

Rearrangement of epoxides to carbonyl compounds in the presence of reusable acidic zeolite catalysts under mild conditions

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Rearrangement of 4-substituted styrene oxides with acidic zeolite catalysts in the presence of polar solvents at room temperature gives the corresponding 4-substituted phenylacetaldehydes in high yields. The procedure has been applied successfully to the rearrangement of disubstituted epoxides. The zeolite can be easily recovered, regenerated by heating and reused.

KEY WORDS: rearrangement; epoxide; 4-substituted styrene oxides; zeolites; carbonyl compounds.

1. Introduction

Substituted epoxides are versatile compounds for organic syntheses due to their ready availability and easy transformation to a wide range of organic compounds [1–4]. Several catalytic systems have been developed for the rearrangement of epoxides to carbonyl compounds. These include Brønsted or Lewis acids [5–8], including $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [9–11], lithium salts [12], MgBr_2 [13,14], $\text{Pd}(\text{OAc})_2$ in the presence of phosphine ligands [15], InCl_3 [16], $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ [17], $\text{Er}(\text{OTf})_3$ [18], $\text{Sn}(\text{OTf})_2$ [19] and hydrated BiOClO_4 [20]. Unfortunately, most such catalytic reagents create a number of environmental disadvantages, such as the production of large quantities of toxic or corrosive waste resulting from the use of stoichiometric quantities. Moreover, the rearrangement reactions mostly need to be carried out at high temperatures for long reaction times.

Major effort has therefore been made to find environmentally friendly processes for the rearrangement of epoxides. The use of solid catalysts can overcome many of the limitations associated with the use of solution phase Lewis or Brønsted acid catalysts. The nature and proportions of the products are dependent largely on the types of catalyst used. In particular, various types of zeolites, such as HY, HZSM-5 and offretite, effect the rearrangement of styrene oxide, at 95 °C in toluene, to give a good yield of phenylacetaldehyde [21–24]. Also, rearrangements of different epoxides have been reported over acidic zeolites at 200–300 °C in the gas phase [25].

We have shown that solid catalysts [26] can have advantages in alkylation [27], acylation [28,29], methanesulfonylation [30], bromination [31], chlorination

[32] and nitration [33,34] of aromatic compounds. Therefore, we decided to investigate the scope and limitations of rearrangement reactions of epoxides and to try to develop a simple process, involving mild conditions. We have already given a preliminary account of some of the results [35]. We now report the full details of this work.

2. Experimental

2.1. Materials

Chemicals were purchased from Aldrich Chemical Company and used without further purification. Commercial zeolites were purchased from Aldrich Chemical Company or provided as gifts from Zeolyst International. All zeolite catalysts were freshly calcined at 400 °C for a minimum of 4 h prior to use.

2.2. Analysis and characterisation of the products

^1H and ^{13}C NMR spectra were recorded on an AV400 Bruker spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C measurement.

Product mixtures from the rearrangement reactions of epoxides (Schemes 1–5) were subjected to gas chromatography on a Philips PU 4400 gas chromatograph, fitted with an HP-1 (100% dimethylpolysiloxane; 30 m, 0.32 mm ID) column. The product from rearrangement of 1,2-epoxyoctane (**7**) was quantified by the use of a DB-225 (50% cyanopropylmethylsilicone, 50% methylphenylsilicone; 30 m, 0.25 mm ID) column. The GC conditions used for analysis were: 100 °C for 1 min, ramped to 160 °C at 15 °C/min and held for 1 min. The injection temperature was 200 °C and the detection temperature 250 °C. Hexadecane was used as an internal standard.

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Styrene oxide (**1a**) is a commercial material and was used without further purification. 4-Substituted styrene oxides **1b–f**, *trans*-stilbene oxide (**3a**), *cis*-stilbene oxide (**3b**), 1,1-diphenylethene oxide (**6**) and 1,2-epoxyoctane (**7**) were prepared according to literature procedures [36–40].

The structures of products **2**, **4**, **5** and **8**, obtained from the rearrangement reactions of the corresponding epoxides **1**, **3**, **6** and **7**, were confirmed by their ^1H and ^{13}C NMR spectra, and were identical to those reported in the literature [41–51].

