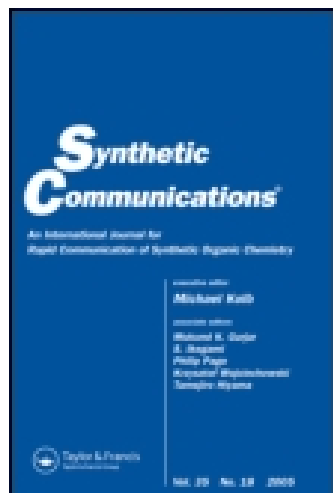


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SYNTHETIC COMMUNICATIONS, 31(17), 2599–2604 (2001)

## ZEOLITE CATALYZED RING OPENING OF EPOXIDES TO ACETYLATED DIOLS WITH ACETIC ANHYDRIDE\*

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### ABSTRACT

HY Zeolite is found to be a versatile catalyst for opening of epoxides to the corresponding acetylated 1,2-Diols with acetic anhydride in good yields.

The opening of epoxides to the corresponding alcohols is one of the most useful reactions in organic synthesis<sup>1</sup> and the acetylation of alcohols is a fundamental process in organic chemistry and provides a cheap and efficient means for protecting hydroxy groups during oxidation, peptide coupling and glycosidation reactions.<sup>2</sup> Thus, it is very important for the epoxide to open for forming a corresponding diacetoxylated selectively instead of a diol. In recent years, there has been a tremendous upsurge of

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interest in various chemical transformations performed in heterogeneous catalysis.<sup>3</sup> Moreover using inexpensive and non-corrosive catalysts, chemical transformations occur with better efficiency, high purity of the products and easier workup, with evident economic and ecological advantages especially in industrial processes.

Zeolites as catalysts for selective organic reactions have received considerable attention in recent decades due to their unique physical and chemical properties such as shape selectivity, acidic and basic nature and their thermal stability.<sup>4</sup> Besides the general advantages associated in using heterogeneous catalysts, like convenient to use, easy separation and being inexpensive further more zeolites can be prepared with different porosity, hydrophobicity, varying acid and basic strength and site distribution, which makes them versatile catalysts for a variety of reactions.<sup>5</sup> In this report, an efficient ring opening of epoxides over HY zeolite as a reusable catalyst is presented. The commercial HY zeolite obtained was from PQ Corporation. The reaction was performed at room temperature for a fixed time and a mixture of epoxide (10 mmol) with acetic anhydride (50 mmol) and the zeolite HY (0.5 g) utilized without previous thermal or chemical treatment, good to high yields (75–95%) were observed in all cases. Under the present conditions chiral epoxides can be easily opened in high yields with complete retention of optical activity (entry 7).<sup>12</sup> In addition, the zeolite HY can be reused many times with no loss in activity and it is simply by filtering the catalyst, washing with acetone, drying and immediately reusing.



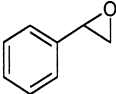
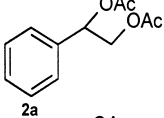
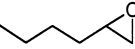
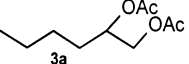
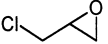
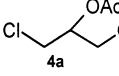
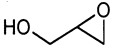
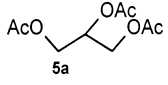
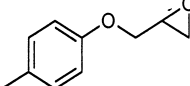
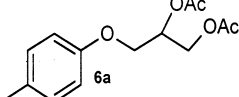
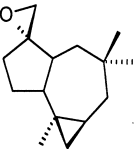
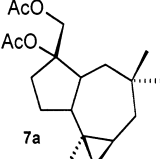
Here zeolite HY shows considerable catalytic activity. As expected the bulkiness of the reagent represents a crucial factor in this process. It limits or completely inhibits its diffusion through the pores of the catalyst and the reaction probably occurs only on the external surface or on the external acidic sites.

## EXPERIMENTAL

In a typical procedure the epoxide (10 mmol) and acetic anhydride (50 mmol) were placed in a flask with stirring. After 5 min zeolite HY (0.5 g) was added and the mixture was stirred at room temperature for the appropriate time (see Table). After completion of reaction, the mixture was poured into an ice cold water and extracted with ethyl acetate and the catalyst filtered off. After evaporation of the solvent, the diacetate could be purified by column chromatography by eluting with Hexane:EtOAc (8:2). In case of 9 $\alpha$ ,15-epoxy africanane (entry 7),<sup>12</sup> 10 mg of the epoxide was taken in a 5 ml round bottom flask contain 0.5 ml of acetic anhydride



**Table.** Ring Opening of Epoxides to Acetylated Diols with Acetic Anhydride over Zeolite HY

Entry	Substrate	Product	Yield (%)	Time (hrs)
1.		 1a	85	10
2.		 2a	90	12
3.		 3a	95	9.5
4.		 4a	95	10
5.		 5a	85	11
6.		 6a	90	14
7.		 7a	85	18

after stirring for 5 min zeolite HY (20 mg) was added and the reaction mixture was stirred for 18 h then after usual work up the corresponding diacetate obtained 85% yield.

In conclusion, we have described a mild, highly efficient and convenient method for the opening of epoxides with acetic anhydride and are promoted by zeolite HY. All the diacetate obtained are in high yields under same experimental conditions studied. The catalyst can be reused without any loss of activity.



