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SYNTHESIS AND CHARACTERIZATION OF *BIS*-ALLYLETHER OF BISPHENOLS*

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ABSTRACT

Bis-allylether of bisphenols were prepared by bisallylation reaction using Palladium(0) catalyst with allyl carbonate. These compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis. Bis-allylether of bisphenol-A could be converted to diglycidyl ether of bisphenol-A (DGEBA) using m-chloroperbenzoic acid as epoxidising agent.

INTRODUCTION

Bis-allylether of bisphenols are important intermediates which find use in a variety of polymer related applications. Bis-allylether of bisphenol-A undergoes a facile thermal Claisen rearrangement to O,O'-bis-allylether of bisphenol-A (2,2'-bis(4-hydroxy-3-allylphenyl) propane[1]. The latter compound is used in the preparation of epoxy resins (Ciba- Geigy Matrimide 5292) for composite applications[2]. It also serves as an important monomer in hydrosilylation

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polymerization[3]. This is an attractive route to functional silicon containing polymers. Bis-allylether of bisphenol-A can be converted to a diglycidyl ether of bisphenol-A (DGEBA) by epoxidation[4] which is an industrially important building block for the preparation of a variety of epoxy resins.

Conventionally, bis-allylether of bisphenol-A is produced by reaction of bisphenol-A with allyl chloride[5]. This method of synthesis uses allyl chloride which is generally produced by vapor phase chlorination of propylene[6]. The efficiency of conversion of propylene to allyl chloride by this process is only 63 %, the balance being a variety of other unwanted halogenated hydrocarbons. Such halogenated hydrocarbons are difficult to dispose off and create a great burden on the environment. The reaction of allyl chloride with bisphenol-A also produces common salt as solid waste which is also difficult to dispose off.

Recently, Palladium (0) catalysed reaction of various phenols with allylmethyl carbonate to form the corresponding phenolallyl ether were reported[7]. We have now extended this method to the synthesis of various bis-allylether of bisphenols[8].

EXPERIMENTAL

Materials and Analyses

4,4'Isopropylidenediphenol (bisphenol-A, BP-A) (Aldrich, USA) was recrystallized from toluene. 2,2'-Bis(4-hydroxy-3-methyl phenyl) propane, 2,2'-bis(4-hydroxy-3,5-methyl phenyl) propane, 1,1'-bis(4-hydroxy phenyl) cyclohexane were prepared according to known literature procedure and purified by recrystallization from acetic acid-water and water-methanol mixtures respectively[9]. Triphenylphosphine (Sisco research laboratory, Bombay, India) was recrystallized from ethanol. *m*-Chloroperbenzoic acid (Aldrich, USA) was used as received. Bis(dibenzylideneacetone)palladium was prepared according to reported procedure[10]. Dichloromethane was dried by distillation over phosphorus pentoxide and stored over 4 Å molecular sieves. Tetrahydrofuran was purified by distillation over sodium. Reaction products were separated by column chromatography using a suitable solvent mixture as eluent and characterized by spectroscopic techniques.

