INTRODUCTION

Epoxides are among the most useful synthetic intermediates towards the synthesis of many biologically active compounds and a large variety of reagents are known for the ring opening of these compounds. Their electrophilic reactions with different nucleophilic anions have been an interesting subject in organic synthesis. Of these anions, the reaction of thiocyanate ion with epoxides has been widely studied and is a suitable method for the preparation of thiiranes. Other reagents such as phosphine sulfide, methylbenzothiazol-2-thione, and dimethylthioformamide have been reported to produce thiiranes from oxiranes. Usually with these sulfitating agents, several different Lewis acids such as RuCl₃, BiCl₃, and TiO(CF₃COO)₂ or a protic acid like TFA or oxalic acid have been employed as catalysts. More recently the β-cyclodextrin complexes and cyanuric chloride have been used for the conversion of oxiranes to thiiranes. However many of these methods suffer from using strongly acidic or oxidizing conditions, undesirable side reactions, long reaction time, high temperature, use of organic solvents and desulfuration of the resulting thiirane to the olefin.

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons, that are widely used in organic synthesis have posed a serious threat to the environment. Consequently methods that successfully minimize their use are the focus of much attention. Water as a solvent is safe, economical and environmentally benign. In view of the advantages of using water as a solvent, we explored the synthesis of various types of thiiranes from oxiranes and potassium thiocyanate in presence of 1,4-bis(triphenylphosphonium)-2-
butene dichloride as an efficient PTC in water at room temperature.

Phase transfer catalysts (PTCs) are powerful reagents in chemical transformations, the characteristics of which include mild reaction conditions, safety, operational simplicity and selectivity. PTCs are often used in nucleophilic displacement reactions to facilitate reactions between organic reactants and ionic inorganic salts. Although many phase transfer catalysts are known, Phosphonium salts are practically important and used in many of organic reactions.

EXPERIMENTAL

All products were characterized by $^1$H NMR, $^{13}$C NMR, IR and by comparison with authentic samples. The IR spectra were recorded on Bomem FT-IR spectrometer. $^1$H NMR and $^{13}$C NMR spectra were taken on a 400 MHz Bruker spectrometer. The C, H, P analyses were performed by the microanalytical service of research institute of petroleum industry (N. I. O. C). Melting points were measured on a mettler FP5 apparatus. 1,4-bis(triphenylphosphonium)-2-butene dichloride was prepared and other chemicals were purchased from the Merck chemical company Darmstadt, Germany. The purity determination of the products and reaction monitoring were accomplished by TLC on polygram SILG/UV 254 plates.

Preparation of 1,4-Bis(triphenylphosphonium)-2-butene Dichloride (BTPBDC)

To a solution of 1,4-dichlorobutene (0.625g, 5 mmol) in CHCl$_3$ (10 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was added triphenylphosphine (2.62g, 10 mmol). The reaction mixture was refluxed on a water bath for 2.5 h. The solution was cooled to room temperature and then, while vigorously stirred, diethylether was added dropwise until an oily product separated. The ether was removed by decantation and acetone (40 mL) was added. Stirring the acetone solution for 40 min afforded a white precipitate which was filtered, washed with acetone (20 mL) and dried. Yield 2.596g (80%), m.p. 278-279 °C. IR (KBr): $\tilde{\nu}$ = 3053(m), 2755(w), 1613(m), 1575(s), 1478(s), 1437(s), 1258(s), 754(s), 693(s), 556(s) Cm$^{-1}$. $^1$H NMR(CDC13): $\ddot{\gamma}$ = 5.7 (dd, JPH=15.7, JHH=8, 4H), 6.3 (m, 2H), 7.7-8.0 (m, 30H). $^{13}$C NMR, (CDCl3): $\ddot{\gamma}$ = 20.7, 120.8, 132.15, 134.2, 137.01, 140.17. Anal. Calcd: C, 73.055; H, 5.5396; P , 9.5421. found: C, 73.9599; H, 5.5469; P , 9.5531%.

RESULTS AND DISCUSSION

1,4-bis(triphenylphosphonium)-2-butene dichloride [BTPBDC] was easily prepared by reacting 1,4-dichlorobutene with triphenylphosphine in chloroform under reflux condition (Scheme 1). The reaction is very clean and phase transfer catalyst can be easily precipitated in acetone.

