Synthesis of Bisphenols

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Section A

General introduction, literature survey and application of bisphenol

Bisphenol are defined as compound containing of two phenols nuclei linked by a hydrocarbon bridge. The importance of bisphenols has increased continually with the growth of the plastic industry from about the end of the 1930 s. bisphenols are useful for the preparation of thermally stable polymer, epoxy resin, paints and varnishes.[1-3] The condensation products of phenols with cyclic hydroaromatic ketones are known as cardo (a loop) monomer. The monomer containing cardo group are very useful in synthesizing polymer with very specific properties such as enhanced thermal stability together with excellent solubility and film forming properties due to the back bone structure [4]. Bisphenols are useful for the preparation of polycarbonates that are useful as binders for charge transport molecules, and photogenerating pigments incorporated, for example, in to layered photoconductive imaging member[5]. 1,1-bis (4-hydroxyphenyl) cyclohexane and 1,1-bis (3-methly-4-hydroxypheny) cyclohexane are important monomer for the synthesis of diphenyl methane-4,4-disulphonyl chloride polymer. The polymer possesses excellent solubility in common solvents, good acid and alkali resistance and moderate biological activities against Escherichia coli and Aspergillus awamori microorganisms [6]. Windows and other articles made from dimethyl bisphenol cyclohexane monomer polycarbonates exhibits enhanced scratch resistance properties and Mw degradation existence properties as compared to traditional polycarbonate such windows and other articles made from dimethyl bisphenol
cyclohexane. Polycarbonate can be used in various applications including building, particularly in agriculture environment and in electronic devices [7]. The presence of cardo group in the polymer increases the softening point of aromatic polysulfon material was tested for Nox detection using a device made by thick layer technology [8]. Bisphenol like 1,1-bis(4-hydroxylphenyl)cyclohexane and 1,1,1-tris (4-hydroxy phenyl) ethane are preferred branching agent used in air craft window for flame resistance [9]. 1,1,1-tris(4-hydroxy phenyl) ethane is used as hardener for epoxy resins and as a branching agent in thermoplastics, polyester resins and thermoplastic molding [10,11]. Tris-hydroxylphenyl lower alkanes are important compounds as sensitivity enhancers for radiation-sensitive composition and elements [12]. 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane is a valuable monomer as polyimide precursors. Polyimide provides good thermal stability, chemical resistance, and excellent mechanical properties. These properties are enhanced by the usage of aromatic based monomer. Polyimide is high performance polymers with inherent radiation shielding properties [13]. Additionally polyimides have high thermal and dimensional stability, high compressive strength, and high flexural modulus, making them extremely useful for this application [14]. They are known to be resistant to solvent, acids, and alkanis, are flame retardant, and maintain their excellent mechanical properties even at high temperatures [15].

Ong et al. [16] reported the synthesis of 1,1-bis (p-hydroxy phenyl) cyclohexane. Charged a mixture of 98.15 gm of cyclohexanone, 470 gm of phenol, 1.0 gm of butanethiol and 150 mL of ethylene dichloride, to the mixture added 108 gm of chloromethyl silane through dropping funnel and reaction mixture was stirred, and
heated at 55-65 °C. After completion of reaction the mixture was filtered by suction filtration and the crude solid product obtained was slurried of in 500 mL of methylene chloride and filtered product was further washed twice with methylene dichloride and recrystalization from methanol water mixture through charcoalization affords with 76% yield [Fig. 4.1].

\[ \text{Fig. 4.1.} \]

Ashok Shyadligeri et al. [17] demonstrated the preparation of bisphenol by condensation of o-cresol with cyclohexenone in presence of HCl and catalyst. o-cresol (1091.4 gm) was treated drop wise with cyclohexanone (196.3 gm) at 60 °C and continued reaction further for 24 h and at 60 °C. The crude solid product obtained was slurried up in 500 mL methylene chloride. The resulting suspension was filtered and the filtered cake was washed with 500 mL methylene chloride then dried over night in a vacuum oven at 90°C. Crude compound was obtained as a pinkish purple solid in a yield of about 419 gm (71%) [Fig. 4.2].

\[ \text{Fig. 4.2.} \]

Kapila et al. [18] reported bis phenol synthesis using dodecyl benzene sulphonic acid as a catalyst and resorcinol as a promoter.
Charged o-cresol (250 gm, 2.3mole), cyclohexanone (45 gm, 0.45 mole), dodecylbenzenesulphonic acid (38 gm) followed by resorcinol (3.0 gm). The reactor contents were stirred at ambient temperature for 4 h. Then heated with stirring up to 55 °C and maintained for 8 h. The reaction mass was poured into 150 mL of toluene and stirred at ambient temp. for about 2 h the solid product was dried and washed with toluene 50mLx3 time. Crude product obtained with 70% yield. . [Fig. 4.3].

![Fig. 4.3.]