**1,2-Diacetoxy-cyclohexane 1a:**<sup>6</sup> Bp 116–118°C, IR (neat)  $\nu_{(\max)}$ : 1735, 1730, 1239, and 1095  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.75 (d, 2H,  $J=16$  Hz), 2.02 (br s, 6H), 1.23–1.75 (m, 8H). EIMS:  $m/z$  (%) 200 [ $\text{M}^+$ ] (3), 142 (87), 141 (5), 99 (45), 81 (80), 70 (8), and 43 (100). Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_4$ : C, 59.98; H, 8.05. Found: C, 59.86; H, 8.08.

**1,2-Diacetoxy-1-phenyl-ethane 2a:**<sup>7</sup> Bp: 119–120°C, IR (neat)  $\nu_{(\max)}$ : 3010, 1738, 1730, and 1360  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.3 (br s, 5H), 6.0 (dd, 1H,  $J=7.2$ , 5.1 Hz), 4.3 (2H, m), 2.08 (br s, 3H), 2.11 (s, 3H). EIMS:  $m/z$  (%) 222 [ $\text{M}^+$ ] (3), 195 (4), 164 (31), 150 (11), 122 (15), 107 (35), 105 (100), 91 (93), 77 (46), 57 (9), and 43 (93). Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ <sup>7b</sup>: C, 68.85; H, 6.35. Found: C, 64.82; H, 6.41.

**1,2-Diacetoxy-hexane 3a:**<sup>8</sup> Bp 107–108°C, IR (neat)  $\nu_{(\max)}$ : 2940, 1736, 1732, 1262, and 1130  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.01 (m, 1H), 3.96 (dd, 1H,  $J=8.1$ , 6.2 Hz), 4.2 (dd, 1H,  $J=5.1$ , 3.2 Hz), 2.05 (d, 6H,  $J=16$  Hz), 1.6 (br s, 6H), 0.89 (t, 3H). EIMS:  $m/z$  (%) 202 [ $\text{M}^+$ ] (2), 171 (51), 158 (4), 142 (3), 129 (8), 127 (10), 111 (25), 97 (12), 69 (75), 57 (18), 55 (41), and 43 (100). Anal. Calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_4$ : C, 59.39; H, 8.97. Found: C, 59.28; H, 8.95.

**1,2-Diacetoxy-3-chloro-propane 4a:**<sup>9</sup> Bp 95–96°C, IR (neat)  $\nu_{(\max)}$ : 1736, 1730, 1240, 1080, and 720  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.18 (m, 1H), 4.19 (dd, 1H,  $J=10$ , 8.1 Hz), 4.36 (dd, 1H,  $J=8.2$ , 4.5 Hz), 3.65 (t, 2H), 2.08 (s, 3H), 2.12 (s, 3H). EIMS:  $m/z$  (%) 135 [ $\text{M}^+$ -AcOH] (10), 119 (22), 76 (14), 60 (6), 57 (70), and 43 (97). Anal. Calcd for  $\text{C}_7\text{H}_{11}\text{ClO}_4$ <sup>9a</sup>: C, 43.20; H, 5.70; Cl, 18.22. Found: C, 43.41; H, 5.92; Cl, 18.25.

**1,2,3-Triacetoxy-propane 5a:**<sup>10</sup> Bp 258–259°C, IR (neat)  $\nu_{(\max)}$ : 1746, 1734, 1728, 1330, 1242, and 1165  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.2 (m, 1H), 4.12 (dd, 2H,  $J=10$ , 6.1 Hz), 4.4 (dd, 2H,  $J=6.1$ , 4.2 Hz), 2.1 (br s, 9H). EIMS:  $m/z$  (%) 218 (28), 176 (27), 148 (8), 129 (12), 120 (9), 102 (20), 85 (47), 72 (27), and 60 (24). Anal. Calcd for  $\text{C}_9\text{H}_{14}\text{O}_6$ : C, 49.54; H, 6.47. Found: C, 49.47; H, 6.50.

**3-(4-Methylphenoxy)-1,2-diacetoxy-propane 6a:**<sup>11</sup> Bp 163–165°C, IR (neat)  $\nu_{(\max)}$ : 3030, 1742, 1733, and 1280  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.05 (d, 2H,  $J=12$  Hz), 7.78 (d, 2H,  $J=10$  Hz), 5.31 (m, 1H), 4.42 (dd, 1H,  $J=7.5$ , 5.1 Hz), 4.23 (dd, 1H,  $J=10$ , 7.5 Hz), 4.18 (t, 2H), 2.3 (s, 3H), 2.1 (s, 3H), 2.08 (s, 3H). EIMS:  $m/z$  (%) 266 (3), 154 (8), 159 (62), 147 (8), 121 (15), 108 (35), 91 (15), 57 (8), and 43 (100). Anal. Calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_5$ : C, 63.15; H, 6.81. Found: C, 63.10; H, 6.84.

**9,15-Diacetoxyafricanane 7a:**<sup>12</sup> IR (neat)  $\nu_{(\max)}$ : 1735, 1740, 1260, and 1095  $\text{cm}^{-1}$ ,  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.62 (d, 1H,  $J=13$  Hz), 4.12 (d, 1H,  $J=13$  Hz), 2.04 (s, 3H), 2.02 (s, 3H), 1.5–1.9 (m, 7H), 0.95 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H), 0.52 (m, 2H), 0.18 (m, 1H). EIMS:  $m/z$  (%) 262



[M<sup>+</sup>-AcOH] (4), 220 (6), 207 (12), 202 (36), 187 (20), 159 (30), 133 (10), 107 (20), 95 (40), and 55 (100). Anal. Calcd for C<sub>19</sub>H<sub>30</sub>O<sub>4</sub>: C, 70.77; H, 9.38. Found: C, 70.80; H, 9.35.

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