We examined the catalytic ability of BTPBDC for conversion of epoxides to thiiranes. Therefore, phenyl glycidyl ether (1 mmol) was reacted with potassium thiocyanate (1 mmol) in the presence of BTPBDC in different solvents. The results were clearly shown water was the best solvent among those tested. TLC analysis was showed at room temperature, conversion was completed after 2.5 h and corresponding thiirane was produced in 87% isolated yield. According to obtained results, this catalyst acted very efficiently and it was observed that only 0.2 M equivalent of the catalyst is enough to convert different epoxides carrying electron donating or with-drawing groups to their corresponding thiiranes in high isolated yields (Scheme 2, Table 1).

It is noteworthy that no evidence for the formation of olefins as by-product of the reaction was observed. In organic solvents; the reaction did not complete after 3 h and was contaminated by diol and thiocyanohydrine formation. In the absence of...
catalyst, the conversion of oxiranes was very slow and the yields were also very low (20% in 6 h). It is believed that BTPBDC can catalyze the formation of thiiranes from epoxides in the aqueous phase in two ways. Firstly by swelling in the aqueous media it can act as phase transfer catalyst for the epoxides, and can therefore provide the necessary microenvironment for the water-soluble nucleophile, that is, SCN\(^-\), to be in the vicinity of the epoxides for the reactions to occur. Secondly, the phosphonium functionalities on these catalyst can interact as a Lewis acid with the oxygens of the epoxides to facilitate the attack of the thiocyanate anion as the nucleophile. It is worthy to note that the reaction medium was almost neutral, sensitive functionalities such as carbon-carbon double bonds remain intact.

Table 1: Reaction of different epoxides with KSCN using BTPBDC as catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product(s)a</th>
<th>Time(h)</th>
<th>Yieldb(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{Ph})</td>
<td>(\text{PhS})</td>
<td>2.5</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>(\text{PhCH}_2)</td>
<td>(\text{PhCH}_2)</td>
<td>2.5</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>(\text{ClCH}_2)</td>
<td>(\text{ClCH}_2)</td>
<td>3</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>(\text{CH}_2\text{CHCH}_2\text{OCH}_2)</td>
<td>(\text{CH}_2\text{CHCH}_2\text{OCH}_2)</td>
<td>2</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>(\text{(CH}_3\text{)_2CHOCH}_2)</td>
<td>(\text{(CH}_3\text{)_2CHOCH}_2)</td>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>(\text{CH}_3\text{CH}_2\text{CH}_3\text{OCH}_2)</td>
<td>(\text{CH}_3\text{CH}_2\text{CH}_3\text{OCH}_2)</td>
<td>2.5</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>(\text{CH}_3\text{H}_2\text{O}\text{O}\text{O}\text{CH}_3)</td>
<td>(\text{CH}_3\text{H}_2\text{O}\text{O}\text{O}\text{CH}_3)</td>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>(\text{CH}_3\text{CH}_2)</td>
<td>(\text{CH}_3\text{CH}_2)</td>
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<td>9</td>
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<td>(\text{CH}_3\text{CH}_2)</td>
<td>3.5</td>
<td>85</td>
</tr>
</tbody>
</table>

*Products were identified by compared of their physical and spectral data with those of authentic samples.

\[\text{Cl}\text{ClCl} + 2 \text{PPh}_3 \xrightarrow{\text{CHCl}_3, \text{Reflex}} \text{PPh}_3 + \text{2Cl}^- + \text{PPh}_3\]

Scheme 1

\[\text{O} \xrightarrow{\text{KSCN, H}_2\text{O, r.t.}} \text{S} \xrightarrow{\text{BTPBDC, r.t.}} \text{R}\]

Scheme 2
In conclusion, we have developed a novel, eco-friendly, and efficient protocol for the synthesis of thiiranes with KSCN using 1,4-bis(triphenylphosphonium)-2-butene dichloride as a catalyst. This method offers several advantages including mild reaction conditions, high conversions, short reaction times and high isolated yields. It can be emphasized that the reaction is clean and from economical and environmental points of view, use of water as solvent is favorable than organic solvents.

ACKNOWLEDGEMENTS

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REFERENCES