Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Advances in Applied Science Research, 2012, 3 (4):2069-2072

ISSN: 0976-8610
CODEN (USA): AASRFC

A simple route to polyethers from *p*-hydroxybenzoic acid

Alok Majumder*, Amitava Mandal, Jayanta Das and Pranab Ghosh

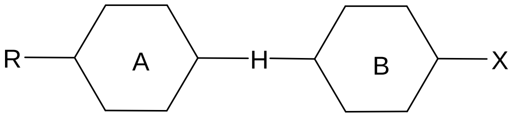
Department of Chemistry, University of North Bengal, Raja Rammohunpur, Darjeeling, West Bengal, India

ABSTRACT

Aryl ethers have been prepared from 1,2-diphenoxy ethane and 1,4-diphenoxy butane. Friedel Craft's acylation of the phenoxy alkanes with acetic anhydride using anhydrous aluminium chloride as catalyst gave 1,2-bis-(p-acetyl)-phenoxy ethane and 1,4-bis-(p-acetyl)-phenoxy butane in 80% yields. Oxidation of diacetyl compounds with either alkaline potassium permanganate or sodium hypobromide yielded the desired compounds. The acids have been identified as their ethyl esters by comparison with authentic samples prepared by condensing ethyl p-hydroxy benzoate with 1,2-bibromo ethane and 1,4-dibromo butane.

INTRODUCTION

In recent years liquid crystalline polymers have received increasing attention because of their scientific and technological importance [1-5]. The liquid crystalline state or more precisely the mesogenic state is a state of matter which is different from the liquid and solid states. Most liquid crystalline molecules are highly anisotropic and to a good approximation they can be regarded as rigid rods or ellipsoids of revolution with lengths greater than their widths. The molecular weight ranges from a few hundreds Daltons for low molecular mass liquid crystals to hundreds of thousands Daltons for polymeric liquid crystals. The basic structure of low molecular mass liquid crystals or monomers of liquid crystalline polymers is schematically shown below where X is a side group, R is a terminal group, A and B are aromatic rings and H is a linking group.



Aryl esters of *p*-alkoxybenzoic acids are known to exhibit tharmotropism, no such work seems to have been done on polyethers based *p*-hydroxybenzoic acid with terminal mesogenic units and a central spacer. These compounds have been reported to exhibit thermotropic properties [6]. The required bis-benzoic acids have been reported as their ethyl or methyl esters mostly in patent literature [7]. These compounds have been prepared by condensing *p*-hydroxybenzoates with appropriate dihaloalkanes. In view of the importance of these compounds, we investigated alternative routes to these compounds.

MATERIALS AND METHODS

General

All the chemicals were reagent grade and were purchased from S. dfine, SRL and Thomas Baker companies limited. The melting points were taken in open capillary meyhod and were uncorrected. ^{1}H NMR spectra were recorded in Bruker-Avance 300 MHz FT-NMR instrument in $CDCl_3$ solvent taking TMS as the internal standard. The coupling constants were expressed in Hertz.

*Preperation of Diphenoxyalkanes (**III** and **IV**)*

A mixture of phenol (0.20 moles), dibromoalkane (0.10 moles), 10% aqueous sodium hydroxide solution and sufficient rectified spirit to make the solution homogeneous was refluxed for a period of five hours. The reaction mixture was cooled and diluted with water to afford the diphenoxyalkane.

Diphenoxyethane (**III**) m.p. 97 °C (Reported m.p. 97 °C, Literature [8])

Diphenoxybutane (**IV**) m.p. 99 °C (Reported m.p. 97 °C, Literature [9])

*Acetylation of phenoxyalkanes: Formation of the acetyl compounds (**V**) and (**VI**) Kosalopoff' procedure [5]*

A mixture diphenoxyalkane (0.1 moles), phosphoric anhydride (0.02 moles) and calcium carbonate (1.0 mole) in anhydrous benzene (100 mL) was refluxed with glacial acetic acid (0.02 moles) with continuous stirring for two hours. Usual working up afforded the diacetyl compounds (**V**) and (**VI**) in approximate 10% yields.

Diacetyldiphenoxyethane (**V**) m.p. 159 °C; IR in cm^{-1} 1680, 1600, 1365, 1310, 1250, 1180, 1030, 960; PMR in ppm 2.48 (s, 6H), 4.44 (s, 4H), 6.8-8.0 (m, 8H); Mass m/e 298, 283, 256, 214, 163, 121, 120.

