CHAPTER – 2

Synthesis of Bisphenol-C and its derivatives
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Synthesis of Bisphenol-C and its derivatives

The current research work is based on synthesis of bisphenol-C and its derivatives. This chapter is further sub-divided into three sections

2.1 Materials and reagents

Benzyl chloride, methyl chlorofomate, ethyl chlorofomate, methyl chloroacetate, ethyl chloroacetate, isopropyl chloroacetate and butyl chloroacetate were purchased from Spectrochem Pvt. Ltd. (Mumbai). Cyclohexanone and o-cresol were purchased from Allied Chemicals (Vadodara). Phenol was purchased from Spectrochem Pvt. Ltd. (Mumbai). Potassium bromide was purchased from RFCL Ltd. (New Delhi). Bromine was purchased from Loba Chemie Pvt. Ltd. (Mumbai). Potassium carbonate (K₂CO₃) was purchased from Siscochem Pvt. Ltd. (Mumbai). Chloroform (CF), tetrahydrofuran (THF), acetonitrile (ACN) and acetic acid (CH₃COOH) were purchased from Allied Chemicals (Vadodara) and used as received. Reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel GF254 plates (E-Merck Co) by using appropriate solvent systems. Melting points were determined in open capillaries and are uncorrected.

Section-I: Synthesis of 1,1’-bis(R, R’-4-hydroxyphenyl)cyclohexane

1,1’-Bis(4-hydroxyphenyl)cyclohexane (BC) and 1,1’-bis(3-methyl-4-hydroxy phenyl) cyclohexane (MEBC) were synthesized according to reported methods [1,2].

Cyclohexanone (0.5 mol) was treated with phenol/o-cresol (1.0 mol) in presence of mixture of HCl: CH₃COOH (2:1 v/v, 100:50 ml) as a Friedel-Crafts catalyst at 55°C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filter through a cotton plug. The yellowish solution obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC/MEBC were crystallized repeatedly from methanol-water system to get pure, white, shining crystals. The yield
and m.p of BC and MEBC were 81 and 77 \%; and 186° and 192°C, respectively. The reaction scheme and plausible reaction mechanism are as under:

\[
\text{Phenol/o-Cresol} \quad 0.5 \text{ mol} \quad \text{Cyclohexanone} \quad 1.0 \text{ mol} \quad \text{HCl : CH}_2\text{COOH} \quad 2:1 \text{ V/V} \quad 55 \text{ °C, 4h}
\]

**Plausible reaction mechanism**


Section-II: Synthesis of 1,1’-bis(3,5-dibromo-4-hydrophenyl)cyclohexane (TBBC)

1-1’-Bis(3,5-dibromo-4-hydrophenyl)cyclohexane was synthesized according to reported method [3].

TBBC was prepared by reacting 10 mmol BC in 15 ml acetonitrile, 40 mmol KBr in 10 ml water and 50 mmol bromine at 30°C. The white precipitates of TBBC was obtained instantaneously following KBr₃ addition. The reaction mixture was stirred for another 5 min at 30°C to complete the reaction. Hydrazine hydrate (80%, 40ml) was added to destroy the residual bromine. The product was separated from the mother liquor by vacuum filter, washed twice with distilled water and dried in an oven at 50°C. TBBC was crystallized repeatedly from methanol to get pure, white and shining crystals. The yield of TBBC was ~96% and m.p. was 137°C.

Plausible reaction mechanism

Section III: Synthesis of bisphenol-C derivatives

Bisphenol-C derivatives were synthesized according to reported methods [4-7].