Weber et al. [19] reported 2, 2,6-bis (4-hydroxyl-3,5-dimethyl phenyl) by condensation of 2,6 xylenol and cyclohexanone using glacial acetic acid concentrated sulphuric acid and dimethyl sulphoxide. By combining 38ml of glacial acetic acid, 20 mL concentrated sulphuric acid and 0.5ml of dimethyl sulphoxide at 15 °C. A mixture of 114.53gm (0.94mol) of 2,6-dimethyl phenol and 20 mL of cyclohexanone were heated until all solid were dissolved. The solution was added drop by drop to the mixture and allowed to stirring for 90 min, the resulting mixture was a brown paste washed by 500mL distilled water and crude crop was washed with 0.5% sodium acetate and crystallization by chlorobenzene (Yield 33%) [Fig.4.4].

![Fig. 4.4.]

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Venkateshwara Rao et al. [20] reported the synthesis of 1, 1-bis (3-methyl-4-hydroxyphenyl) cyclohexane by condensing o-cresol and cyclohexanone using a mixture of hydrochloric acid and acetic acid. Cyclohexanone (49.0gm, 0.5mol) was treated with o-cresol (104 gm, 1.0 mole) in presence of a mixture of hydrochloric acid and acetic acid (150 mL, 2:1v/v) at room temperature for a week. Pink colored product separated out was dissolved in 2 molar NaOH solution and filtered to remove gummy product and then acidified to yield a yellowish product. Repeatedly leaching with benzene removed impurities of the product. Methanol solution of the residue was charcoalisde and then concentrated to gives product yield 77% [Fig. 4.5].

\[
\begin{align*}
\text{Acetic Acid} \\
\text{Hydrochloric Acid} \\
\text{At RT / one week}
\end{align*}
\]

Fig. 4.5.

Papava G.Sh et al. [21] reported the synthesis of bisphenol by condensing cyclopentanone with phenol and o-cresol using hydrochloric acid and butylmercaptan in 30.0% yield. [Fig. 4.6].

\[
\begin{align*}
\text{Acetic Acid} \\
\text{Hydrochloric Acid} \\
\text{BuSH}
\end{align*}
\]

Fig. 4.6.

Kozlov et al. [22] demonstrated synthesis of bis phenol by condensing o-cresol and cyclohexanone using polyphosphoric as a catalyst with moderate yield [Fig. 4.7].
McCloskey et al. [23] demonstrated the synthesis of tris(4-hydroxy phenyl)ethane by condensation of 194 moles of phenol, 345 gm sodium 3-mercaptopropanesulfonate as catalyst in the presence of sulphuric acid with 25 moles of 2,4 pentanedione at 50°C over a period of 22 h. compound was isolated by methylenedichloride. The crude product further washed with methylenedichloride. Isolated compound gave 55% yield and 95% purity with 4-5 %bisphenol [Fig. 4.8].

Udayakumar et al. [24] reported condensation of phenol and benzaldehyde using supported hetropolyacid at 100-110°C in the presence of solvent media such as benzene and toluene. After completion of the reaction, the mixture was poured in to 40% ethyl acetate solution. The obtained crude product was purified with the mixture of ethanol, ethylacetate and hexane .the process was repeated three times.gave isolated yield up to 42% [Fig.4.9].
Section B

Synthesis of bisphenol by using cyclic ketones

Introduction

From literature review it is quite clear that bisphenols are one of the extensively studied molecules and still there is scope for the development of improved methodology for its synthesis. With the present growing concern about controlling environmental pollution, safety aspect with respect to energy efficiency, operational simplicity, health and protecting future resources, the design of environmentally friendly chemical process has attracted considerable interest in organic synthesis.

Bisphenols have been synthesized by condensation of phenols with cyclic ketones, aliphatic ketones, aldehyde and acetophenone in the presence of various catalysts. Although these methods are suitable for synthesis of bisphenols but many of these methods are associated with one or more disadvantages such as prolonged reaction time, harsh reaction conditions and unsatisfactory yields, use of halogenated hydrocarbons solvent, excess use of phenols, tedious workup, charcoailiation, and generation large quantity of hazardous phenolic residue, multistep purifications and heavy pollution of chlorinated solvents.

Herein we wish to report for further development of better yields, short reaction time, mild reaction condition, simple purification methodology, and separation method, halogenated hydrocarbons solvent-free process, no use of charcoal using selective phase transfer catalyst. Phase transfer catalyst is one of the most important
and useful methods in synthetic organic chemistry because of its preparative advantages [25]. As a general technique for catalyzing reaction, phase transfer catalyst has been quite successfully used in a wide range of reactions, such as SN$_2$ type alkylations using C-, O-, S- and N-nucleophiles [26], dehydrohalogenations[27], oxidations and epoxidations [28], o-acylations [29], etherification reactions [30], aldol condensations [31] and isomerizations [32]. Transformation of starting materials in to desired final product usually required a number of chemical operations in which additional reagents, solvents etc are used. Thus, in the course of synthesis, besides the desired products, many waste materials are produced because transformation of educts in to products is not quantitative and selective process, particularly due to the use of these additional components. These wastes should be regenerated, destroyed and disposed, consuming much energy and creating heavy burden on the environment. Perhaps one of the most general and efficient methodologies that fulfill this requirements is phase transfer catalyst[33,34] It is therefore easy synthetic procedure which is applicable for industries with respect to reduce pollution, depletion of our finite environmental resources, optimal use of material and energy, efficient waste management can be recognized as important factor for environmental protection.