Diacetyldiphenoxybutane (**VI**) m.p. 133 °C; IR in cm^{-1} 1680, 1600, 1365, 1330, 1290, 1260, 1180, 990; PMR in ppm 2.45 (s, 3H), 3.8-4.2 (m, 8H), 7.0-8.0 (m, 8H); Mass m/e 326, 192, 149, 121, 119, 107.

Friedel Craft's acylation procedure

To a miture of diphenoxyalkane (0.05 moles) and acetic anhydride (0.01 moles) in carbon disulphide (100 ml) was added with cooling and stirring anhydrous aluminium chloride (0.15 moles) in small lot. After the addition, the reaction mixture was stirred for a period of three hours and left overnight at room temperature. Usual working up gave the acetyl compounds in nearly 80% yields. They were found to be identical with the ones obtained from the previous methods.

Dicarboxydiphenoxy alkane (**I**) and (**II**)

Oxidation of the acetyl compounds with alkaline potassium permanganate

The acetyl compound (500 mg) was refluxed with 10% potassium permanganate in 10% aqueous potassium hydroxide solution for two hours. Acidification of the reaction mixture gave the crude diphenoxy acids which were redissolved in sodium carbonate solution and filtered to remove suspended impurities. Acidification gave the acids (**I**) and (**II**) as very high melting solids.

1,2-Bis-(*p*-carboxyphenoxy)-ethane (**I**) m.p. 250 °C; PMR in ppm□ 4.36 (m, 4H), 6.98 (m, 4H), 8.02 (m, 4H), 11.0 (s, 2H); Mass m/e 302, 298, 283, 211, 210, 182, 160, 152, 122

1,4-Bis-(*p*-carboxyphenoxy)-butane (**II**) m.p. 250 °C; PMR in ppm 2.43 (m, 4H),4.36 (m, 4H), 6.98 (m, 4H), 8.02 (m, 4H), 11.0 (s, 2H); Mass m/e 330, 238, 222, 207.

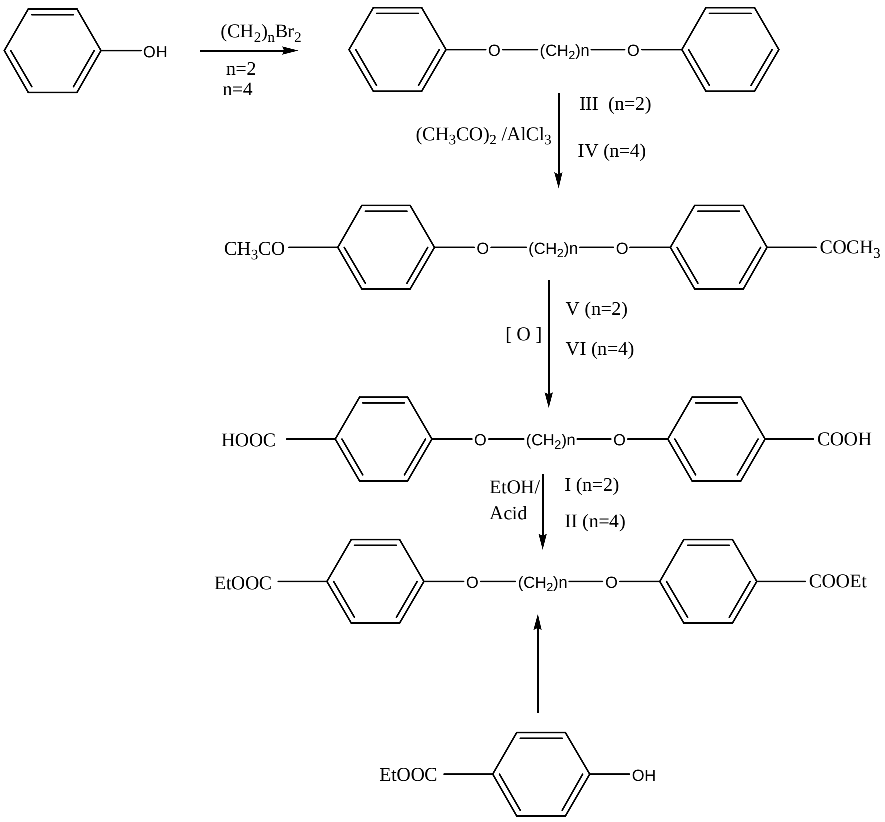
Oxidation with sodium hypobromide

To a cooled solution of sodium hydroxide (20 g) in water (175 mL) was added bromine (9.5 mL) with stirring. Into this was introduced a solution of diacetyl compound (0.05 moles) in dioxane with stirring and cooling over a period of one hour. The stirring was continued for a further period of two hours. Usual working up gave the dicaboxylic acids in approximately 30% yields. The acids were converted in to their ethyl esters by standered procedure.

