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## Ring opening of epoxides with alcohols using $\text{Fe}(\text{Cp})_2\text{BF}_4$ as catalyst

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## ABSTRACT

$\text{Fe}(\text{Cp})_2\text{BF}_4$  is an efficient catalyst for the alcoholysis of aromatic, aliphatic, and cyclic epoxides giving excellent yields of the corresponding  $\beta$ -alkoxy alcohols under ambient conditions. The methanolysis of styrene oxide using  $\text{Fe}(\text{Cp})_2\text{BF}_4$  as a catalyst (5 mol %) gave excellent yield of 2-methoxy-2-phenylethanol with complete regio-selectivity. The ring opening of cyclic epoxides gave 77–97% yields of *trans*- $\beta$ -methoxy alcohols, in 0.5–6 h. The use of 1,2-epoxyhexane and 1,2-epoxydodecane as substrates gave both regioisomers in excellent yields. The first order rate of reaction with respect to catalyst was observed for the kinetics of ring opening of 1,2-epoxyhexane with methanol.

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The ring opening of epoxides with various nucleophiles gives a variety of 1,2-disubstituted compounds.<sup>1</sup>  $\beta$ -Alkoxy alcohols are valuable intermediates in the direct synthesis of  $\beta$ -alkoxy ketones<sup>2</sup> and also this functionality is present in some natural products.<sup>3</sup> The ring opening of epoxides with alcohols requires either strongly acidic or basic conditions due to the poor nucleophilicity of alcohols.<sup>4</sup> The harsh conditions associated with this process have provided the impetus to develop mild methodologies.

Various heterogeneous catalysts<sup>5</sup> have been successively developed for the ring opening of epoxides with primary alcohols. Simple, general and efficient catalysts for the alcoholysis of epoxides have also been developed using transition metals and lanthanides salts,<sup>6</sup> porphyrin metal complexes,<sup>7</sup> salen and salophen complexes,<sup>8</sup> DDQ,<sup>9</sup> tetracyanoethylene (TCNE)<sup>10</sup> and organotin phosphate condensates.<sup>11</sup>

Some of these methods suffer from the use of expensive, hazardous and moisture sensitive catalysts, long reaction times and use of high catalyst loading. In our earlier reports we have used  $\text{Fe}(\text{Cp})_2\text{PF}_6$  as a catalyst for the cyanosilylation and the Strecker reaction of ketones and aldehydes under solvent-free conditions at room temperature.<sup>12</sup> Recently, we have reported  $\text{Fe}(\text{Cp})_2\text{BF}_4$  as a catalyst for the ring opening of epoxides with amines.<sup>13</sup> Herein, we report the use of commercially available  $\text{Fe}(\text{Cp})_2\text{BF}_4$  as an efficient catalyst for the ring opening of epoxides with representative alcohols at 25 °C (Fig. 1).

In our initial investigations, we have carried out the ring opening of styrene oxide with methanol (5 mL, 61.8 equiv) using

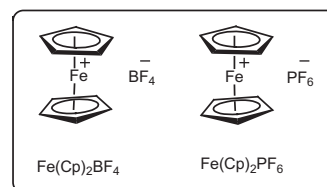


Figure 1. Structure of catalysts.

$\text{Fe}(\text{Cp})_2\text{BF}_4$  (5 mol %) as a catalyst at 25 °C.<sup>14</sup> The styrene oxide **1** was converted to 2-methoxy-2-phenyl ethanol (**2a**) in >99% after 5 min. The catalyst loading was decreased to 2 mol % and also gave 98% conversion after 40 min. The amount of methanol was decreased to 8 equiv, styrene oxide **1** was completely consumed and gave 81% yield of the desired product **2a** with 19% other impurities (Table 1, entry 4).

We have compared the reactivity of  $\text{Fe}(\text{Cp})_2\text{BF}_4$  (5 mol %) for the methanolysis of styrene oxide with various catalysts under identical reaction conditions, which has been reported in the literature. The catalyst  $\text{Fe}(\text{Cp})_2\text{BF}_4$  shows a better reactivity compared to  $\text{Fe}(\text{Cp})_2\text{PF}_6$ ,  $\text{InCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$  and  $\text{ZrCl}_4$  (Table 1, entries 2 and 5–10). In the absence of catalyst the conversion of product was determined to be only 4% after 24 h.