To realize this goal, we describe our successful results that led to an extremely convenient method for the synthesis of Bisphenols with appropriate quantity of catalyst, appropriate quantity of phenols, halogenated hydrocarbon solvent-free process, no charcoalization, and simplicity of the procedure, low energy consumption, minimization of industrial wastes in high isolated yields and purity of products.
Reaction scheme of Bisphenol synthesis [Fig 4.10]

\[ \text{OH} \ R \ (\text{CH}_2)_n \ \text{OH} \]
\[ \overset{\text{OH} \ R}{\overset{\text{Dry HCl}}{\text{(CH}_2)_n}} \overset{\text{OH}}{\text{OH}} \]
\[ n = 2 \text{ or } 4 \]

Fig.4.10.

Mechanism. [Fig.4.11]

\[ \overset{\text{O}^-}{\overset{\text{H}^+}{\overset{\text{HCl}}{\text{(CH}_2)_n}}} \overset{\text{H}^+}{\overset{\text{HCl}}{\text{(CH}_2)_n}} \overset{\text{H}^+}{\overset{\text{HCl}}{\text{(CH}_2)_n}} \overset{\text{H}^+}{\overset{\text{HCl}}{\text{(CH}_2)_n}} \]
\[ n = 2 \text{ or } 4 \]

Fig.4.11.
Cetyl trimethyl ammonium chloride catalyzed synthesis of 4, 4′-(cyclohexane-1, 1-diyl) bis (2-methylphenol)

To prove the catalytic activity of cetyl trimethyl ammonium chloride in the synthesis of 4,4′-(cyclohexane-1,1-diyl)bis(2-methylphenol), we initially conducted a blank reaction, in which o-cresol was reacted with cyclohexanone at 38-40 °C. in the presence of 3- mercaptopropionic acid and dry hydrochloric acid gas and after completion of reaction NaHCO₃ was added. The results showed that the reaction was very sluggish with fewer yields and formation of impurities was observed. However, addition of a catalytic amount of cetyl trimethyl ammonium chloride resulted in the yield improvement. The effect of amount of catalyst on the yield and rate was also investigated. It was found that 2.19x10⁻⁴ of catalyst was enough for fairly high yield. The lesser amounts gave a low yield even after long reaction time, and the more amounts could not cause the obvious increase in the yield of product. When the reaction was carried out at 38-40 °C with 2.19x10⁻⁴ mmole catalyst the maximum yield was obtained in a short reaction time (Table 1, entry 4). We chose to perform this reaction at 38-40 °C in the presence of 2.19x10⁻³ mmole of catalyst under solvent-free conditions. After optimizing the reaction conditions, series of bisphenols were synthesized and the results are summarized in Table 4.1.

\[ \text{Cetyl trimethyl ammonium chloride} \]

\[ \text{3-mercaptopropionic Acid} \]

\[ \text{Dry HCl} \]

\[ n = 2 \text{ or } 4 \]
Table 4.1

Reaction of 4, 4’-(cyclohexane-1, 1-diyl) bis (2-methylphenol) under different reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temperature °C</th>
<th>Time (h)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>60-65</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>No catalyst</td>
<td>38-40</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>9.38x10⁻⁵ mmol</td>
<td>38-40</td>
<td>6</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>2.19x10⁻⁴ mmol</td>
<td>38-40</td>
<td>4</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>4.38x10⁻⁴ mmol</td>
<td>38-40</td>
<td>4</td>
<td>94</td>
</tr>
</tbody>
</table>

Experimental

Melting point was determined in open capillaries and is uncorrected. 

¹H NMR spectra were recorded at room temperature on a Bruker “AVANCE 400” MHz spectrometer in DMSO-D6 using TMS as an internal standard. Reaction was monitored by Gas chromatography (Agilent7890/BP-5). Phenols and Ketones were purchased from Merck, India.
Typical experimental procedure for the synthesis of 4, 4’-(cyclohexane-1, 1-diyl) bis (2-methylphenol)

A 500 mL four-necked round bottom flask, fitted with an overhead stirrer, a gas inlet, a dropping funnel, a thermometer and a reflux condenser vented to a scrubber containing aqueous sodium hydroxide solution was assembled. Flask was charged with o-cresol (248 gm, 2.3 mole) 3-mercaptopropionic acid (2.7 gm) and cetyltrimethylammonium chloride (0.07 gm, 2.19x10^-4 mmole). The mechanical stirrer was turned on and saturated o-cresol with dry HCl at 38-40°C. Then added cyclohexanone (45 gm, 0.46 mole) through dropping funnel within 2 h at 40-42°C and the reaction mass was maintained for 4 h for completion of reaction. The progress of reaction was monitored by following the disappearance of cyclohexanone using Gas chromatography. After completion of reaction NaHCO₃ (10 gm) added slowly and reaction mixture was filtered using Buchner funnel. The wet cake was suction dried and washed with 25% aqueous methanol (50 mLx3).