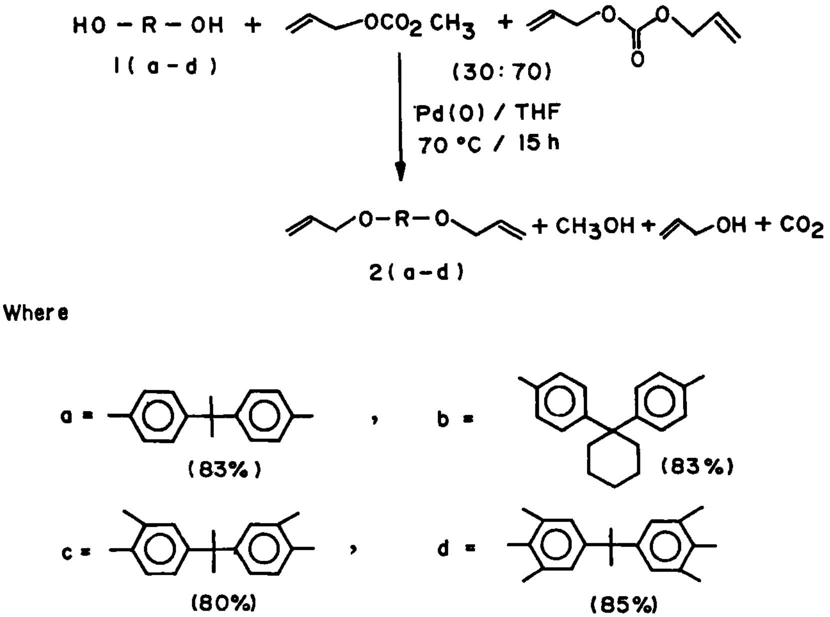
Allylation Reaction

A 50 mL three neck round bottom flask was flame dried and cooled under nitrogen. Bisphenol-A (0.228 g, 1×10^{-3} mol), bis(dibenzylideneacetone)palladium(0.005 g, 1.47×10^{-5} mol), triphenylphosphine (0.02 g, 7.6×10^{-5} mol) and a mixture (70:30 mol%) of diallyl and allyl methyl carbonate (0.8 g, 0.75 mL, 5.6×10^{-3} mol) were reacted in 5 mL of dry tetrahydrofuran under nitrogen atmosphere. Reaction mixture was stirred at 75^{0}C for 15 h. The product was purified by column chromatography on silica using petroleum ether-ethyl acetate (98:2) solvent mixture as eluent. The yield of 2,2'-bis(4-allyloxy phenyl)propane obtained was 0.25 g (83%).

The reaction with other bisphenols was conducted in the same manner.

Epoxidation Reaction using m-Chloroperbenzoic Acid

2,2'-Bis(4-allyloxy phenyl)propane (0.11 g, 3.6×10^{-4} mol) in 10 mL of dry dichloromethane was added to a 50 mL of two neck round bottom flask equipped with a nitrogen inlet, stirring arrangement, dropping funnel and guard tube. *m*-Chloroperbenzoic acid (0.3 g, 1.8×10^{-3} mol) dissolved in 10 mL of dry dichloromethane was added dropwise over 30 min to the reaction mixture at 0°C. After completion of addition, reaction mixture was stirred at room temperature for 24 h. TLC of reaction mixture indicated formation of two products alongwith unreacted bis-allylether of bisphenol-A. Reaction mixture was washed thrice with saturated solution of $NaHCO_3$ (to remove m-chlorobenzoic acid, generated during reaction). The organic layer was washed repeatedly with water and dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded a viscous oil which was purified by column chromatography. The first fraction was eluted with petroleum ether:ethylacetate (97:3) which gave unreacted bis-allylether of bisphenol-A (0.031 g) and mono-epoxidised product of bis-allylether of bisphenol-A (0.0266 g). The later fraction eluted with petroleum ether:ethylacetate (90:10) gave diglycidyl ether of bisphenol-A (DGEBA) (0.058 g). These were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra.



Scheme 1 : Synthesis of Bis-allylether of Bisphenols

RESULTS AND DISCUSSION

A 70:30 mole % mixture of diallyl carbonate and allylmethyl carbonate was prepared in 70 % yield by the reaction of allyl alcohol with dimethyl carbonate[11]. This mixture was used as such for the allylation of bisphenol-A. Various bisphenols were reacted with a mixture of diallyl carbonate and allylmethyl carbonate (70:30 mol%) using Pd(0) catalyst (Scheme 1). After the reaction, the byproduct allyl alcohol, methanol and solvent were removed. Thereafter the reaction mixture was analyzed by TLC which showed formation of bis-allylether of bisphenols, unreacted bisphenols and the catalyst. The bis-allylether of bisphenols were purified by column chromatography on silica (60 - 120 mesh) using petroleum ether:ethylacetate (98:2) solvent mixture as eluent. The yield of bis-allylether of bisphenols after purification were in the range of 80 - 85% (Table 1).Even sterically hindered bisphenols such as

