)</th>
<th>Lit. Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>O</td>
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<tr>
<td>b</td>
<td>O</td>
<td>OH</td>
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<tr>
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<td></td>
<td></td>
<td>5</td>
<td>71</td>
<td>26a</td>
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</tbody>
</table>

[a] Allyl aryl ether: 2.5 mmole, Zeolite: 0.3 g (activated overnight at 120°C), Temperature: 80°C. [b] Isolated and unoptimised yield. [c] All compounds were characterized by IR and ¹H NMR spectroscopy and compared with literature reports.

Table III —Microwave-assisted o-Claisen rearrangement of allyl aryl ethers using Hβ-zeolite at 80°C in absence of solvent[bd]
3.2, 1.6 Hz), 5.37 (ddd, 1H, J = 16, 3.2, 1.6 Hz), 5.92-6.07 (m, 2H), 6.64-6.07 (m, 3H).

Conclusion

In conclusion, a methodology has been developed involving Hβ zeolite as an effective catalyst for the selective Claisen rearrangement of allyl aryl ethers to 2-allyl phenols under microwave irradiation in the absence of solvent. The protocol has advantages like short reaction time, good to moderate yield of products, cleaner reaction, applicability towards a wide range of allyl aryl ethers and above all, the use of mild, cheap, recyclable and green catalyst.

References