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ORIGINAL ARTICLE

Structural and orthoselectivity study of 2-hydroxybenzaldehyde using spectroscopic analysis

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Abstract The orthoselectivity and high yield are two significant subjects which should be studied more in the process of hydroxybenzaldehydes or salicylaldehyde production. In this work, salicylaldehyde was synthesized by the reaction of formaldehyde and phenol magnesium methoxide complex, in an anhydrous medium. In order to achieve a selectively orthoformylated product, at first the hydroxyl group of phenol was rearranged by magnesium methoxide. The phenol magnesium salt was then formylated by paraformaldehyde. Impurities of the resulted salicylaldehyde were removed by several steps of liquid extracting via water and acid washing. The spectroscopic data of FT-IR, ^{1}H NMR (500 MHz), and GC/MS on the final product were recorded and interpreted. The results of FT-IR spectrum and integration value of ^{1}H NMR spectrum imply on the high conversion of reaction. The GC/MS spectrum also shows that the amounts of by products are low enough.

1. Introduction

The O-hydroxybenzaldehyde or salicylaldehyde has many applications as an intermediate in chemical industries. The largest single use of salicylaldehyde is in the manufacture of coumarin. Coumarin is an important commercial chemical used in soaps, flavors and fragrances and electroplating (Kirk and Othmer, 1991). Furthermore, salicylaldehyde is the forerunner of aspirin (Thoer et al., 1988). In another application, salicylaldoximes bearing branched alkyl chains are used as extractants to effect the separation and concentration operations in the hydrometallurgical recovery of copper and other accounting for around 30% of annual production (Ocio et al., 2004; Wood et al., 2006).

The main processes for the manufacture of hydroxybenzaldehyde are based on phenol. The most widely used industrial process for the production of salicylaldehyde is Saligenin process (Kirk and Othmer, 1991). The different methods for preparation of hydroxyl benzaldehyde and its derivatives were reported in different literatures (Aldred et al., 1994; Dimmit et al., 2001; Forgan, 2008; Furniss et al., 1978; Levin, 1996;

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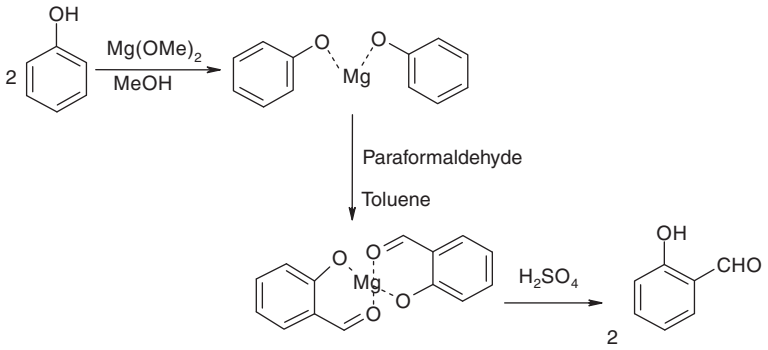

Figure 1 The reactions of salicyaldehyde production.

Matsuda and Murata, 1980; Paliwal et al., 2007; Selvam and Mahalingam, 2003; Willemse, 2003).

Phenolic aldehydes have so far been synthesized according to the well-known Reimer-Tiemann reaction in which phenol reacts with chloroform in the presence of a powerful base such as potassium hydroxide. This process besides having the difficulty in handling chloroform, has some significant problems such as low yield of the reaction, unselectively and the necessity of a large amount of chloroform consumption (Ahluwalia and Goyal, 2000; Thoer et al., 1988; Wynberg and Meijer, 1982).

A modified Duff reaction, as described by Lindoy et al. (1998) is a simple procedure, but its main disadvantage is the lack of regioselectivity in the formylation process so substitution occuring in the both ortho and para positions to the phenol and hence diformylated products are common.

Casiraghi et al. (1978) reported that the reaction of paraformaldehyde and magnesium phenoxide produced from phenol and ethylmagnesium bromide in benzene as solvent in the presence of stoichiometric amount of hexamethylphosphoric triamide (HMPTA) resulted in formylation exclusively at the ortho position. An improved method by Hofsløkken and Skattebøll (1999) in the absence of HMPTA has been reported. The ortho-formylation successfully was carried out by paraformaldehyde and magnesium bis (phenoxides) which prepared from phenols and magnesium methoxide in methanol as the cosolvent instead of HMPTA (Aldred et al., 1994; Levin 1996)

Therefore, when selective mono-formylation was desired and more than one site for incorporation of the -HC = O group is possible, the Levin method is chosen, which involves magnesium-mediated ortho-formylation.

The purpose of this research is to study the ortholformylation of phenol to salicylaldehyde by direct reaction of solid paraformaldehyde. In this process the effect of preparation of magnesium phenoxide will be investigated on the ortholformylation of phenol at first. The yields of orthoselectivity of this reaction will be investigated secondly, and the yield of overall reaction or decreasing the amount of by products will be revised thirdly.