General reaction procedure

A 100 ml round bottomed flask containing 1 mmol BC or MEBC, 2.5 mmol anhyd. K$_2$CO$_3$, 0.1 mmol PEG-600 and 2.5 mmol benzylchloride (Scheme-I) or alkylchloroacetates (Scheme-II) or alkyl chloroformates (Scheme-III) in 15 ml THF was placed in a water bath and temperature was raised to reflux with stirring for 1-2.5 h. The reaction was monitored by TLC. The reaction mixture was poured in a large excess of cold water and transferred into a 500 ml separating funnel. Chloroform (25ml) was added into the separating funnel, and organic layer was washed with water (50 ml x 3). The organic solvent was removed under vacuum to afford crude compounds. The compounds were crystallized three times from ethyl acetate. The analytical data are reported in Table 2.1

![Scheme-I](image1)

**Scheme-I**

![Scheme-II](image2)

**Scheme-II**


Plausible reaction mechanisms

**Ar = Phenyl rings**

**Sn^2 transition state**

- **Cl^-**

**Sn^1 transition state**

**Ar = Phenyl rings, R = Methyl & Ethyl**

**Sn^2 transition state**

- **Cl^-**

**Ar = Phenyl rings, R = Methyl, ethyl, isopropyl, & butyl**

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Structures of different bisphenol-C derivatives
### Table 2.1. Analytical data of bisphenol-C derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.F.</th>
<th>M.W.</th>
<th>M.P. °C</th>
<th>Reaction Time, h</th>
<th>% Yield</th>
<th>R&lt;sub&gt;f&lt;/sub&gt; value</th>
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</thead>
<tbody>
<tr>
<td>BC-1</td>
<td>C&lt;sub&gt;32&lt;/sub&gt;H&lt;sub&gt;32&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>448</td>
<td>195</td>
<td>2.5</td>
<td>83</td>
<td>0.63(B)</td>
</tr>
<tr>
<td>BC-2</td>
<td>C&lt;sub&gt;22&lt;/sub&gt;H&lt;sub&gt;24&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>384</td>
<td>123</td>
<td>1.0</td>
<td>78</td>
<td>0.74(A)</td>
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<td>BC-3</td>
<td>C&lt;sub&gt;24&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>412</td>
<td>107</td>
<td>1.0</td>
<td>80</td>
<td>0.69(A)</td>
</tr>
<tr>
<td>BC-4</td>
<td>C&lt;sub&gt;24&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>412</td>
<td>88</td>
<td>1.0</td>
<td>94</td>
<td>0.82(A)</td>
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<td>BC-5</td>
<td>C&lt;sub&gt;24&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>440</td>
<td>70</td>
<td>1.0</td>
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<td>C&lt;sub&gt;24&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>468</td>
<td>59</td>
<td>1.5</td>
<td>93</td>
<td>0.61(B)</td>
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<td>C&lt;sub&gt;30&lt;/sub&gt;H&lt;sub&gt;40&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>496</td>
<td>244</td>
<td>2.5</td>
<td>91</td>
<td>0.70(B)</td>
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<td>MEBC-1</td>
<td>C&lt;sub&gt;34&lt;/sub&gt;H&lt;sub&gt;36&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>476</td>
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<td>2.0</td>
<td>84</td>
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<td>412</td>
<td>126</td>
<td>1.0</td>
<td>87</td>
<td>0.64(A)</td>
</tr>
<tr>
<td>MEBC-3</td>
<td>C&lt;sub&gt;26&lt;/sub&gt;H&lt;sub&gt;32&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>88</td>
<td>1.0</td>
<td>94</td>
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<td>C&lt;sub&gt;26&lt;/sub&gt;H&lt;sub&gt;32&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>496</td>
<td>122</td>
<td>1.5</td>
<td>89</td>
<td>0.69(B)</td>
</tr>
<tr>
<td>MEBC-7</td>
<td>C&lt;sub&gt;32&lt;/sub&gt;H&lt;sub&gt;44&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>524</td>
<td>243</td>
<td>2.5</td>
<td>91</td>
<td>0.79(B)</td>
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</table>

(A) Hexane : Ethyl acetate (80:20 v/v)
(B) Chloroform : Methanol (70:30 v/v)