SYNTHESIS OF 2,3-DI(FURAN-2-YL)-5,6-DIHYDRO-1,4-DIOXINE

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Abstract : Furoin transfers into enol-form under the alkali environment,responds with 1,2 saturated dihalide to obtain 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine.The structure of the compound was confirmed on the bases of elemental analysis and spectral studies.And tetrabutylammonium bromide has been found to promote the yields significantly.

Introduction

The furol is one kind of extremely important organic industrial chemicals.It is necessary to carry on the deep processing for furol uses by synthesizing more precious organic industrial chemicals.Because furoin and its derives has sensitization for the photoreactions(1).

And the reaction rate of 2,3-diphenyl-5,6-dihydro-1,4-dioxine and the singlet oxygen is very high(2),in photosensitive redox,it may process catching singlet oxygen to evaluates the response efficiency.We first prepare the 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine has the similar structure with it,and higher electron density.It may provide the higher response activeness.It is also reported 2,3-diphenyl-5,6-dihydro-1,4-dioxine has widely applies in the preparation of antiseptic-germicide(3)(4)(5).

Experimental

All ^{1}H NMR were performed in $CDCl_3$. ^{1}H NMR spectra was recorded using a Bruker spectrometer operating at 500 MHz (^{1}H).Chemical shifts (δ) were given in ppm relative to TMS.Infrared spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a ATI UNICAM 1000 spectrometer.Melting points were measured in open capillaries and uncorrected.Elemental analysis were performed by CE Instruments elemental analyzer FLASH EA1112.Mass spectra was recorded by Applied Biosystems Q-trap LC/MS/MS SYSTEM.

The furfural is the Nongan county furfural factory product and has been purified by distillation in vacuum(6).For all procedures,the submitters employed reagents and solvents as supplied from commercial suppliers without purification.

Preparation of Furoin

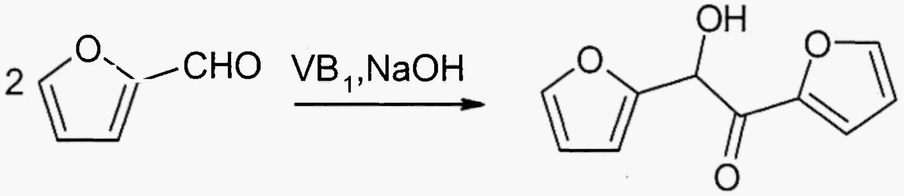

Figure-1 : Synthesis for furoin.

A 250mL,four-necked,round-bottomed flask equipped with condenser,a thermometer,and a mechanical overhead stirrer is charged with 20.0g of distilled or deionized water and 6.8g of vitamine B_1(VB_1).The mixture is stirred at room temperature for 10 min,allowing the solids to dissolve.After the addition of 60.0ml of 95% alcohol,the solution is stirred as aqueous 3mol/L NaOH is added carefully in one portion to adjust the pH of the aqueous between 9-10.50ml of furol is added.The solution is heated to 65°C-70°C with stiring and the addition of aqueous 3mol/L NaOH to keep the pH between 9-10,over 3 to 4 hr. Product begins to precipitate after about 30min.The solution undergoes a sequence of color changes from yellow to orange to brown.

The mixture of the reaction is cooled to room temperature.The product is isolated by filtration.The filter cake is washed with 50 mL of cold water followed by 2×50mL portions of cold alcohol.The product is dried at ambient temperature to give 49.58 g (89.1%) of the furoin as a white crystal.The product has the following characteristics: mp 138-139°C(6)(7).

Preparation of 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine

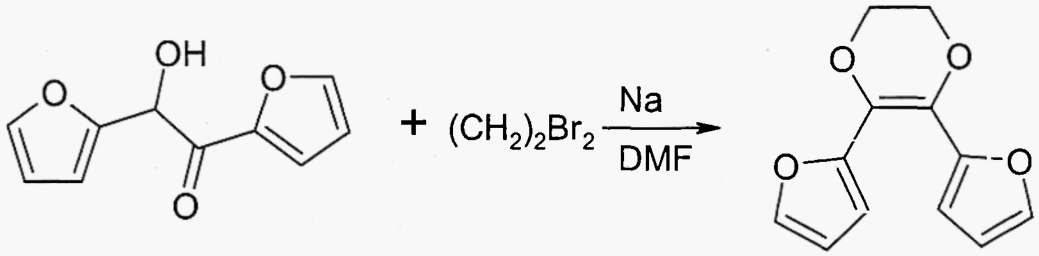

Figure-2 : Synthesis for 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine.