Instrumental analysis such as ^{1}H NMR[1] and FT-IR[2] and GC/MS[3] and interpretation of their spectra could be useful for obtaining the structural information and the quantitative determination of the achieved product.

[1] Hydrogen – Nuclear Magnetic Resonance.
[2] Fourier Transfer Infra Red.
[3] Gas Chromatography- Mass Spectroscopy.

2. Experimental

2.1. Materials

Phenol (with the melting point of 40-43 °C and boiling point of 182°C) and magnesium powder (with the melting point of 650°C) were prepared from Merck chemical company. Commercial grade of paraformaldehyde was applied. Industrial grades of toluene and methanol were prepared from Iranian petrochemical companies and used after twice distillation (the boiling point of toluene and methanol after purification were about of 110.5 °C, 64.7 °C, respectively).

2.2. Equipments

A Fourier Transfer Infrared (FTIR) spectrophotometer, Bomem model MB100, and a Nuclear Magnetic Resonance (NMR) spectrometer, Bruker Avance Drx-500, were used. GC/MS data were recorded on a Agilent 6890 series GC system and Agilent 5973 network MSD using a 30 m HP-1MS column, 0.25 mm inner diameter, and program temperature 50-275 °C (15 °C/min).

2.3. Procedure and Mechanism of Reaction

At first, magnesium methoxide is prepared from the reaction of magnesium powder in methanol at reflux temperature. Magnesium bis(phenoxides) is then is formed by addition of magnesium methoxide to phenol or alkyl phenols in methanol. It then is reacted with paraformaldehyde in toluene. Finally, the acidic workup removes magnesium and other impurities (as seen in Fig. 1).

Fig. 2 shows the mechanism of this reaction. The main product was obtained after some acidic work up. Acidic treatment of the produced salicylaldehyde magnesium salt is performed in order to separate the magnesium ions as magnesium sulfate in aqueous phase. Then, the aqueous layer should be extracted with toluene or ether. Afterwards, all organic layers should be washed with distilled water for completion of washings. Finally, the obtained organic layer is evaporated under reduced pressure to yield pure salicylaldehyde.

2.4. Synthesis of Salicylaldehyde

12 gram of magnesium powder in methanol (405 gr) reacted at reflux temperature (63 °C) for up to 15 hr. This is an autocatalytic reaction; therefore, after the formation of magne-

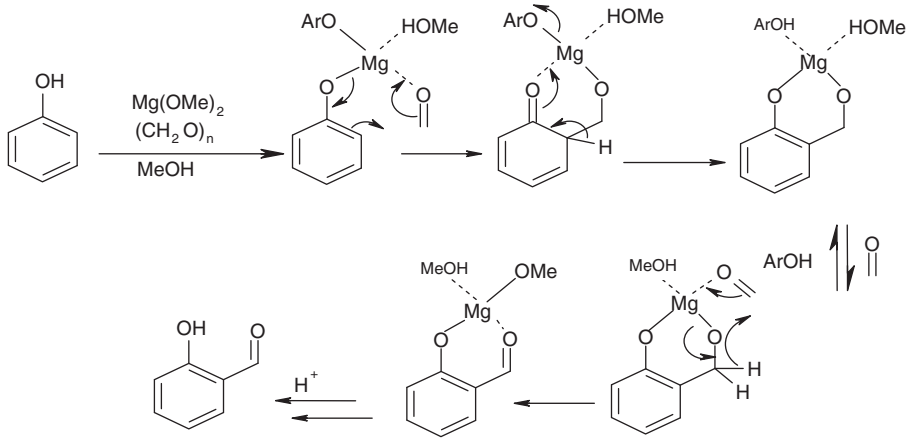

Figure 2 Proposed mechanism of salicyaldehyde production (Aldred et al., 1994).

sium methoxide, the rate of reaction will be accelerated than the start of reaction. Hence, in order to reduce the duration of this reaction, it is suggested that some amounts of magnesium methoxide are used as catalyst. When the color of mixture becomes milky and all the magnesium dissolves, phenol (80 gr) was added to magnesium methoxide (43 gr) solution in methanol. The mixture was refluxed for 3 hr. When, more than the half of methanol was distilled off, toluene (400 gr) was added to the residue in two steps. The rest of toluene (up to 100gr) was added at about the end of distillation. When the temperature of reaction mixture reached to about 95 °C, paraformaldehyde (75 gr) was added over 4 hr. After cooling the mixture to 50°C, a solution of 10% sulfuric acid (1000 cc) was added. The resulting mixture was stirred at 30-50 °C for 2 hr. Organic layer was washed with distilled water two times and filtered through filter paper for separation of unchanged formaldehyde and other impurities. Then the product was extracted with toluene and evaporated under reduced pressure to separate its solvent to give the 2-hydroxybenzaldehyde.

3. Results and Discussion

The ^{1}H NMR, FT-IR, and GC/MS spectra of the product are shown and interpreted in this section. The boiling point of the obtained salicyladehyde is about 200 °C.

