

Synthesizing of salicylaldehyde using magnesium phenoxide and its mass analyzing characterization

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ABSTRACT

Phenolic derivatives can be formylated in the ortho position selectively. In this research at first magnesium phenoxide was synthesised by the reaction of white powder of magnesium methoxide and phenol in toluene as a non-polar solvent. Secondly para-formaldehyde was reacted with magnesium phenoxides. The resulting product was purified after several times washing with acid and distilled water and then its characterization by MS and FTIR spectrum analysis. FTIR spectrum deliberation shows the good orthoselectivity of the product. MS spectrum Deliberation shows an ionic peak in m/z 122 as phenolic base peak and with abundances of 100%, another peak in m/z 121 with abundance of 93.75 elucidate the elimination of phenolic proton % and the final peak in m/z 93 with abundance of 87.5 assigned to the elimination of CHO from deprotonated phenol. These analyzing which has less been asserted in the articles show the synthesis of product with this method besides of having high orthoselectivity has about 87% yields. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Salicylaldehyde;
Magnesium methoxide;
Magnesium phenoxide;
Ortho-formylation.

INTRODUCTION

Salicylaldehyde as intermediates in the chemical industry has many applications. Most of its usage is in producing coumarine. Coumarin is a chemical that is used in most commercial soaps, spices, perfumes and plating^[1].

Furthermore it is a starting material in synthesis of Asprine^[2]. Salicylaldehyde is also known as a characteristic component of buckwheat grouts aroma. Common buckwheat has been grown in Europe for centuries and is now an important alternative crop; its products have been associated with preventative nutrition. In Central and Eastern Europe and in some parts of Japan, buckwheat grain is cooked and use as a feed or make it into powder form^[3]. Working methods of

Formylation of Aromatic Compounds (such as Duff, Riemer-Tiemann, Vilsmeier, Gattermann), can be effective when phenol hydroxyl derivative produce but free phenol formylation via this methods, most of the time has low yield or weak ortho-formylation or dominant para-formaldehyde. Phenol can be ortho-formylated by formaldehyde in the presence of a catalyst such as metal salts (for example using the salt of Sn, Fe, Ti, Cr, Zr) but some of these reactions generally require high pressure^[4-5]. The purpose of this research is to introduce the method of synthesis of salicyl aldehyde from para-formaldehyde, that has not the problems of former methods such as Poor quality product and Low efficiency of the reaction.

Vilsmeier reagent (DMF-POCl₃) was used as an efficient formylating agent. Several sterols having *sec-*

hydroxyl group at 3/17-position have been modified into respective formate esters. The method is simple, mild, chemoselective and provides *sec*-alcoholic protection in good yields.

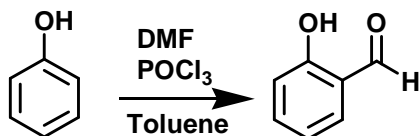


Figure 1 : Formylation of salicyl aldehyde using vilsmeier reagent

Gattermann reaction is mainly given by alkyl benzenes, phenols and phenolic ethers. In this method poor yield, low selectivity and separation problem show itself^[6].

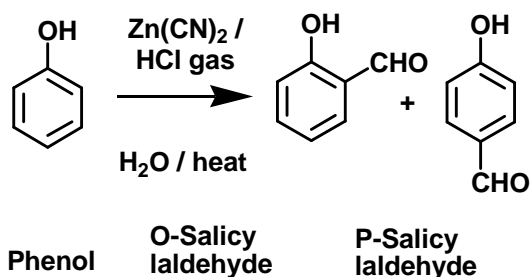


Figure 2 : Formylation of salicylaldehyde using gattermann reaction

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 occurring in the both ortho and para positions to the phenol and hence diformylated products are common. This method leads waste water pollution and small yield^[5,6].

The Reimer-Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols. The reaction was discovered by Karl Ludwig Reimer and Ferdinand Tiemann. In the simplest case, the product is salicylaldehyde:

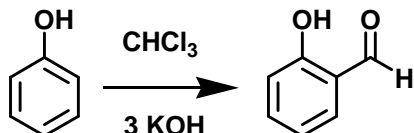


Figure 3 : Formylation of salicylaldehyde using reimer-tiemann reaction

The mechanism of the reaction reveals that Chloroform reacts with strong base to form the chloroform carbanion, which will quickly alpha-eliminate to give

dichlorocarbene. Dichlorocarbene will react in the ortho-position of the phenate to give dichloromethyl substituted phenol. After basic hydrolysis, the desired product is formed.

It has been found that when the above reaction is carried out in certain organic solvent mixtures appreciably higher yields of salicylaldehyde are obtained Compared with previous methods and in addition, the amount of p-hydroxybenzaldehyde produced as an undesirable by-product is sharply reduced.

This process besides having the difficulty in handling chloroform, has some significant problems such as low yield of the reaction compared with this assay method, unselectively and the necessity of a large amount of chloroform consumption^[5,7,8].