2.3. Typical experimental procedure for the rearrangement of 4-substituted styrene oxides **1** in the presence of acidic zeolite catalysts

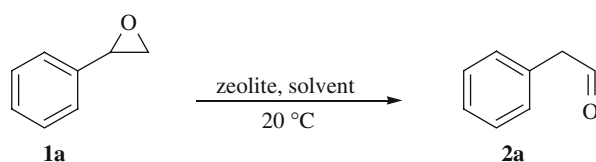
Quantities are recorded in the footnotes to the appropriate tables or text. All reactions were carried out under a nitrogen atmosphere in a 100 ml two necked round bottomed flask equipped with a water condenser and a magnetic stirrer. In a typical experiment, epoxide **1** (8.3 mmol) was directly added to a mixture of freshly calcined zeolite catalyst and chloroform (10 ml) and the mixture was stirred at 20 °C for the appropriate reaction time. Samples (1 ml) were withdrawn periodically, hexadecane (0.2 g) was added as internal standard, and the aliquot was filtered to remove the zeolite before analysis by gas chromatography. When the reaction was complete, the bulk sample was filtered and the catalyst was washed with CHCl_3 (3×30 ml), then the solvent was removed under reduced pressure. ^1H NMR spectroscopy was used to identify and quantify the product **2** [41–46].

2.4. Experimental procedure for the rearrangement of *trans*-stilbene oxide (**3a**), *cis*-stilbene oxide (**3b**) and 1,1-diphenylethene oxide (**6**) in the presence of acidic zeolite catalysts

The procedure was identical to that used for the rearrangement of 4-substituted styrene oxides **1**, except that **3a**, **3b** or **6** (1.0 g, 5.1 mmol) was used in CHCl_3 (10 ml) at 20 °C under nitrogen. The reaction mixture was worked up and the product was identified and quantified by GC and NMR [47–50].

2.5. Experimental procedure for the rearrangement of 1,2-epoxyoctane (**7**) in the presence of acidic zeolite catalysts

A mixture of **7** (1.0 g, 7.0 mmol) and zeolite catalyst (0.5 g) in CHCl_3 (10 ml) was heated at the appropriate temperature for the appropriate reaction time under a nitrogen atmosphere. The reaction mixture was worked up and the product was identified and quantified by GC and NMR [51].



Scheme 1. Catalytic rearrangement of styrene oxide (**1a**).

3. Results and discussions

Initially, we investigated the rearrangement of styrene oxide (**1a**) to phenylacetaldehyde (**2a**) (Scheme 1), over the zeolite HZSM-5 (Si/Al = 75) in toluene as solvent at 95 °C, as described in the literature [21]. The yield of phenylacetaldehyde (**2a**) was 77%. Although the yield was good, and the GC trace showed no other products, the yield was much less than the quantitative yield reported in the literature. Further investigation revealed that the remaining styrene oxide was converted into polymeric material that did not show up in the gas chromatographic analysis.

In order to test the effect of the solvent in this process, several reactions of styrene oxide (**1a**) were carried out over zeolite HZSM-5, under identical conditions except for the nature of the solvent. The reactions were conducted at 20 °C in order to allow differences in rates of reaction to be revealed. The results obtained are recorded in Table 1.

The results indicated that the yield of **2a** obtained was high after just 30 min when the reaction was carried out in diethyl ether (entry 6), acetone (entry 10), chloroform (entry 11) or dichloromethane (entry 12). However, the yield was low in methanol (entries 8 and 9), even after 4 h, presumably due to the weakening of the acidity of the catalytic sites by hydrogen bonding to methanol.

Table 1
Influence of solvent on the rearrangement of styrene oxide (**1a**) according to Scheme 1 in the presence of HZSM-5^a

Entry	Solvent	Reaction time (h)	Conversion (%) ^b	Yield (%) of 2a ^c
1	Toluene	0.5	28	26
2	Toluene	2	47	37
3	Toluene	5	71	59
4	Hexane	0.5	16	15
5	Hexane	5	82	78
6	Et ₂ O	0.5	94	88
7	Et ₂ O	1	97	85
8	MeOH	0.5	17	16
9	MeOH	4	49	47
10	MeCOMe	0.5	100	77
11	CHCl_3	0.5	100	79
12	CH_2Cl_2	0.5	70	66
13	CH_2Cl_2	2	96	84

^aHZSM-5 (Si/Al = 75; 0.5 g) and **1a** (8.3 mmol) in solvent (10 ml) at 20 °C under N_2 for the indicated reaction time.

^bDecrease in amount of **1a** by quantitative GC.

^cCalculated from GC and ^1H NMR. Numbers expressed as percentages have been rounded to the nearest whole number.