CHAPTER 4

SYNTHESIS OF INTERMEDIATE II: TETROL
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4.0 Introduction

As discussed in the last chapter, the formation of diol from chloroepoxyalkane resulted in an increase in the refractive index from 1.430 of chloroepoxyalkane to 1.534 of diol. Beside this, diol formation is accompanied by the incorporation of –SH group in the molecule, which is important for achieving monomer with high refractive index to develop the plastics of desired quality. In order to take it further towards the development of the desired monomer, it was essential to enhance the number of –SH groups per molecule. For this, diol has been further reacted for its dimerisation to form the tetrol. In this chapter, the synthesis of tetrol is discussed.

Tetrol is the second intermediate formed during the synthesis of polythiols. Tetrols belong to the class of polyhydric alcohols, which contain three or more –OH groups. Examples of polyhydric alcohols are pentaerythritol, di-pentaerythritol and tri-pentaerythritol. Tetrol has been synthesized as intermediate – II from diol. The formation of the second intermediate from the first intermediate involves parameters such as molar ratio of reagents, temperature and time of the reaction. The effect of various parameters involved in the formation of the second intermediate from diol has been studied.
4.1 Preparation of tetrol

Sodium sulfide has been used to introduce thio ether links during the dimerization of diol. The use of sodium sulfide for the introduction of sulphide bonds has been well reported in literature such as the sulphide bonds being formed during the formation of diethylmercaptoacetal from diethyl bromoacetal as described in Fig. 4.1.

![Chemical Structure](image)

**Diethyl bromoacetal**

**Diethyl mercaptoacetal**

Fig. 4.1: An example of formation of sulfide linkage for dimerization of halo compounds such as diethyl bromoacetal to form diethyl mercaptoacetal.

The reaction of sodium sulfide with halo alkanes involves the formation of thio ether bonds. Taking this knowledge further, in the present work reactions were carried out to convert diol into tetrol by the use of sodium sulfide. The effect of reaction parameters such as molar ratio of sodium sulfide, reaction temperature and reaction time were studied. The results obtained are presented in the following sections:

During gradual addition of sodium sulfide to diol, a continuous change in pH of the solution was observed. The initial pH of the reaction mixture which consists of the diol only, was 5.2 indicating the acidic nature. The pH of sodium sulfide solution used for the reaction was 13.0. As the addition of sodium sulfide to diol was started a change in pH was observed as indicated in the graph (Fig.4.2).
Fig. 4.2: Effect of addition of Na$_2$S on pH of tetrol indicating that with the addition of Na$_2$S, the pH of the reaction mixture increases sharply to 10.0 in the beginning of addition. The pH remains around 10.0 till the end of the addition carried out in an hour. The change in the pH of the reaction mixture during reaction is presented in Fig. 4.3.

It could be seen that the pH of the solution as addition took place increased from 5.2 to 10.0, during the initial addition of sodium sulfide. The pH remained around 10.0 till the complete addition of sodium sulfide. When reaction mixture was allowed to react and pH of the mixture studied with time, the reduction of pH was observed. As indicated in Fig. 4.3, the pH falls to 8.0 after half an hour of reaction.
time. This clearly indicates that a reaction is taking place between
diol and sodium sulfide, within half an hour of the reaction time as
seen from the change in the pH of the solution from 10.0 to 8.0. When
the reaction was allowed to proceed for longer time the pH of the
solution remains unchanged (Fig 4.3).

![Graph showing pH of tetrol over time](image)

**Fig. 4.3:** Effect of reaction time on pH of tetrol of the reaction
mixture to obtain tetrol. The decrease in pH from 10.0
to 8.0 indicates the formation of tetrol and
disappearance of sodium sulfide.

The change in pH of the reaction mixture could possibly be due to the
reaction taking place as per the scheme presented in **Fig. 4.4.**
Fig. 4.4: Scheme of reaction taking place between diol and sodium sulfide. Disappearance of sodium sulfide and formation of sodium chloride

First, the sodium sulfide dissociates into the sodium and sulfide ions. Then the sulfide ion dimerized the diol while the sodium ion combine with the chloride ion. By the way, the formation of sodium of sodium chloride with the disappearance of sodium sulfide can also be understood from the fact that the sodium chloride is known to have a pH of 8.17 (Table-4.1). The formation of sodium chloride was further confirmed by the confirmatory qualitative test for chloride.