A 125mL,one-necked,round-bottomed flask,equipped with a magnetic stirring bar,is charged with 20.0mL of DMF and 0.92g (0.04mol)of Na.The flask is immersed in an ice-water bath and the solution of furoin (3.84g,0.02mol) in DMF(30ml) is added dropwise through an addition funnel.After the mixture is stirred for 10 min, 5ml of ethylene bromide is added.The mixture is stirred at room temperature overnight.

Most of the DMF is removed by low pressure distillation followed by rotary evaporation of the residual solvent.The resulting residue is dissolved in (3:1 v/v)light petroleum:ethyl acetate.The resulting oil is purified by passing it down a short silica gel column (elution with the same aqueous).The appropriate fractions are pooled and freed of solvent under reduced pressure to give 0.45g (13.5%) of 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine.The product has the following characteristics:^{1}HNMR(CDCl$_3$ 500MHz):δ:4.314(4H,CH$_2$),δ:6.278(2H,4-furan),δ:6.377 (2H,3-furan),δ:7.366(2H,5-furan); MS m/z:218(M$^+$); Anal.caled for $C_{12}H_{10}O_4$:C 66.05%,H 4.62%,O 29.33%;Found:C 66.12%,H 4.83%,O 29.05%. IR:3432,1654,1481,1284,1159,968, 875,835,734(cm^{-1}).

Preparation of 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine with phase transfer catalysis

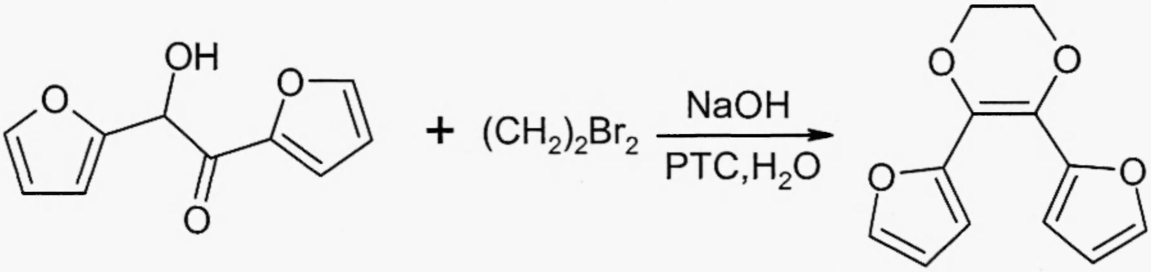

Figure-3 : Synthesis for 2,3-di(furan-2-yl)-5,6-dihydro-1,4-dioxine with phase transfer catalysis.

A mixture of furoin (3.84g,0.02mol),tetrabutylammonium bromide(0.5g,0.002mol), ethylene bromide (3.5ml,0.04mol),and a little water is heated to 35°C-40°C with stirring for 3hr.And 10ml of aqueous 10% NaOH is added in the first 0.5hr.The resulting solution is extracted by ethyl acetate.After removal of the solvent,the residue was chromatographed on the silica gel.The solvent is removed by rotary evaporation to yield the product 0.70g(20%).

Results and Discussions

1. The synthesis carried out in two ways and the identity of it has been confirmed by elemental analysis,high-resolution mass spectrometry,^{1}H NMR spectrum and infrared spectrum.
2. Phase transfer catalyst enhances the reaction rate and the yield of the synthesis.
3. The reaction temperature should below 40°C.If the fural ring of furoin is overheated,it could be destoried.
4. Furoin has two isomers(A)(B) in alkalic environment(8).The reaction product of (B) has more stability under our studying condition.

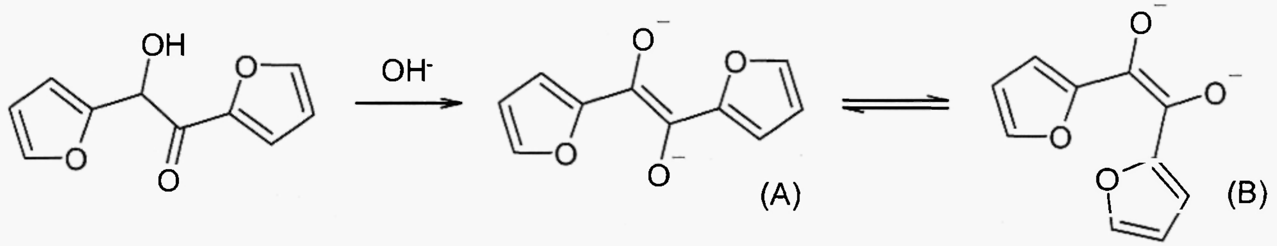

Figure-4 : Furoin's two isomers in alkalic environment.

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