Phenol can ortho-formylate by formaldehyde in the presence of a catalyst such as metal salts (for example using the salt of Sn, Fe, Ti, Cr, Zr) but some of these reactions generally require high pressure^[4,5]. Purpose of this research is to introduce the method of synthesizing of salicylaldehyde from para-formaldehyde, that has not the problems of former methods such as Poor quality product and Low efficiency of the reaction.

Instrumental analysis such as FT-IR and MS and interpretation of their spectra could be useful for obtaining the structural information and the quantitative determination of the achieved product.

MATERIAL AND METHODS

Materials

The materials that used in this research include: magnesium powder, phenol, para-formaldehyde and sulfuric acid, which all of them prepared from Germany's Merck companies and reaction solvents (methanol and toluene) prepared from Iranian companies and were used after two times distillation.

Equipment

Two necks round bottom flask, condenser, mercury thermometer, mantle stirrer were applied in this research.

Experiment method

All glass containers must be completely dried in an oven over 150 c for an hour. From 3 days ago phenol

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was dried in the presence of CaCl_2 and para-formaldehyde was placed in desiccator in the presence of P_2O_5 to lose its moisture. 200 ml methanol in a Round-bottom flask equipped with a condenser, is heated with mantle stirrer up to its boiling point. Then 12 gr magnesium powder was slowly added to boiling methanol and was stirred for 8 hours. One mole (about 80 gr) phenol was weighed and added to the reaction flask and the reaction was continued for 3 hours at reflux temperature. After that the solvent of the reaction i.e. methanol has to be replaced by toluene by changing to setup into distillation mode. When almost half of methanol was distilled, 400 milliliter toluene was charged till all the methanol-toluene azeotrope in the system was gone. After that 2/5-3 mol (75 gr) weighted para-formaldehyde was added to magnesium phenoxide produced in last stage in optimal temperature of 95 c in 6-8 hours. Reaction mixture was cooled to room temperature and was stirred with sulfuric acid 10% for 2 h at the same temperature. The organic and aqueous phases were

separated and the aqueous phase was extracted with toluene and organic phase entered to the reaction flask and 250 g of saturated brine was added to it. After half an hour of mixing, the organic phase is separated and washed 2 times and each time with 250 gr of distilled water. The final product, salicylaldehyde, was then distilled under vacuum and was extracted with ether.