Attachment of sulfide ion to diol resulting in the formation of a C-S-C bond between two diol moieties leading to the formation of tetrol. The sodium ions react with chloropropane diol to form sodium chloride. The sulfur atom forms a covalent bond between two diol moieties to form a tetrol having four hydroxyl groups and three thio ether bonds.
The analysis of tetrol for parameters such as elemental content, hydroxyl value and sulfur content could not be carried out due to the presence of water in the reaction mixture, which interfered with the analysis. Sulfur content was tried to be determined by bomb calorimeter as per ASTM 1448(1991), outlined in Chapter 2. On combustion in the bomb calorimeter, the sample was burnt out completely leading to charring of the sample. Further analysis of the sample, therefore, could not be carried out.

**Table-4.1: pH of reactants and products: indicating the formation of sodium chloride as a by-product.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol</td>
<td>5.47</td>
</tr>
<tr>
<td>Aqueous sodium sulfide solution (40% by weight)</td>
<td>13.09</td>
</tr>
<tr>
<td>Aqueous sodium chloride solution (40% by weight)</td>
<td>8.17</td>
</tr>
<tr>
<td>Tetrol</td>
<td>7.95</td>
</tr>
</tbody>
</table>

Even though, the effect of molar ratio of sodium sulfide to diol could not be studied for the various compositional parameters, the mixture of sodium sulfide and diol having different ratios were studied for the formation of polythiol which was ultimate objective of this work. As can be seen from the **Table-4.2** the ratio of 0.5 mole of the sodium sulfide and 1.0 mole of diol gives the yield of polythiol (Chapter 6) as per the expected times. Any further rise in sodium sulfide content resulted in no additional advantage. This further demonstrates that for dimerization, half a mole of sodium sulfide per mole of sodium
sulfide is sufficient for the diol formation of tetrol as the reaction scheme presented in Fig.4.4.

In order to understand the degree of conversion of diol to tetrol the techniques were adopted as a) HPLC b) TLC c) NMR spectroscopy d) Yield of polythiol.

Table-4.2: Effect of molar ratio of sodium sulfide on the yield of polythiol: The yield of polythiol remains approximately the same for all molar ratios indicating the molar ratio of 0.5:1.0 of sodium sulfide and diol is the optimum for this purpose.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Molar ratio (M) Na₂S:Diol</th>
<th>Yield (%) of polythiol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.5:1.0</td>
<td>86.16– 86.30</td>
</tr>
<tr>
<td>2.</td>
<td>0.6:1.0</td>
<td>86.30 – 86.50</td>
</tr>
<tr>
<td>3.</td>
<td>0.7:1.0</td>
<td>86.30 – 86.50</td>
</tr>
<tr>
<td>4.</td>
<td>0.8:1.0</td>
<td>86.80 – 87.00</td>
</tr>
<tr>
<td>5.</td>
<td>0.9:1.0</td>
<td>86.80 – 87.00</td>
</tr>
<tr>
<td>6.</td>
<td>1.0:1.0</td>
<td>86.85 – 87.00</td>
</tr>
</tbody>
</table>

4.2 Effect of molar ratio

To study the effect of molar ratio of sodium sulfide on tetrol formation, sodium sulfide solutions of 0.5 M- 1.0M were used for converting the diol into tetrol. The tetrol that was formed during the reaction was analyzed for parameters such as elemental content, hydroxyl value and sulfur content. However, probably due to the presence of water in the reaction mixture leading to interference the analysis could not be carried out.
Analysis of the above parameters involved heating the sample which in turn leads to charring of the sample accompanied by the emission of strong sulfur smelling fumes. An attempt was made to separate water from the reaction mixture by carrying out azeotropic distillation using toluene as a solvent.

This again leads to charring and decomposition of the sample due to which the process of distillation could not be completed. Sulfur content was tried to be determined by bomb calorimeter as per ASTM 1448(1991), outlined in Chapter two. On combustion in the bomb calorimeter, charring of the sample took place. Further analysis of the sample, therefore, could not be carried out.

Since all the known methods applied for the studying the compositional parameters of tetrol failed, the effect of molar ratio on tetrol formation was studied by studying its effect on the formation of the final product i.e., polythiols as already stated above.

Since the yields of polythiols obtained with all the molar ratios of sodium sulfide are similar, it is evident that 0.5 M of sodium sulfide is sufficient to give good yields of polythiol. The yield of polythiols that was obtained from the yield of tetrol, it is clear that the tetrol is completely formed using 0.5 M of sodium sulfide.