Table 1

Characterization of Bis-allylether of Bisphenols

Code No.	Yield (%)	^{1}H-NMR ($CDCl_3$, δ, ppm)	IR (Neat,ν, Cm^{-1})	^{13}C-NMR ($CDCl_3$, δ, ppm)	Elemental Analysis Calc./Found C, H	Mass m/z, (%)
2a	83	1.6 (s, 6H), 4.5 - 4.6 (d, 4H), 5.25 - 5.55 (m, 4H), 6.1 -6.2 (m , 2H), 6.8 -6.95 (d, 4H, ortho to $-C(CH_3)_2$), 7.15 -7.25 (d, 4H, ortho to ether)	1645 (-C=C-) 1246 (-C-0-C-) 808 (=CH_2) 926 (-CH)	31.25($-C(\underline{C}H_3)_2-$), 41.85($-\underline{C}(CH_3)_2-$), 68.95($-0\underline{C}H_2-$), 133.76($-\underline{C}H=$), 117.56($=\underline{C}H_2-$), 114.29, 127.87, 143.44 & 156.66(Ar-$\underline{C}$-)	81.52/81.81, 7.90/8.01	308, (30)
2b	83	1.45- 1.5 (bs, 6H),1.65- 1.7 (s, 6H), 2.2 -2.3 (bs, 4H),4.5 - 4.55 (d, 4H), 5.25 - 5.5 (m, 4H), 6. -6.1 (m , 2H), 6.8 -6.85 (d, 4H, ortho to $-C(CH_3)_2$), 7.15 -7.2 (d, 4H, ortho to ether)	1646 (-C=C-) 1246 (-C-0-C-) 824 (=CH_2) 926 (-CH)	23.14($-\underline{C}H_2-$), 26.64($-\underline{C}H_2-$), 37.63($-\underline{C}H_2-$), 45.27($-\underline{C}-$), 68.93($-0\underline{C}H_2-$), 133.78($-\underline{C}H=$), 117.56($=\underline{C}H_2-$), 114.48, 128.24, 141.40 & 156.43(Ar-$\underline{C}$-)	82.37/82.75, 8.04/8.13	---
2c	80	1.6 - 1.65 (s, 6H), 2.2 -2.3 (s, 6H), 4.5 - 4.55 (d, 4H), 5.2 - 5.5 (m, 4H), 6.15 -6.25 (m , 2H), 6.7 - 6.75 (d, 2H, ortho to $-C(CH_3)_2$), 7. - 7.1 (d, 4H, ortho to ether)	1646(-C=C-) 1254 (-C-0-C-) 808 (=CH_2) 924 (-CH)	16.75(Ar-$\underline{C}H_3$), 31.39($-C(\underline{C}H_3)_2-$), 41.76($-\underline{C}(CH_3)_2-$), 68.99($-0\underline{C}H_2-$), 134.13($-\underline{C}H=$), 116.93($=\underline{C}H_2-$), 110.89, 124.94, 126.35, 129.60, 143.20 & 154.89(Ar-$\underline{C}$-)	82.14/82.23, 8.23/8.75	---
2d	85	1.6 - 1.7 (s, 6H), 2.25 -2.35 (s, 12H), 4.3 - 4.4 (d, 4H), 5.15 - 5.55 (m, 4H), 6.15 -6.2 (m , 2H), 6.85 - 6.95 (s, 4H, ortho to $-C(CH_3)_2$),	1646 (-C=C-) 1224 (-C-0-C-) 794 (=CH_2) 924 (-CH)	16.84(Ar-$\underline{C}H_3$), 31.32($-C(\underline{C}H_3)_2-$), 41.98($-\underline{C}(CH_3)_2-$), 73.20($-0\underline{C}H_2-$), 134.64($-\underline{C}H=$), 116.90($=\underline{C}H_2-$), 127.36, 130.12, 146.22 & 153.97(Ar-$\underline{C}$-)	82.32/82.41, 8.79/9.0	---

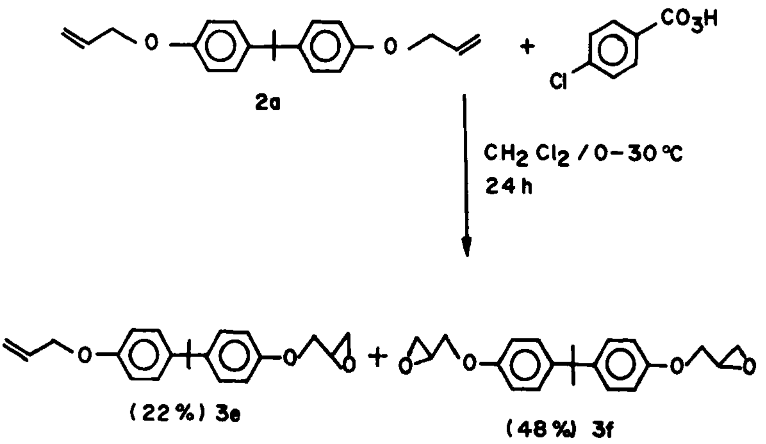
--- = not recorded.

