INTRODUCTION

There is a continued interest in the regioselective ring opening of oxiranes to the corresponding vicinal halohydrins. Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations. The reaction is typically performed with hydrogen halides, but the harsh reaction conditions and the low observed regioselectivity in the opening of unsymmetrical epoxides have prompted a search for more selective and milder procedures. Recently, it has been found that epoxides can be converted into halohydrins by means of elemental halogen, but this method has limitations such as low yield, long reaction times, low regioselectivity and formation of acetonide byproducts in addition to the expected iodo adduct. Furthermore, iodination does not occur in aprotic solvents other than acetone.

ABSTRACT

There is a continued interest in the regioselective ring opening of oxiranes to the corresponding vicinal halohydrins. Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations. The ring opening of epoxides with elemental bromine and nano catalyst ZrO₂ affords vicinal bromo alcohols in high yields. This new procedure occurs regioselectively under neutral and mild conditions in various aprotic solvents even when sensitive functional groups are present.

Key words: Ring opening, epoxides, regioselective, bromine, nano catalyst, alcohols.
In conjunction with ongoing work in our laboratory on the synthesis and formation of complex heterocyclic compounds containing donor nitrogen atoms, with neutral molecules such as iodine,[3-5] we found out that ZrO₂ with frame nano efficiently catalyzed the addition of elemental bromine to epoxides under mild reaction conditions with high regioselectivity (Scheme 1).

**EXPERIMENTAL**

NMR spectra were recorded by a Bruker Avance 300 MHz spectrometer locked on deuterium from solvent. Chemical shifts (δ [ppm]) were calculated from chemical shift of deuterium lock and were not calibrated. FTIR spectra were measured on Perkin Elmer 2000 spectrometer in KBr pellets (1/200).

Epoxide (1 mmol) in CH₂Cl₂ (5 mL) was added to a stirred ZrO₂ catalyst (0.15 mmol) in at room temperature. Next, a solution of elemental Bromine (1 mmol) in CH₂Cl₂ (5 mL) was added portion-wise (15 min) to the above mixture. The progress of the reaction was monitored by TLC. After complete disappearance of the starting material, the reaction mixture was washed with 10% aqueous Na₂S₂O₃ (2×10 mL) and water (2×10 mL). The aqueous layer was extracted with CH₂Cl₂ (2×10 mL). The combined organic layer was dried over anhydrous MgSO₄ and evaporated to give crude alcohol–catalyst.

**RESULTS**

In this study, we wish to report the results of the reactions of some epoxides with elemental bromine and Iodine in the presence of a sub-stoichiometric amount of ZrO₂ (Scheme 1, Table 1).

![Scheme 1: Synthesis bromohydrin by ZrO](image.png)

R = Alkyl, Aryloxy, Phenyl

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>(%mol) catalyst</th>
<th>Time (h)</th>
<th>Isolate yield (%)</th>
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<tr>
<td>1</td>
<td>-</td>
<td>10</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>10</td>
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<td>50</td>
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<tr>
<td>3</td>
<td>MeOH</td>
<td>10</td>
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<td>30</td>
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<tr>
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<tr>
<td>5</td>
<td>CCl₄</td>
<td>10</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>CH₃CN</td>
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</tr>
<tr>
<td>7</td>
<td>H₂O</td>
<td>10</td>
<td>24</td>
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<tr>
<td>8</td>
<td>CH₂Cl₂</td>
<td>10</td>
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<td>80</td>
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<tr>
<td>9</td>
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<td>15</td>
<td>5min</td>
<td>98</td>
</tr>
<tr>
<td>10</td>
<td>CH₂Cl₂</td>
<td>20</td>
<td>5min</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 1: Ring opening 3-phenoxy-1,2-epoxypropane
The crude products were purified on a column of silica gel. The solvent was evaporated and pure halohydrin was obtained. The halohydrins obtained throughout this procedure were identified by comparison, where possible, with authentic samples prepared in accordance with literature procedures.