1,2-Bis-(*p*-ethoxycarbonylphenoxy)-ethane m.p. 70 °C

1,4-Bis-(*p*-ethoxycarbonylphenoxy)-butane m.p. 85 °C

The esters showed no depression in melting point on admixture with authentic samples prepared by condensing ethyl p-hydroxybenzoate (0.1 moles) with dibromoalkane (0.08 moles) in presence sodium carbonate (0.5 g) in methanol (50 mL) containing a little diglyme.



RESULTS AND DISCUSSION

Condensation of phenol with 1,2-dibromoethane and 1,4-dibromobutane yielded 1,2-diphenoxyethane [8] (**III**) (m.p. 97 °C) and 1,4-diphenoxybutane [9] (**IV**) (m.p. 99 °C) respectively in appreciable yields.

It has been reported that aryl ethers are extremely sensitive to acylation and that acylation may occur in presence of less powerful catalysts than anhydrous aluminium chloride; even free carboxylic acid have been used as an acylating agent. Kosolapoff has reported [9,10] that anisole can be acetylated by refluxing it with a mixture of glacial acetic acid and phosphoric anhydride in presence of calcium carbonate. In view of the extreme simplicity of this procedure and the reported very high yields, we attempted the acylation of diphenoxyethane and diphenoxybutane by this procedure. A mixture of diphenoxyalkane, glacial acetic acid and phosphoric acid anhydride was refluxed in presence calcium carbonate for two hours. The acetyl compounds (**V** & **VI**) could be isolated in approximately 10% yields. Increasing the time of reflux or using varying proportion of the reactants has no marked effect on the overall yields.

Friedel Craft's acylation procedure using acetic anhydride and anhydrous aluminium chloride gave the diacetyl compound in excellent yields.

Oxidation of the diacetyl compounds with alkaline potassium permanganate [11] or sodium hypobromide gave 1,2-bis-(p-carboxy)-phenoxyethane (**I**) and 1,4-bis-(*p*-carboxy)-phenoxybutane (**II**) as high melting compounds. They were identified as their ethyl esters by comparing with authentic samples prepared by condensing ethyl-p-hydroxybenzoate with dibromoethane or dibromobutane.

Acknowledgement
The authors are thankful to UGC, India for financial support to carry out the work.

REFERENCES

[1] P. Ghosh, A. Mandal, *Adv. Appl. Sci. Res*., **2011**, 2, 255.
[2] D. S. bhavsar, *Adv. Appl. Sci. Res*., **2012**, 3, 1250.
[3] P. Ghosh, T. Das, *Adv. Appl. Sci. Res*., **2011**, 2, 272.
[4] M. E. Mohammed, C. Y. Ishak, *Adv. Appl. Sci. Res*., **2011**, 2, 32.
[5] F. Yogam, I. V. Potheher, A. Cyrae Peter, S. Tamilselvan, A. L. Rajesh, M. Vimalan. P. Sagayaraj, *Adv. Appl. Sci. Res*., **2011**, 2, 261.
[6] J. Il, Y. Seogchung, J. S. Kang, *Mol. Cryst. Liq. Letters*, **1983,** 82, 261.
[7] I. Norio, K.Toshio, I. Hirofumi, F. Yohei, *Chem. Abs*., **1976**, 84**,** 135319
[8] S. Saburo, K. toshio, K. Naskazu, I. Mirataka, S. Kenichiro *Chem. Abs*., **1974**, 80, 26925.
[9] H. B. Henbest, J. A. W. Reid, *J. Chem. Soc*., **1961**, 5239
[10] E. Welthius, B. Bouma, *Tetrahedron Lett*., **1970**, 1651
[11] A. I. Vogel, A Text Book of Practical Organic Chemistry (ELBS & Longman, London) **1978**, 1111 & 476