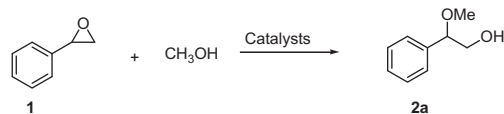
We have also studied the ring opening of styrene oxide **1** with primary, secondary and tertiary alcohols using  $\text{Fe}(\text{Cp})_2\text{BF}_4$  (5 mol %) as a catalyst at 25 °C. The excellent conversions of styrene oxide to 2-alkoxy-2-phenyl ethanol (**2b–e**) were observed in 15–30 min. (Table 2).

The ring opening of 1,2-epoxyhexane **3** with methanol was carried out using  $\text{Fe}(\text{Cp})_2\text{BF}_4$  (2 mol %) as a catalyst at 25 °C.<sup>14</sup> We

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**Table 1**  
Ring opening of styrene oxide **1** with methanol using various catalysts<sup>a</sup>



Entry	Catalyst	Time	Conversion <sup>b</sup> (%)
1	Fe(Cp) <sub>2</sub> BF <sub>4</sub>	5 min	>99
2	Fe(Cp) <sub>2</sub> PF <sub>6</sub>	12 min	99
3	Fe(Cp) <sub>2</sub> BF <sub>4</sub>	40 min	98 <sup>c</sup>
4	Fe(Cp) <sub>2</sub> BF <sub>4</sub>	20 min	81 <sup>d</sup>
5	InCl <sub>3</sub>	3 h	81
6	FeCl <sub>3</sub>	3 h	99
7	CoCl <sub>2</sub>	24 h	9
8	Ti(O <sup>i</sup> Pr) <sub>4</sub>	24 h	–
9	ZrCl <sub>4</sub>	20 min	98
10	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	20 min	91
11	No catalyst	24 h	4

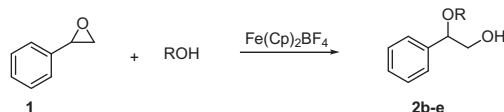
<sup>a</sup> Epoxide (2 mmol) was cooled to 0–5 °C then catalyst (5 mol %) and methanol (61.8 equiv, 5 mL) were added and stirred at 25 °C for the specified time.

<sup>b</sup> The conversion of epoxide to the product **2a** was determined by GC.

<sup>c</sup> Catalyst (2 mol %) was used.

<sup>d</sup> Methanol (8 equiv) was used and epoxide was consumed, but 19% impurities were observed.

**Table 2**  
Fe(Cp)<sub>2</sub>BF<sub>4</sub> catalysed ring opening of styrene oxide with different alcohols<sup>a</sup>



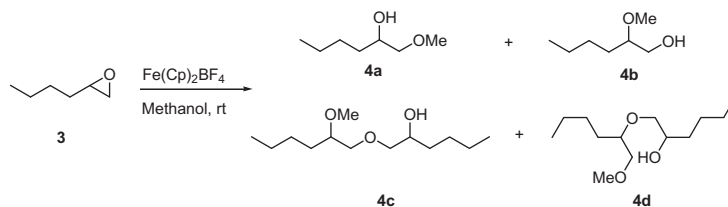
Entry	R	Time (min)	Yield <sup>b,c</sup> of <b>2b–e</b> (%)
1	Et	15	98 (99)
2	<sup>n</sup> Pr	30	98 (>99)
3	<sup>i</sup> Pr	30	99 (99)
4	<sup>t</sup> Bu	30	98 (99)

<sup>a</sup> Epoxide (2 mmol) was cooled to 0–5 °C, then Fe(Cp)<sub>2</sub>BF<sub>4</sub> (5 mol %) and alcohols (5 mL) were added and stirred at 25 °C for the specified time.

<sup>b</sup> The reaction was monitored by GC and conversions are shown in parenthesis.