**Purification:** The crude cake was dissolved in methanol (~375 mL at 50°C) and filtered through whatman 42. 1.5 gm Na₂SO₃ and 4.3 mL 25%H₂SO₄ were then added to the filtered solution and stirred for 1 h followed by addition of 3.4 mL 46% caustic lye solution. Then precipitation was carried out at 50 °C by addition of water and cooled to 40 °C and filtered using a Buchner funnel. The wet filtered cake was suctioned dried and washed with 25% aqueous methanol solution and dried in vacuum to afford the pure white crystalline compound in 94% yield. The purity of compound was checked by HPLC. The structure of compounds was confirmed on the basis of IR, ¹H NMR and mass spectra. Similarly the compounds of the
series shown in the Table 4.2 were synthesized by using above procedure and characterization data of same compound are given in Table 4.3.
Table 4.2

Percentage yield & reaction temperature in synthesis of bisphenols.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Phenol used</th>
<th>Cyclic ketone Used</th>
<th>Temp, °C</th>
<th>Time h</th>
<th>Product obtained</th>
<th>% Yield</th>
<th>% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o-Cresol</td>
<td>Cyclohexanone</td>
<td>40 - 42</td>
<td>4</td>
<td>![Product Image 1]</td>
<td>94</td>
<td>99.9</td>
</tr>
<tr>
<td>2</td>
<td>o-Cresol</td>
<td>Cyclopentanone</td>
<td>40 - 42</td>
<td>4</td>
<td>![Product Image 2]</td>
<td>88</td>
<td>99.75</td>
</tr>
<tr>
<td>3</td>
<td>o-Cresol</td>
<td>4-methyl cyclohexanone</td>
<td>40 - 42</td>
<td>4</td>
<td>![Product Image 3]</td>
<td>88</td>
<td>99.76</td>
</tr>
<tr>
<td>5</td>
<td>Phenol</td>
<td>Cycloheptanone</td>
<td>40 - 42</td>
<td>4</td>
<td>![Product Image 5]</td>
<td>87</td>
<td>99.80</td>
</tr>
<tr>
<td>Entry No.</td>
<td>Phenol used</td>
<td>Cyclic ketone Used</td>
<td>Temp °C</td>
<td>Time h</td>
<td>Product obtained</td>
<td>% Yield</td>
<td>% Purity</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>--------------------</td>
<td>--------</td>
<td>--------</td>
<td>------------------</td>
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<td>---------</td>
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<tr>
<td>7</td>
<td>Phenol</td>
<td>Cyclohexanone</td>
<td>40-42</td>
<td>4</td>
<td><img src="image1.png" alt="image" /></td>
<td>91</td>
<td>99.81</td>
</tr>
<tr>
<td>8</td>
<td>Phenol</td>
<td>4-methyl cyclohexanone</td>
<td>40-42</td>
<td>4</td>
<td><img src="image2.png" alt="image" /></td>
<td>89</td>
<td>99.86</td>
</tr>
<tr>
<td>9</td>
<td>2,6-Xylenol</td>
<td>Cyclohexanone</td>
<td>50-52</td>
<td>8</td>
<td><img src="image3.png" alt="image" /></td>
<td>60</td>
<td>98.82</td>
</tr>
<tr>
<td>10</td>
<td>2,6-Xylenol</td>
<td>Cyclopentanone</td>
<td>50-52</td>
<td>8</td>
<td><img src="image4.png" alt="image" /></td>
<td>61</td>
<td>99.77</td>
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</table>
Table 4.3
Characterization data of Bisphenols.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Product Obtained</th>
<th>Melting range °C</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
<th>λ max (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td>187-188</td>
<td>C₂₀H₂₄O₂</td>
<td>296.4</td>
<td>279</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image 2" /></td>
<td>161-162</td>
<td>C₁₉H₂₂O₂</td>
<td>282.37</td>
<td>279</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image 3" /></td>
<td>180-181</td>
<td>C₂₁H₂₆O₂</td>
<td>310.42</td>
<td>279</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image 4" /></td>
<td>158-160</td>
<td>C₂₁H₂₆O₂</td>
<td>310.42</td>
<td>278</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image 5" /></td>
<td>168-170</td>
<td>C₁₉H₂₂O₂</td>
<td>282.37</td>
<td>277</td>
</tr>
<tr>
<td>Entry</td>
<td>Product obtained</td>
<td>Melting range °C</td>
<td>Molecular formula</td>
<td>Molecular weight</td>
<td>λ max (nm)</td>
</tr>
<tr>
<td>-------</td>
<td>------------------</td>
<td>------------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td>6</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td>157-158</td>
<td>C_{17}H_{18}O_{2}</td>
<td>254.32</td>
<td>278</td>
</tr>
<tr>
<td>7</td>
<td><img src="image2.png" alt="Image 2" /></td>
<td>196-197</td>
<td>C_{18}H_{22}O_{2}</td>
<td>268.35</td>
<td>279</td>
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<tr>
<td>8</td>
<td><img src="image3.png" alt="Image 3" /></td>
<td>179-180</td>
<td>C_{19}H_{22}O_{2}</td>
<td>282.37</td>
<td>278</td>
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<tr>
<td>9</td>
<td><img src="image4.png" alt="Image 4" /></td>
<td>199-201</td>
<td>C_{22}H_{28}O_{2}</td>
<td>224.45</td>
<td>277</td>
</tr>
<tr>
<td>10</td>
<td><img src="image5.png" alt="Image 5" /></td>
<td>173-174</td>
<td>C_{21}H_{26}O_{2}</td>
<td>310.42</td>
<td>279</td>
</tr>
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</table>

