

# A Convenient Method for the Preparation of Bisphenols

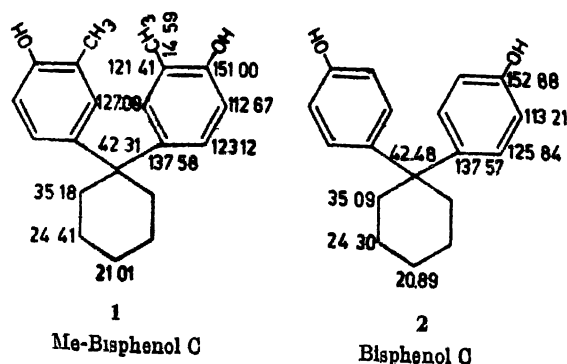
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Synthesis of two bisphenols having a 'cardo' group was carried out from phenol and *o*-cresol using cyclohexanone and a mixture of hydrochloric acid and acetic acid in the ratio 2 : 1 (v/v) at different temperatures to optimise the condition. The products have been characterised by ir,  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra.

THE condensation products of phenols with cyclic hydroaromatic ketones are known as 'cardo' (a loop) monomers. The monomers containing cardo group are very useful in synthesising polymers with very specific properties such as enhanced thermal stability together with excellent solubility due to the backbone structure<sup>1</sup>. Bisphenols have been synthesised by the condensation of phenols with cyclohexanone or aliphatic ketones using boron trifluoride<sup>2</sup>, polyphosphoric acid<sup>3,4</sup>, dry hydrochloric acid<sup>5,6</sup> and acetic acid<sup>7</sup>. We have synthesised two cardo bisphenols **1** and **2** by condensing cyclohexanone with *o*-cresol and phenol, respectively, in presence of a mixture of hydrochloric acid and acetic acid in 2 : 1 proportion at different temperatures, room temperature, 40, 50 and 60°. The optimum temperature for synthesis of the compounds **1** and **2** was found to be (i) at room temperature and (ii) 40°, respectively. A decrease in yield was observed with increase in temperature. The methods reported in the literature are having a disadvantage that the completion of the reaction takes place after four to several weeks. The method modified is more convenient as compared to the methods reported earlier in terms of time, isolation technique and purity of products. The structure of the compounds was supported by ir,  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectral study. Me-bisphenol C (**1**) exhibited eleven carbon signals while bisphenol C (**2**) showed eight carbon signals. Their shift assignments followed from consideration of the effect of substituents on aromatic moiety in **1**.



## Experimental

Ir spectra (KBr) were taken on a Shimadzu DR-1.  $^1\text{H}$  nmr spectra were taken on a XL-100A spectrometer operating at 100.1 MHz and  $^{13}\text{C}$  nmr spectra on a Varian CFT-20 spectrometer using DMSO- $d_6$  as solvent. The chemical shifts are in ppm downfield from TMS used as internal reference. All the chemicals used were of laboratory grade and were purified prior to use by the methods reported in the literature<sup>8</sup>.

**Preparation of 1,1-bis(3-methyl-4-hydroxyphenyl)cyclohexane (Me-bisphenol C) (1):** Cyclohexanone (49 g, 0.5 mol) was treated with *o*-cresol (104 g, 1.0 mol) in presence of a mixture of hydrochloric acid and acetic acid (150 ml, 2 : 1 v/v) at room temperature for a week. Pink coloured product separated out was dissolved in 2 M 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 charcoaled and then concentrated to give Me-bisphenol C as fine white shining crystals (77%), m.p. 186° (lit.<sup>9</sup> 186°) (Found : C, 80.4 ; H, 7.6.  $\text{C}_{20}\text{H}_{24}\text{O}_2$  calcd. for : C, 81.08 ; H, 8.1%) ;  $\nu_{\text{max}}$  3 500, 3 400, 2 900, 2 850, 1 250, 1 000, 900, 860, 735, 635 and 600  $\text{cm}^{-1}$  ;  $\delta$  8.98 (2H, s, 2  $\times$  OH), 7.0–6.8 (6H, m, ArH), 2.08 (10H, s, cyclohexyl H) and 1.43 (6H, s, 2  $\times$  CH<sub>3</sub>).

**Preparation of 1,1-bis(4-hydroxyphenyl)cyclohexane (Bisphenol C) (2):** Cyclohexanone (49 g, 0.5 mol) was treated with phenol (94 g, 1.0 mol) in presence of a mixture of hydrochloric acid and acetic acid (150 ml, 2 : 1 v/v) at 40° for 5 h and kept overnight at room temperature. Treatment of the product separated as above afforded bisphenol C (82%), m.p. 185° (lit.<sup>7</sup> 186°) (Found : C, 80.41 ; H, 6.91.  $\text{C}_{18}\text{H}_{20}\text{O}_2$  calcd. for : C, 80.59 ; H, 7.46%) ;  $\nu_{\text{max}}$  3 580–3 200 and 830  $\text{cm}^{-1}$  ;  $\delta$  8.5 (2H, s, 2  $\times$  OH), 6.9–6.6 (8H, m, ArH) and 2.14 (10H, s, cyclohexyl H).

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