<sup>c</sup> The % yield was measured after filtration of crude material through a pad of Celite.

**Table 3**  
Ring opening of 1,2-epoxyhexane (**3**) with methanol using Fe(Cp)<sub>2</sub>BF<sub>4</sub> as a catalyst<sup>a</sup>



Entry	CH <sub>3</sub> OH equiv	Time (h)	Conversion of epoxide <sup>b</sup>	Ratio <sup>c</sup> of <b>4a:4b</b>	Selectivity of products <b>4a</b> and <b>4b</b> <sup>d</sup> (%)	Selectivity of products <b>4c</b> and <b>4d</b> <sup>d</sup> (%)
1	1	4.5	91	2.47:1	57	43
2	2	5	94	1.77:1	80	20
3	4	4.15	82	1:57:1	90	10
4	6	5.15	78	1.66:1	93	7
5	8	7	89	1.65:1	95	5
6	Excess (10 mL)	20	95	1.47:1	99	1

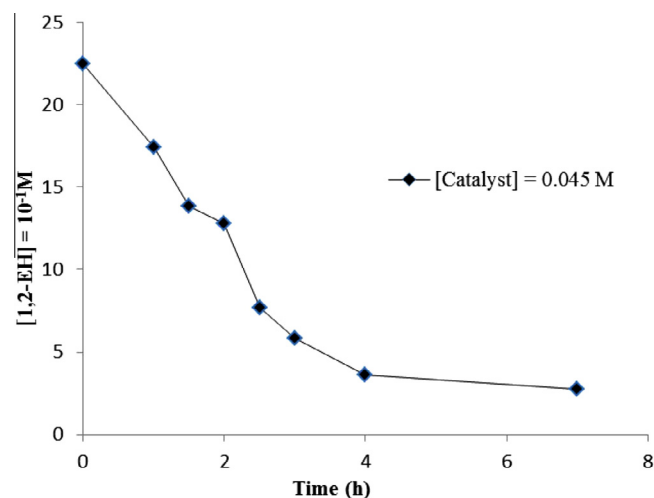
<sup>a</sup> Epoxide (2 mmol) was cooled to 0–5 °C, Fe(Cp)<sub>2</sub>BF<sub>4</sub> (2 mol %), then methanol were added and stirred at 25 °C for the specified time.

<sup>b</sup> The conversion of epoxide to products was monitored by GC.

<sup>c</sup> The ratio of regioisomers **4a:4b** was determined by GC.

<sup>d</sup> The products **4c** and **4d** were confirmed by GCMS and the % selectivity of products **4a** and **4b** = (GC area of **4a** and **4b**/GC area of all products **4a–4d**) × 100.

have obtained four products in which the major two are regioisomeric products **4a** and **4b**, which are obtained from the ring opening of 1,2-epoxyhexane **3** by an attack of methanol at the terminal carbon, as well as the secondary carbon. Other by-products **4c** and **4d** were formed by the ring opening of 1,2-epoxyhexane (**3**) with initially formed products **4a** and **4b**. The regioisomers **4a** and **4b**, which were isolated and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy and GCMS data. The by-products **4c** and **4d** were not possible to isolate by column chromatography and instead were characterized only by GCMS. We have investigated the effect of methanol on the rate of reaction and selectivity of the products. The ring opening of 1,2-epoxyhexane (**3**) with methanol (1 equiv) gave 91% conversion of epoxide and a ratio of regioisomeric product **4a:4b** of 2.47:1 with a poor selectivity (57%) (Table 3, entry 1). The amount of methanol was increased up to 8 equiv was increased the reaction time and the selectivity of products (**4a** and **4b**) was improved up to 95% with a comparable regioisomeric ratio (Table 3, entries 2–5). When we used a large excess of methanol (10 mL) the reaction time was increased to 20 h and



**Figure 2.** Time dependent plot of conversion of 1,2-epoxyhexane (**3**) to products catalysed by Fe(Cp)<sub>2</sub>BF<sub>4</sub>; [catalyst] = 0.045 M and [1,2-EH] = 22.50 × 10<sup>-1</sup> M.

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