Melting point of synthesized compounds was taken by open capillary method and are uncorrected.
Spectral discussion [35-38]

IR spectra [Fig. 4.13].

Representative of synthesized compounds were scanned for IR spectra on FTIR Model-Spectrum one, Make- PerkinElmer, using KBr. The characteristic absorption band of **1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane** are as follows and spectra are included after IR discussion of compound 1 and 2.

![Chemical structure](image)

1) 3406 cm\(^{-1}\) -Ar-O-H Stretching 
2) 3063 cm\(^{-1}\) Stretching aromatic ring. 
3) 2858 cm\(^{-1}\) –CH\(_3\)- Stretching in CH\(_3\). 
4) 1608 cm\(^{-1}\) –C=C Aromatic ring Stretching. 
5) 1451 cm\(^{-1}\) –C-C- Stretching in CH\(_3\). 
6) 1244 cm\(^{-1}\) -C-O- Phenolic stretching. 
7) 675-1000 cm\(^{-1}\) Aromatic ring bending.
Compound 2: **IR-spectra [Fig. 4.14].**

**1,1-bis(3-methyl-4-hydroxy phenyl)4-methyl cyclohexane**

![Chemical structure](image)

1. 3536 cm\(^{-1}\) –Ar-O-H Stretching frequency.

2. 3063 cm\(^{-1}\) (C-H) Stretching frequency in aromatic ring.

3. 2864 cm\(^{-1}\) –CH- Stretching in CH\(_3\).

4. 1607 cm\(^{-1}\) –C=C Aromatic ring Stretching.

5. 1107 cm\(^{-1}\) –C-C- Bending in CH\(_3\).

6. 1272 cm\(^{-1}\) -C-O- Phenolic stretching.

7. 817 cm\(^{-1}\) Aromatic ring bending.
Fig. 4.13 IR Spectrum of 1,1-bis (3-methyl-4-hydroxy phenyl) cyclohexane
Fig. 4.14 IR Spectrum of 1,1-bis (3-methyl-4-hydroxy phenyl) 4-methyl cyclohexane
$^1$H NMR Spectra [Fig. 4.15 and 4.16].

Purified compounds were scanned for $^1$H-NMR Spectra were recorded at room temperature on Brucker “AVANCE” 400 MHz in DMSO-D$_6$ using TMS as an internal standard. They show following characteristics peak.

The characteristic $^1$H NMR resonance peak values in $\delta$[ppm] of 1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane are as follows and spectra are included after $^1$H NMR discussion.

![Chemical Structure](image)

1) 1.40 ppm (s, 6H, methyl proton).
2) 2.10 ppm (t, 6H, cyclohexyl proton).
3) 2.50 ppm (t, 4H, cyclohexyl proton).
4) 6.63 ppm (d, 2H Aromatic proton).
5) 6.85 ppm (d, d, 2H Aromatic proton).
6) 9.01 ppm (2H, Phenolic proton).
7) 6.92 ppm (d, 2H Aromatic proton).
1,1-bis(3-methyl-4-hydroxyphenyl)-4-methyl cyclohexane [Fig. 4.17]

1. 1.44 ppm (m, 1H, cyclohexyl proton).
2. 1.54 ppm (q, 2H, cyclohexyl proton).
3. 2.50 ppm (t, 2H, cyclohexyl proton).
4. 6.95 ppm (d, 1H Aromatic proton).
5. 6.86 ppm (dd, 1H Aromatic proton).
6. 6.68 ppm (d,1H, aromatic proton).
7. 9.00 ppm (s,1H phenolic -OH proton)
Fig. 4.16 Expanded 'H NMR Spectrum of 1,1-bis (3-methyl-4-hydroxy phenyl)cyclohexane
Fig. 4.17 $^1$H NMR Spectrum of 1,1-bis (3-methyl-4-hydroxy phehnyl) 4-methyl cyclohexane
Mass Spectra Fig.[4.18].

