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Environmental friendly synthesis of dihydroxy monomer containing sulphonyl group

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ABSTRACT

An efficient and new green synthetic protocol has been developed for the synthesis of bisphenol derivative containing sulphonyl group as pendent unit. This method uses solid p-toluene sulphonic acid and avoids the use of HCl gas or H_2SO_4 which are corrosive in nature and can be implemented in large scale for industrial applications.

Key Words: *p*-Hydroxyacetophenone, Phenol, Toluenesulphonic acid, Dihydroxy monomer.

INTRODUCTION

Polymers having high glass transition temperature, high indices of refraction and low birefringence have immense applications in advanced polymer science and technology. Polycarbonate is known for its dimensional stability and mechanical properties and is used in many optical applications, such as compact discs. The high stress optical sensitivity of bisphenol-A polycarbonate, however also poses a problem for certain applications, where the requirements for the preservation of polarization of light is stringent[1-3]. The residual birefringence in BPA polycarbonate has been investigated earlier and shown that the interpretation of the birefringence distributions is not straightforward and cannot be explained in the same way as for polystyrene. The origin of birefringence in BPA polycarbonate is believed to be due to positive anisotropy or higher polarizability along the chain backbone. By introducing chemical bonds, which are oriented on an average perpendicular to the backbone, the anisotropy and consequently the stress optical coefficient in the melt can be reduced. Moreover, toxicity of monomer might get reduced as molecule becomes less planar due to the presence of orthogonal substitutents. In this background, it is essential to obtain new monomers having unique structures and by using eco-friendly methods, which would meet the required property after polymerization.

Synthesis of bisphenol and related monomers are achieved by the condensation of a ketone like acetone with phenols in the presence of an acid catalyst at higher temperatures[4-6]. Usually the reaction requires the addition of another compound, methanesulphonic acid and mercaptopropanoic acid as promoters. Popular acid catalyst that is being used is dry HCl or sometimes, conc H_2SO_4. The handling of these catalysts either requires stringent pollution control requirements or suitable engineering design to prevent corrosion. Bisphenol derived polyesters and polycarbonates (**Fig I**) are widely used as engineering thermoplastics finding application as optical disks, roofing systems etc. Recently, bisphenol-A is suspected to possess adverse impact on human health[7-8]. In this context, it is imperative to find newer dihydroxy compound which has the potential of replacing present monomer, but possess less toxic effects, cost effective to find economic use and that can be made by environmental friendly process.

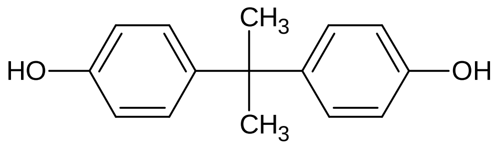


Fig 1

With these observations in mind it was contemplated to design some newer bisphenol derivatives using alternate solid catalysts like p-toluene sulphonic acid which is non corrosive and easy to handle in large quantities. Additional benefit of this catalyst system is that being organic in character; it would help easy mixing of the reactants thus enhancing the rate of the reaction.

EXPERIMENTAL SECTION

Step-1: Preparation of 4-tosyloxyacetophenone (1):

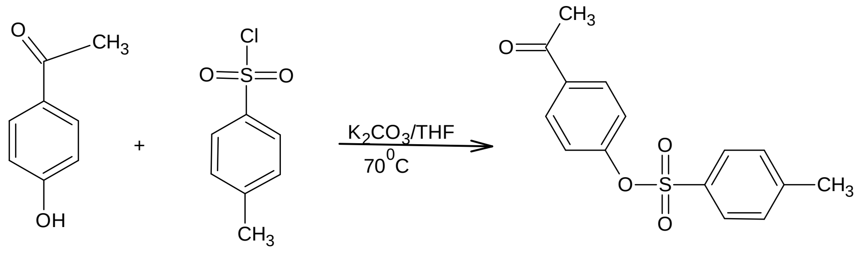
Procedure: To a mixture of 4-hydroxyacetophenone(13.6grams, 1mole)) and p-toluenesulphonyl chloride (19.5grams; 0.1mole, purity >97%) in tetrahydrofuran was added potassium carbonate (0.1mole) under stirring (**Scheme 1**). The reaction mixture was heated at 75^0C for 6 hrs. After reaction was completed (by thin layer chromatography), the solvent was distilled out under reduced pressure. Resulting solid was poured into ice-cold water and stirred well. The product was filtered and washed with water; dried and taken for next step without further purification.