Based on the results of yields of polythiols from the tetrol obtained from the different molar ratios of sodium sulfide and diol (0.5:1.0, 0.6:1.0, 0.7:1.0, 0.8:1.0, 0.9:1.0, 1.0:1.0) it was evident that for the desired quality and yield of polythiols (final product), the optimum molar ratio of sodium sulfide and diol was 0.5:1.0 and hence, all
other necessary studies related to process optimization of tetrol were conducted keeping this ratio constant. The effect of temperature and effect of time, thus, were studied by taking 0.5 mole of sodium sulfide per mole of diol and the reaction was carried out of different temperature ranges and time period. Here, it may be noted again that the synthesis of tetrol were carried out under different conditions of reactions but the optimization was done only through the results of formation of polythiol.

4.3 Effect of temperature

Following the optimization of molar ratio of reagents, the effect of temperature on color yield and its values are given in the Table 4.3. The polythiol obtained at temperatures of 25-30°C, 30-35°C and, 35-40°C, was found to be clear and transparent as indicated by the b values while the product obtained at a reaction temperature of 45-50°C and 55-60°C, was found to be deep yellow as indicated by the “b” values. This could be due to the decomposition of tetrol at higher temperatures of 45-50°C and 55-60°C leading to the formation of colored by-products such as disulfides. Since the highest yield of polythiol was obtained at a temperature range of 30-40°C, it clearly indicates that a temperature range of 30-40°C is the most suitable temperature for tetrol formation.
Table-4.3: Effect of temperature on tetrol formation understood through the color and yield of polythiol synthesized from the tetrol obtained under different temperature conditions. The b-values determined on the UV spectrophotometer indicates that colorless polythiol could only be obtained from tetrol synthesis at temperature < 40 °C; Tetrol synthesized at > 40 °C gave yellow colored polythiol.

<table>
<thead>
<tr>
<th>Molar ratio Na₂S:Diol</th>
<th>Temp. (°C)</th>
<th>Yield (%) of polythiol</th>
<th>b-value</th>
<th>Color of polythiol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1.0</td>
<td>25 - 30</td>
<td>86.70</td>
<td>23.5</td>
<td>Colorless</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>30 - 35</td>
<td>88.00</td>
<td>24.1</td>
<td>Colorless</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>35 - 40</td>
<td>88.00</td>
<td>23.7</td>
<td>Colorless</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>40 - 45</td>
<td>86.00</td>
<td>30.5</td>
<td>Light yellow color</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>45 - 50</td>
<td>85.00</td>
<td>38.2</td>
<td>Light yellow color</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>50 - 55</td>
<td>--</td>
<td>--</td>
<td>Discoloration</td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>55 - 60</td>
<td>--</td>
<td>--</td>
<td>Discoloration, decomposition with irritating odor.</td>
</tr>
</tbody>
</table>

*Note: b-value of distilled water was 23.9.

4.4 Effect of reaction time

After having optimized the molar ratio and reaction temperature required for the formation of tetrol, studies were carried out to study the effect of reaction time on tetrol formation again through the yield and quality of polythiol. For this, polythiol was synthesized from the tetrol obtained by the reaction of sodium sulfide and diol for a period of 1 hour, 2 hour and 3 hours. The results of the yield and the color of polythiol obtained from the tetrol synthesized at 35°C – 40°C for different time periods have been seen in Table-4.4. It is evident that
the desired time for formation is one hour. There is no change if the
tetrol is synthesized for longer period.

The optimization of the reaction of tetrol has been done by the two
ways: a) through the evaluation of the yield and quality of polythiol
and b) through the evaluation of tetrol by HPLC and TLC. The molar
ratio of 0.5:1.0 of sodium sulfide and diol respectively and
temperature range of 35°C – 40°C were kept constant and the HPLC
and TLC studies of the reaction mixture were carried out at different
time intervals. The results of the HPLC and TLC present here have
been used to study formation of tetrol.

**Table-4.4: Effect of time on tetrol formation understood through
the –SH (%) and yield of polythiol synthesized from
the tetrol obtained under different time conditions. There is not much change in the yield of polythiol and
–SH %.