Representative of the synthesized compounds of Bisphenols series (Table 4.4 and 4.5) were scanned for mass spectrum on Shimadzu GCMS QP 5050A make Shimadzu Corporation Japan, mode-DI. The probable fragments ions of 1,1-bis(3-methyl-4-hydroxy phenyl)cyclohexane Spectra are included after Table.

![Chemical Structure](image)

Table 4.4

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>M/Z</th>
<th>Probable fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>296</td>
<td><img src="image" alt="Structure" /> + *</td>
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<td>281</td>
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<td>5</td>
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<td><img src="image" alt="Molecule 5" /></td>
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<td>7</td>
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<td><img src="image" alt="Molecule 9" /></td>
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<td><img src="image" alt="Molecule 10" /></td>
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<tr>
<td>11</td>
<td></td>
<td><img src="image" alt="Molecule 11" /></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td><img src="image" alt="Molecule 12" /></td>
</tr>
</tbody>
</table>
C) Mass spectra [Fig. 4.19]

1,1-bis(3-methyl-4-hydroxy phenyl)4-methyl cyclohexane

![Chemical structure](image)

**Table 4.5**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molecular ion / fragment</th>
<th>m/z ratio</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td><img src="image" alt="Molecular ion structure" /></td>
<td>310 (Molecular ion)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Fragment structure" /></td>
<td>293</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>253 (Base peak)</td>
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<tr>
<td>---</td>
<td>-------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>254</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Molecular Structure" /></td>
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<td><img src="image" alt="Molecular Structure" /></td>
<td>227</td>
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<td>7</td>
<td><img src="image" alt="Molecular Structure" /></td>
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<tr>
<td>10</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>77</td>
</tr>
</tbody>
</table>
C.C. SHROFF RESEARCH INSTITUTE

Sample Information

Sample Name: SPL M-04.
Injection Volume: 1.000
Data File: D:\GC MS DATA\ACADEMIC\PATIL25.qgd
Method File: D:\GCMS METHODS\DI Ei(DB-5MS).qjm
Tuning File: C:\GCMSsolution\System\Tune1\PTBA\DB5MS.qgt

[Spectrum]

DI Ei MODE/(SCAN).

Fig. 4.18 Mass Spectrum of 1,1-bis (3-methyl-4-hydroxy pehenyl) cyclohexane
Fig. 4.19 Mass Spectrum of 1,1-bis (3-methyl-4-hydroxy phehyl) 4-methyl cyclohexane
Section C:

Synthesis of Bisphenols by using aromatic aldehydes and Ketones

Introduction:

While referring literature of the above class of compounds it was found wide applications as a hardener for epoxy resins and as a branching agent in thermoplastic resins. Such as polycarbonates and polyester resins. As such it is important that the material be pure and free of various possible isomers and impurities in the final product. A number of scientists in the past have tried to develop good synthetic path of such class of compound. Still there is scope for the development of improved methodology for its synthesis.

One of the challenges to research workers during the recent years has been to develop green procedures that are both environmentally desirable and economically acceptable. “Green chemistry” is considered as an integral part of a comprehensive program to protect the human health and the environment. Chlorinated hydrocarbon solvents used in industry are toxic, costly and problematic to use. Carrying out reaction with lesser amount or no solvent would lead to clean, efficient and economical process with the increasing environmental concerns and the regulatory constraints faced by chemical and pharmaceutical industries, development of environmentally benign organic reactions has become a crucial and demanding research in modern organic chemical research [39]. Considering these importance in mind, we have developed an improved simple, efficient procedure under solvent free reaction conditions with simple purification
methodology and minimum use of phenol and substituted phenol quantity in high yield and extremely high purity compounds.

**Reaction Scheme:**

![Reaction Scheme](image)

(where R = H, -CH₃)
(where R¹ = H, -CH₃)
(where R² = H, -OH)

**Fig.4.20.**

**Typical experimental procedure for the synthesis of 1, 1, 1-tris (4-hydroxy phenyl) ethane**

A 500 mL four-necked round bottom flask, fitted with an overhead stirrer, a gas inlet, a dropping funnel, a thermometer and a reflux condenser vented to a scrubber containing aqueous sodium hydroxide solution was assembled. Flask was charged with Phenol (122 gm, 1.2 mole) 3-mercaptopropionic acid (5.0 gm) and cetyl trimethyl ammonium chloride (0.025 gm, 7.82x10⁻⁵mmole). The mechanical stirrer was turned on and saturated Phenol with dry HCl at 40-42°C. Then added a mixture of 4-hydroxy acetophenone (50.0 gm, 0.36 moles) and Phenol (85.0 gm, 0.9 moles) through dropping funnel within 6.0 h and reaction mass was maintained for 20 h for completion of reaction. The progress of reaction was monitored by HPLC. After completion of reaction Sodium bicarbonate (10 gm) was added and reaction mixture was filtered.
The wet filtered cake was suctioned dried and washed with aqueous methanol.