1-Bromo-2-boutanol (99%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 0.95 \text{ (t, 3H, } J=7.2\text{Hz), 1.55-1.7 (m, 2H), 3.05-3.25(m, 1H), 3.3-3.5 \text{ (m, 1H), 3.75-3.8(m, 1H).} \]
\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 0.95 \text{ (t, 3H, } J=7.2\text{Hz), 1.55-1.7 (m, 2H), 3.05-3.25(m, 1H), 3.3-3.5 \text{ (m, 1H), 3.75-3.8(m, 1H).} \]

2-Bromo Cyclohexanol (97%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 1.2-1.6(m, 4H), 1.8-1.9 (m, 1H), 2.0-2.2(m, 2H), 2.4-2.5(m, 1H), 3.5-3.65(m, 1H), 3.95-4.05(m,1H);MS(EI) M/Z 226( M+); IR(KBr) 3425, 2960 cm-1 \]

2- Bromo -1-(4-Chlorophenyl)ethanol (96%):

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.45(br, 1H), 3.45-3.5 (m, 2H), 4.80-4.88(m, 1H), 7.2-7.4(m, 4H);MS(EI) M/Z 226( M+); IR(KBr) 3460, 2960 cm^{-1} \]

2- Bromo -1-phenyl ethanol (98%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.50(br, 1H), 3.39-3.55 (m, 2H), 4.75(m, 1H), 7.25-7.4(m, 4H);MS(EI) M/Z 282( M+); IR(KBr) 3460, 2960 cm^{-1} \]

1- Bromo-3-(4-methoxyphenyl)2-propanol (98%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.05(br, 1H), 2.85(d, 2H, J=6.2, 9.2Hz), 3.25 (dd, 1H, J=4.8,9.2 Hz), 3.35 (dd, 1H, J=3,8,9.2Hz), 3.6-3.75(m, 1H), 3.80(S, 3H),6.85(d, 2H,J=8.2Hz), 7.15(d, 2H, J=8.2 Hz); ^13\text{CNMR (CDCl}_3,50\text{Hz}) \delta 14.67, 41.66, 55.10, 71.62, 113.92, 128.98, 130.12, 158.25;MS (EI) M/Z 292 (M+); IR(KBr) 3560, 3050, 2960 cm^{-1} \]

1- Bromo -3-(4-acetylphenoxy)2-propanol (99%)

yellow Solid, mp 68-700 C, \[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.55(S, 3H), 3.30-3.50 (m,2H), 3.90-4.05 (m, 3H), 6.90(d, 2H,J=7.8Hz), 7.9(d, 2H, J=7.8Hz); ^13\text{CNMR (CDCl}_3,50\text{Hz}) \delta 8.84, 26.21, 69.12, 70.15, 114.66, 130.64, 162.75, 196.96; MS (EI) M/Z 320 (M+); IR(KBr) 3460, 3020, 2970, 1710 cm^{-1} \]

1- Bromo -3-(4-Chlorophenoxy)2-propanol (97%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.40 (br, 1H), 3.35-3.40 (m,2H), 3.45-3.50 (m, 1H), 3.95-4.0 (m, 1H), 4.05-4.10(m, 2H), 6.85(d, 2H, J=8.2 Hz), 7.15(d, 2H, J=8.2 Hz); MS (EI) M/Z 312 (M+); IR(KBr) 3515 cm^{-1} \]

1-Bromo-3-phenoxo-2-propanol(98%)

\[ ^1\text{HNMR (CDCl}_3, 300\text{MHz}) \delta 2.40(br, 1H), 3.30-3.55 (m, 2H), 3.8-4.1(m, 3H), 6.75-7.0(m, 3H) 7.15-7.35(m,2H);MS(EI) M/Z 278(M+); IR (KBr) 3500 , 2985 cm^{-1} \]

**DISCUSSION**

In conclusion, this new method appears to be highly competitive with the other methods reported in the literature. The reaction occurs in neutral and mild conditions on the acid-sensitive substrates and vicinal halohydrins were obtained in high yields and region-selectivity. In addition, in comparison with our previous methods, ZrO₂ is cheaper, less step need for preparation, and overall yield is higher.

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**REFERENCES**