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Molar ratio Na₂S:Diol</th>
<th>Temp. (°C)</th>
<th>b value</th>
<th>Yield (%) of polythiol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5:1.0</td>
<td>35-40</td>
<td>23.7</td>
<td>86.70</td>
</tr>
<tr>
<td>2</td>
<td>0.5:1.0</td>
<td>35 – 40</td>
<td>23.7</td>
<td>87.00</td>
</tr>
<tr>
<td>3</td>
<td>0.5:1.0</td>
<td>35-40</td>
<td>23.7</td>
<td>88.00</td>
</tr>
</tbody>
</table>

**Formation of tetrol as studied by HPLC and TLC:**

The HPLC analysis of the tetrol after a reaction time of 1 hr, 2 hrs and
3 hrs is shown in **Fig.4.5 (a-d)**. HPLC analysis indicates the
disappearance of the peak due to diol within one hour indicating the
formation of tetrol to be taking place within an hour.

First peak was observed at a retention time of 11.21 minutes, second
peak was observed at a retention time of 28.30 minutes and the third
peak was observed at a retention time of 43.39 minutes as shown in Fig. 4.5 (b-d). The peak at 48.39 minutes was observed to be the most intense peak, which could be attributed to the presence of tetrol as the major component. The other peaks could be due to the presence of by-products formed during the reaction the nature of which has not been identified. By the way, the tetrol obtained from the reaction at different time interval provided the right quality of polythiol indicating that these by-products and did not affect the quality of the product. The HPLC analysis therefore, indicates that one-hour is the optimum time required for the tetrol formation.

TLC of tetrol synthesized at one hour of reaction time indicated the presence of two spots having a retention factor (Rf) of 0.91 and 0.81

Fig. 4.6. Since TLC is not as sensitive a technique as HPLC only two spots are observed in TLC indicating the presence of two components while three peaks were observed in HPLC. This clearly indicates that one of the three components is present in such low amounts, that it could not be observed in TLC.

Structural elucidation of tetrol was carried out by $^{13}$C-NMR spectroscopy.

The NMR confirmed that tetrol is the major product as indicated in Fig. 4.7. The presence of five major peaks at the following peak positions confirms the presence of five different carbon atoms as follows:
Peaks due to impurities were also present in the spectra. The spectra Fig.4.7 also indicate the presence of other impurities in minor amounts which, however, does not interfere in the formation of the final product.

The sp³ hybridized carbon at C₁ and C₄ absorb upfield and show absorption value at 61.71 ppm and 70.97 ppm respectively. There are five equivalent sp³ hybridized carbons in tetrol. The presence of substituent affects the nature of the absorption. There are three electronegative groups in tetrol with hydroxyl group being the most electronegative followed by sulfur. C₃ shows absorption at 35.39 ppm. C₂ and C₅, which are attached to sulfur atom, show a downfield absorption at 38.28 ppm and 38.95 ppm respectively.
Fig. 4.5(a-d): HPLC spectra of tetrol: Effect of reaction time on the synthesis of tetrol indicating the reaction of diol to form tetrol
**Fig. 4.6:** TLC of diol and tetrol indicating the formation of tetrol from diol: two spots indicate the formation of tetrol and other by-products formed during the reaction.

**Fig. 4.7:** $^{13}$C- NMR spectra of tetrol indicating the presence of 4 hydroxyl groups at C1 and C4 and the presence of two thio-ether group at C3 and C5.
4.5 Conclusion

From the results of the studies presented here, following conclusions can be drawn:

a) The diols having \(-\text{C} - \text{S} - \text{C} -\) linkage can be dimerized by creating a linkage at the carbon atom having halogen group (Chlorine), using sodium sulfide. The dimerization of diol, which means formation of four hydroxyl groups having \(-\text{C} - \text{S} - \text{C} -\) linkages, takes place with exothermic reaction when diol is reacted with sodium sulfide.

b) Formation of sodium chloride, lowering of pH, change in viscosity are found to be the major process control parameters.

c) The following process conditions are found to be optimum for the desired results:

<table>
<thead>
<tr>
<th>Process condition</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol: Na$_2$S ratio</td>
<td>1: 0.5 mole</td>
</tr>
<tr>
<td>Temperature range</td>
<td>35-40°C</td>
</tr>
<tr>
<td>Time of addition</td>
<td>1 hour</td>
</tr>
<tr>
<td>Time of reaction</td>
<td>3 hours</td>
</tr>
</tbody>
</table>

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