**Purification**

The crude cake was dissolved in methanol (~180 mL) and filtered through whatman 42. 10 mL aqueous solution containing 0.1%Na$_2$SO$_3$, 0.1%Na$_2$S$_2$O$_5$, 1% NaOH, and 0.1% hydrose were then added to the filtered solution and stirred for 15 min. followed by addition of catalytic amount of sodium borohydried. Then precipitation was carried out by water and cooled, filtered, washed with water and dried in vacuum to afford the pure crystalline in 70.0 % yield. Similarly the compounds of the series shown in table 4.6 were synthesized by using above procedure.

**Table 4.6 Synthesis of 1,1,1-tris (4-hydroxy phenyl) alkanes.**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Phenol used</th>
<th>Aldehyde/ Ketone used</th>
<th>Temp. range °C</th>
<th>Time h</th>
<th>Product obtained</th>
<th>% Yield</th>
<th>% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>o-Cresol</td>
<td>4-hydroxy bezaldehyde</td>
<td>40-42</td>
<td>12</td>
<td><img src="https://via.placeholder.com/50" alt="image" /></td>
<td>76</td>
<td>99.5</td>
</tr>
<tr>
<td>2</td>
<td>Phenol</td>
<td>4-hydroxy bezaldehyde</td>
<td>40-42</td>
<td>12</td>
<td><img src="https://via.placeholder.com/50" alt="image" /></td>
<td>70</td>
<td>99.6</td>
</tr>
<tr>
<td>3</td>
<td>Phenol</td>
<td>4-hydroxy acetophenone</td>
<td>40-42</td>
<td>20</td>
<td><img src="https://via.placeholder.com/50" alt="image" /></td>
<td>70</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Section D

Methanol recovery from Bisphenol aqueous stream and characterization of methanol and aqueous.

Introduction

The industrial waste management is a major factor in any industrial business to maintain its efforts and ability to maintain its ISO 14001 accreditation. All industrial companies are expected to improve their waste and environmental performance and efficiency in a regular basis.

Typically recycling is the most favored solution in the industrial waste management system. And, many environmental groups agree with the idea because of the main advantages that it brings to the people and to the environment. Primarily, recycling is an environmentally waste strategy; it converts used products into usable material all over again. Next, recycling can be a source of income to many people in the society. It helps people to establish waste or recycling business in a very low capital or investment. Aside from that, there are many industrial companies that can benefit from their waste products. They can still turn them into re-use or recyclable material in their own production process. This strategy can help the company to reduce their budget for buying new material for their manufacturing process. As well as the industrial companies can have the opportunity to increase their revenues or profits.

Taking this fact into consideration it was thought worthwhile that to establish recovery of methanol present in bisphenols aqueous generated via bisphenol purification.
Typical method for recovery of pure methanol from Bisphenols aqueous

100 mL aqueous solution containing 20-24% methanol was taken in 250 mL round bottom flask equipped with 2 ft packed Colum, Reflux divider with chilled water condenser, further it was heated T upto 70-75 °C and recovered pure methanol through reflux divider slowly maintaining vapor temp. 63-64°C and L/D ratio. When vapor temp increased above 65°C stopped recovery of methanol.

Recovered methanol analyzed purity by Gas chromatography and moisture by Karl fisher method and estimated COD of aqueous stream before methanol recovery and after methanol recovery. The results are included in (Table 4.7).

**Table 4.7**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Parameter</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Analysis of recovered methanol</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Color</td>
<td>Clear colorless liquid</td>
</tr>
<tr>
<td>2</td>
<td>%Purity</td>
<td>99.9</td>
</tr>
<tr>
<td>3</td>
<td>%Moisture</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>COD of aqueous stream</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>COD before methanol recovery</td>
<td>3,75,806 ppm</td>
</tr>
<tr>
<td>2</td>
<td>COD after methanol recovery</td>
<td>10,260 ppm</td>
</tr>
</tbody>
</table>
Spectral discussion [40-41]

IR-spectra [Fig. 4.21] Representative of synthesized compounds were scanned for IR spectra on FTIR Model-Spectrum one, Make Perkin Elmer, using KBr. The characteristic absorption band of \textbf{1,1,1-tris(4-hydroxy phenyl) methane} are as follows.

\begin{itemize}
  \item 1) 3259 cm\(^{-1}\) -Ar-O-H Stretching
  \item 2) 3063 cm\(^{-1}\) Stretching aromatic ring.
  \item 3) 1360 cm\(^{-1}\) -CH- Stretching in CH\(_2\).
  \item 4) 1509 cm\(^{-1}\) -C=C Aromatic ring Stretching.
  \item 5) 1173 cm\(^{-1}\) -C-C = benzyl bending.
  \item 6) 1014 cm\(^{-1}\) -C-O- Phenolic stretching.
  \item 7) 780 cm\(^{-1}\) Aromatic ring bending.
\end{itemize}


1H NMR Spectra [Fig.4.22].