2,2' bis(4-hydorxy-3-methylphenyl)propane and 2,2' bis(4-hydorxy-3,5-dimethylphenyl)propane reacted well under the same experimental condition. This is attributed to the higher nucleophilicity of the bisphenolates.

All products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis. IR spectra showed absorption bands at 1645 (C=C), 1246 (C-O-C), 808(=CH_2) & 926 (-C-H) which are characteristic of allyl groups. ^{1}H-NMR of bis-allylether of bisphenols showed peaks at 4.5 - 4.6 (d, 4H), 5.25 - 5.55 (m, 4H) and 6.1 - 6.2 (m, 2H) which are again characteristic of allyl group. In aromatic region at 6.8 - 6.95 (d, 4H) and 7.15 - 7.25 (d, 4H) which is AB type pattern observed. The ^{13}C- NMR spectra showed peaks at 68.95 (-$O\underline{C}H_2$), 133.76 (=$\underline{C}H$) 117.56 (=$\underline{C}H_2$), which are due to allyl group carbons and the peaks at 114.29, 127.87 & 156.66 are due to aromatic carbons. The downfield shift of aromatic carbon peaks is observed due to the ether linkage. The elemental analysis of the bis-allylether of bisphenols confirmed the structures (Table 1).

As a representative example the bis-allylether of bisphenol-A was epoxidised using excess m-chloroperbenzoic acid. This reaction resulted in the formation of mono- and bis-epoxidised product of bisphenol-A in 70 % conversion (Scheme 2).

These products were separated by column chromatography and characterized by IR, ^{1}H NMR and mass spectra. IR spectra of mono-epoxidised product showed bands at 1646, 808 & 926 due to C=C and a characteristic band of epoxide at 832 cm^{-1}. IR spectrum of bis-epoxidised product showed absence of C=C bands and characteristic band of epoxide group at 832 cm^{-1}. ^{1}H-NMR of mono-epoxidised product showed peaks at 4.5-4.6 9(d,2H), 5.4 - 5.45 (m, 2H), & 6.1 -6.2 (m, 1H) which are characteristic of allyl group and peaks at 2.75 - 2.80 (t, 1H), 2.85 - 2.9 (t, 1H), 3.4 - 4 5 (m, 1H), 3.9 - 4(q,1H), 4.2 - 4.3 (q, 1H) which are observed due to epoxide groups whereas bis-epoxidised product showed absence of peaks due to allyl groups. These spectral data are in agreement to the structures proposed. The mass spectra of mono and bis-epoxidised product showed molecular ion peaks at 324 (25%) and 340 (10%) which corresponds to the formulae weights. These mass spectra confirmed the structures proposed (Table 2).



Scheme 2 : Epoxidation of Bis-allylether of Bisphenol-A

Table 2

Characterization of Epoxidised Products

Code No.	Yield (%)	^{1}H-NMR ($CDCl_3$, δ, ppm)	IR (Neat,ν, cm^{-1})	Mass m/z, (%)
3e	22	1.6 (s, 6H), 2.75 - 2.8 (t, 1H), 2.85 - 2.9 (t, 1H), 3.4 - 4.5 (m, 1H), 3.9 - 4 (q, 1H), 4.2 - 4.3 (q, 1H), 4.5 - 4.6 (m, 2H), 5.4 - 5.45 (m, 2H), 6.1 - 6.15 (m, 1H), 6.8 - 7.2 (dd, 8H)	1646 (-C=C-) 918 (-C-H) 1246 (-C-O-C-) 832 (-C--C-) \/ O	324, (25)
3f	48	1.6 (s, 6H), 2.75 - 2.8 (t, 2H), 2.85 - 2.9 (t, 2H), 3.4 - 4.5 (m, 2H), 3.9 - 4 (q, 2H), 4.2 - 4.3 (q, 2H), 6.8 - 7.2 (dd, 8H)	1248 (-C-O-C-) 832 (-C--C-) \/ O	340, (10)

CONCLUSIONS

In conclusion, the present method offers a chlorine free approach to the synthesis of bis-allylether of bisphenols and DGEBA. Thus it promises to be a more environmentally friendly process for the synthesis of valuable intermediates which find diverse applications in polymer science and technology.

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