3.1. ^{1}H NMR Data for the Product

Fig. 3 shows the ^{1}H NMR (500 MHz) spectrum of salicylaldehyde. The multiple peaks appeared at the chemical shifts of 7-7.6 ppm could be assigned to aromatic protons. The sharp peak appeared at 9.9 ppm is due to the resonance of aldehyde proton. The sharp peak that is shown at the chemical shift 11.07 ppm could be assigned to the proton of phenolic hydroxyl group. There are many ways to investigate the orthoselectivity and conversion of this reaction using the ^{1}H NMR spectra. One of them could be the comparison of aldehyde and unreacted phenolic protons, and the other is the comparison of aldehyde and hydroxyl group of orthoformylated protons. Furthermore, ^{1}H NMR comparison against a reference standard confirms the formation of the desired product (Kasler, 1973; Silverstein et al., 2005). The phenolic proton of unreacted phenol appeared at 4.02 ppm. Their integration values are too small to be accounted. The integration value of aldehyde protons is about 0.94 and for the phenolic one in orthoformylated product is about 0.92. These similarities imply on the high conversion of reaction. As a result it could be concluded that the conversion of reaction is very high. For studying of the selectivity one can see that there is any multiple peaks at the other positions of phenolic or aldehyde protons (i.e. meta and para). It could be deduced that the production of other formylated sequences is so few that it

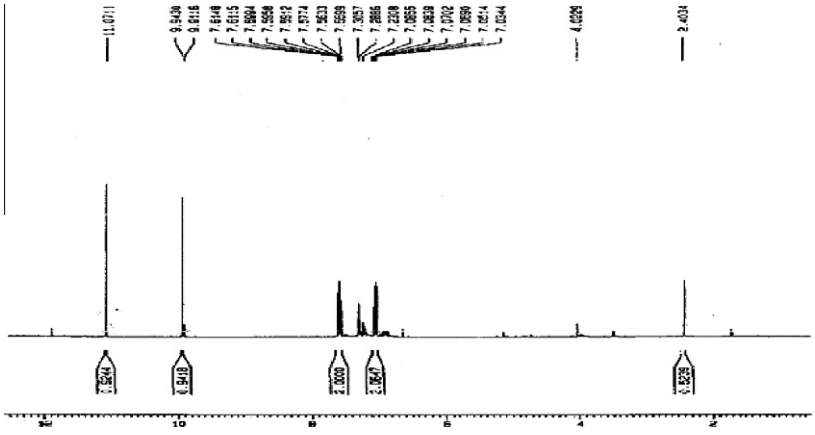

Figure 3 Assignment of ^{1}H-NMR spectrum for salicylaldehyde.

could not be considered (Kasler, 1973; Silverstein et al., 2005).

3.2. FT-IR Spectrum of the Product

The FT-IR spectra of the final product were recorded too. The peak which appeared at 2847cm^{-1} should be due to the C-H band of aldehyde group. Carbonyl group should have a lower stretching frequency due to the presence of phenolic hydroxyl group. Hence, the band appeared at 1664 cm^{-1} should be due to aldehyde carbonyl group. Therefore, by comparing the obtained spectroscopic data with the literature data it is evident that salicylaldehyde was produced accompanying with a high conversion and selectivity (Janes and Kreft, 2008; Mohan, 2000; Pavia et al., 1996; Silverstein et al., 2005).

3.3. GC/MS Analysis of Product

The GC-MS chromatogram of product was used for detection of salicylaldehyde in the obtained product. The GC-MS chromatogram consists of a main peak at 6.48 min, which is due to the 2-hydroxybenzaldehyde product. In addition, the peak appeared at retention time 5.59 min could be due to the presence of unreacted phenol in product, but as seen by GC-MS its extent is too little. The major by product from the reaction could be the 2,2́-dihydroxydiphenilmethane which was identified at retention time 14.77 min and its percent of area is 10.72. The amount of by products calculated from the area of their peaks which was given from quantitative chromatographic analysis is up to 20%. The extent of detected p-hydroxybenzaldehyde at 8.97 min is less than 0.6% (w/w). Therefore, approximately 80% of the product is salicylaldehyde. This can be confirmed from the result of ^{1}H NMR spectrum. The high yield of synthesized salicylaldehyde, indeed confirms the method that has been described in this paper (Pavia et al., 1996; Silverstein et al., 2005).

It could be concluded that the distillation of methanol should be done slowly so that the concentrations of methanol in the solution should be maintained in an appropriate value, because the high concentration of methanol can result in competition with the phenoxides for magnesium coordination and hence it acts as an inhibitor. Therefore this is a controlled reaction, which yields primarily a monoformylated product (Aldred et al., 1994).

4. Conclusion

It was recognized that magnesium phenoxide could be orthoformylated by paraformaldehdye in a high yield and high selectivity, while phenol could not be formylated alone. Carrying out the reaction at suitable conditions of time and temperature and the collecting of methanol solvent on time and slowly lead to a high yield and high selective product. The extraction procedure has a good effect in this issue. The accurate and exact interpretation of the obtained spectra which were taken by high performance equipments has been less asserted in other articles. The results of these spectra imply on the high conversion of reaction and high selectivity of reaction i.e. the production of by products is low.

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