1: Yield: 25.8g(90%); ^{1}H NMR(δ, DMSO-d_6): 2.41(3H, CH_3), 2.51(3H, CH_3), 7.19 (2H, ArH), 7.48(2H, ArH), 7.74(2H, ArH) 7.73(2H, ArH); LCMS: 290(M^+).

Step-2: Synthesis of 4-tosyloxy-4,4'-dihydroxyphenylethane(2):

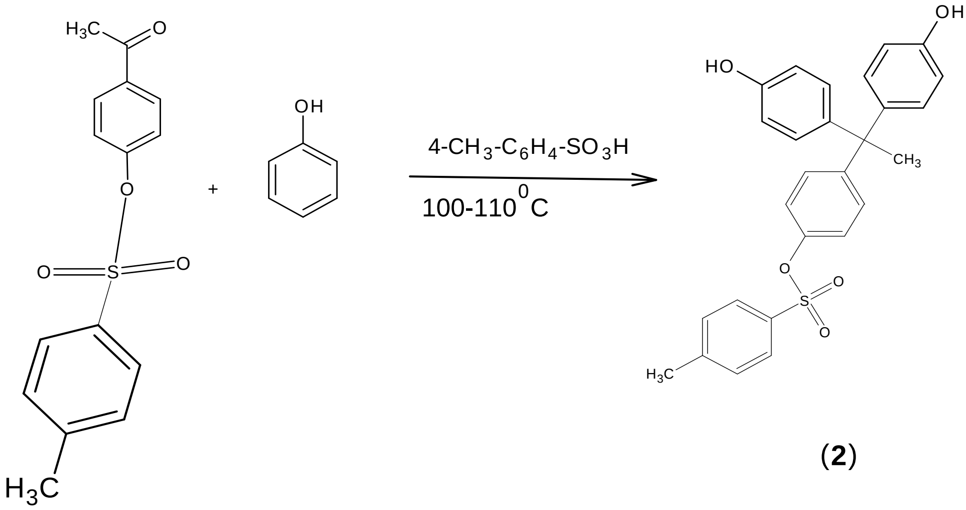
Procedure: To a mixture of 4-tosyloxyacetophenone(7.5g, 0.025mole) and phenol(14.2g, 0.15mole) catalytic amount of toluene sulphonic acid and few drops of mercapto propanoic acid was added and the contents were heated at 100-110^0C for 24hrs (**Scheme 2**). After the reaction was completed, the reaction mixture was cooled. This mixture was stirred with toluene for 2hrs. The solid product thus obtained was filtered and washed several times with hot water to remove the phenol if any. Crude yield: 9.2g(86%). Crude material was crystallized from isopropyl alcohol.

^{1}H NMR(δ, DMSO-d_6): 9.37(2H, OH), 7.45-7.85(4H, ArH), 6.60-7.10(12H, ArH), 2.36(3H, CH_3), 1.98(3H, CH_3);



(**1**)

Scheme-1



(**2**)

Scheme 2

RESULTS AND DISCUSSION

Synthesis of the monomer involves two step reactions as shown in **Scheme 1**. The first step of the synthesis involves the base catalyzed condensation of hydroxyacetophenones with p-touenesulphonyl chloride in the presence of potassium carbonate to get 4-tosyloxyacetophenone (**1**).

Acid catalysts that are generally used for the bisphenol synthesis include HCl gas in combination with anhydrous zinc chloride/ methane sulphonic acid/ trifluoromethane sulphonic acid/ ion exchange resin. The compound (**1**) was then condensed with phenol using methane sulphonic acid as catalyst and mercapto propanoic acid as the promoter to get the bisphenol (**2**). Present method using p-toluenesulphonic acid does not require the use of gaseous HCl. Moreover, the method gives white crystalline substituted bisphenol derivative on stirring with hot toluene. Hence, this is recommended for large scale preparation in laboratory and pilot scale synthesis.

CONCLUSION

In conclusion, we have reported a novel bisphenolic compound using an eco-friendly synthetic method. The new compound could be a potential monomer for the polyester and polycarbonate synthesis. The monomer may find applications for synthesis of polymers having high refractive indices, making them useful in ophthalmic applications. Also this compound has the potential to find use as an intermediate for epoxy coating formulations. Moreover, this monomer has the potential to be used in large scale applications as raw materials are cost effective and synthetic process is simple.

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