Purified compounds were scanned for 1H NMR Spectra were recorded at room temperature on Brucker “AVANCE” 400 MHz in DMSO-D$_6$ using TMS as an internal standard. They show following characteristics peak.

The characteristic 1H NMR resonance peak values in δ[ppm] of 1,1,1-tris (4-hydroxy phenyl) methane are as follows.

![Fig 4.22](image)

1) 5.22 ppm (s, 1H, methylene proton).

2) 6.65 ppm (d, 6H, aromatic protons).

3) 6.84 ppm (d, 6H, aromatic proton).

4) 9.20 ppm (s, 3H Phenolic-OH protons).
Fig. 4.22: $^1$H NMR Spectrum of 1,1-tris(4-hydroxy phenyl) methane
Representative of the synthesized compounds of Bisphenols series were scanned for mass spectrum on Shimadzu GCMS QP 5050A make Shimadzu Corporation Japan, mode–DI. The probable fragments ions of 1,1,1-tris(4-hydroxy phenyl)methane are as follows.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molecular ion / fragment</th>
<th>m/z ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="" alt="Molecular ion" /></td>
<td>292 (Molecular ion &amp; Base Peak)</td>
</tr>
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<td>2</td>
<td><img src="" alt="Fragment 2" /></td>
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</tr>
<tr>
<td>3</td>
<td><img src="" alt="Fragment 3" /></td>
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<tr>
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<td><img src="" alt="Fragment 6" /></td>
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</tr>
</tbody>
</table>
Fig. 4.23 Mass Spectrum of 1,1,1-tris (4-hydroxy phehyl) methane
**Result and discussion**

Herein, we report the simple and effective method for the synthesis of bisphenols by condensation of substituted phenols with corresponding cyclic ketones, aromatic ketone and aldehyde in presence of suitable catalyst under solvent free condition and no charcoaization.

Use of halogenated hydrocarbon solvents for synthesis of bisphenols involve multiple operation like filtration, purification which resulted in to low yield, pollution, corrosion of equipment and possibility of iron contamination during acidic material processing and removal of residual halogenated hydrocarbon from products is very difficult. The presence of halogenated hydrocarbon or aromatic solvent in finish bisphenols is not advisable as a view of polymerization. To avoid these problems Sodium bicarbonate is studied in place of halogenated hydrocarbon solvents and it is economical and safe method.

We have developed methanol recovery method from aqueous in pure form and it can be recycled in the process without suffering quality and product yield. Methanol recovery method help to reduce COD load from waste effluent and made economical and clean process. This method can be used at commercial scale for the recovery of methanol from aqueous stream. To optimize the reaction condition, we examined the condensation reaction between phenol and cyclic ketone in the presence of phase transfer catalyst and results shows that cetyl trimethyl ammonium chloride is powerful catalyst to enhance the yield and high quality product. Purification of crude mass by charcoal makes tedious workup and resulted in to lot of pollution, material loss and increases multi operation step. Herein we have developed very simple reagents for purification of crude bisphenol; these reagents are water soluble and requirements in small quantity, easy for handling and no generation of
industrial waste as compared to charcoal. This methodology seems to be more effective, efficient and economical with extremely pure compound with short reaction time and simple operation, minimum exposure to human, no need to handle halogenated hydrocarbon solvents, charcoal and multiple purification steps in the process.

**Conclusion**

In summary, an improved highly efficiently method for the preparation of bisphenols by condensation of substituted phenol with corresponding ketones and aldehydes in presence of catalyst under solvent free condition with simple purification method was developed in high yield with extremely high purity in first time.

This method seems to be superior to the reported methods with respect to clean reaction profile. The attractive features of this procedure are

1) Easy synthetic procedure with high yield and purity.
2) Simple purification technique.
3) Mild reaction condition and short reaction time.
4) Free of halogenated hydrocarbon solvent.
5) Charcoal free process.
6) High reactivity and selectivity of the active species.
7) Low energy consumption process.
8) Minimum exposure to human at commercial scale.
9) Methanol can be recovered from aqueous stream and recycled in the process.
10) Industrial point of view these processes are very attractive.

We believe that this procedure provides a valuable addition in current methodologies of bisphenol synthesis and good contribution for polymer chemistry as raw material and additives.
References:


34. Dehmlow E.V., Dehmlow S.S., *Phase transfer catalysis*,3rd Ed,verlag chemic, Weinheim **1993**.