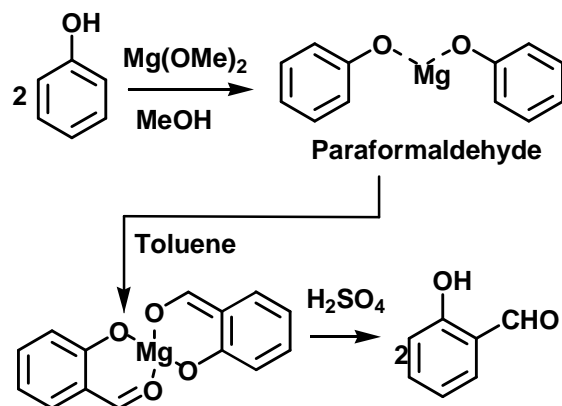


Figure 4 : Formylation of salicylaldehyde using magnesium phenoxide

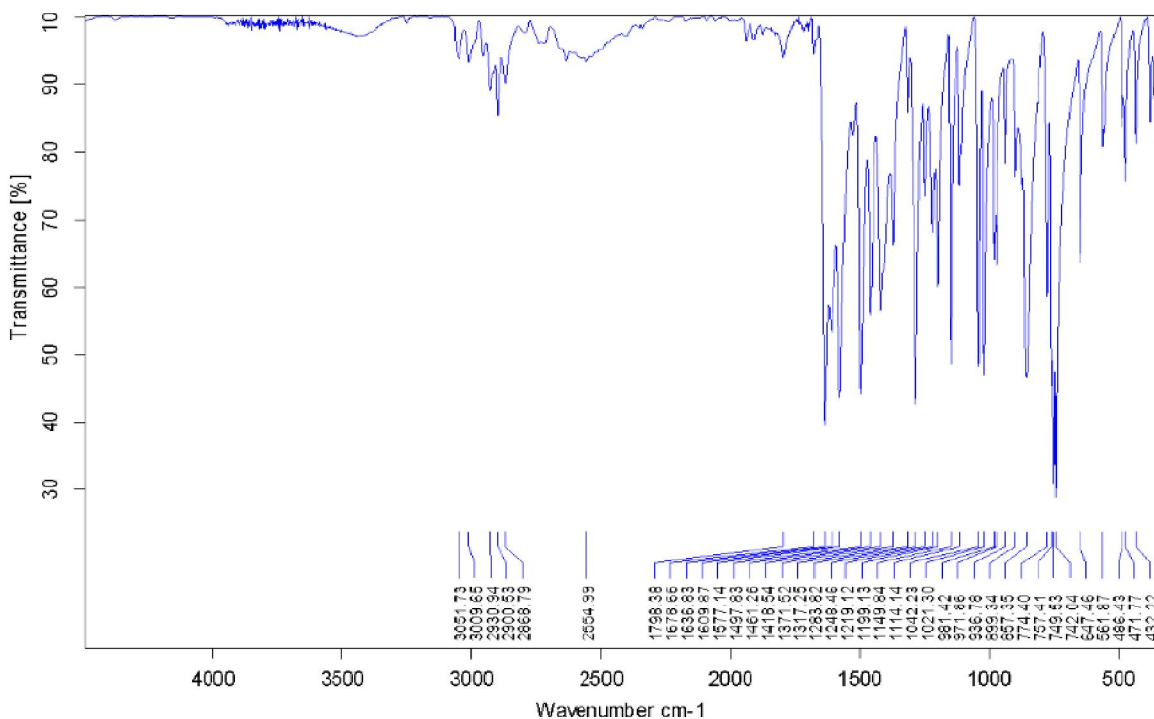


Figure 5 : FTIR spectrum analysis of salicylaldehyde

RESULT AND DISCUSSION

The result of FTIR analyzing for produced salicylaldehyde was shown in figure 5. This figure shows that

the CH bending mode of aldehyde appeared in the 2847.45 cm^{-1} , the broad band of phenolic OH appeared in the 3179.14 cm^{-1} and the aldehyde carbonyl group appeared in 1660.43 cm^{-1} . Since the OH peak is broad and is drowned to 3200 cm^{-1} this reveals that there is

a hydrogen bond here and the yield of ortho-product is high^[14].

The MS spectroscopy of salicylaldehyde has been shown in figure 6. This figure which confirms with the chemical structure of product shows an ion peak in m/z 122 as basic peak and with abundance of 100%. The

peak M-1 which appeared in m/z 121 and with abundance 93.75% reveals that the elimination of phenolic proton and finally the M-30 appeared in m/z 93 with abundance of 87.5% emphasis on the elimination CHO group. The other peaks assigned to the breaking of phenol ring is well appeared in the mass of 65 and 76.

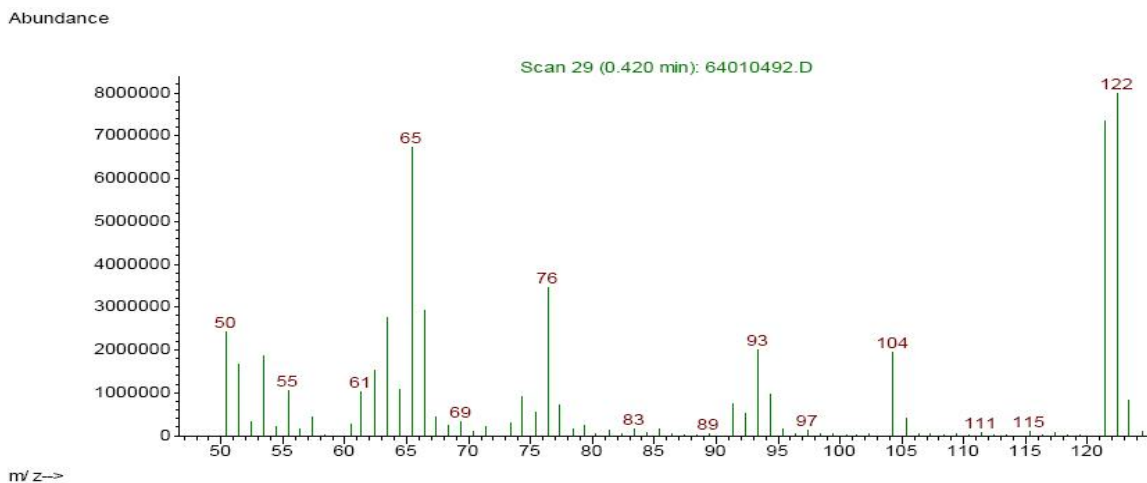


Figure 6 : MS spectrum analysis of salicylaldehyde

CONCLUSION

In this research 2 - hydroxy benzaldehyde was prepared using para-formaldehyde and magnesium phenoxide which attained a high quality product with high yield of 87%, and gave up orthoformylation and lower cost (Compared with other methods). Therefore it could be superior of previous methods. During reaction procedure it was realized that usage of pure reactants attained the high yield of reaction. Timely removal of solvents in its place and Precise control of temperature are really important factors which should be kept.

REFERENCES

- [1] T.Matsuda, T.Murata; Process for Producing Salicylaldehyde, US Patent 4231967, Sumitomo Chemical.Co., (1980).
- [2] Z.Pouramini, A.Moradi; Structural and Orthoselectivity Study of 2-Hydroxybenzaldehyde Using Spectroscopic Analysis, Arabian Journal of Chemistry, **5**(201), 99-102 (2012).
- [3] J.Damjan, S.Kreft; Salicylaldehyde as a Characteristic Aroma Component of Buckwheat Groats, Food Chemistry, **109**, 293-298 (2008).
- [4] R.Aldred, R.Johnson, D.Levin, J.Neilan; Magnesium-Mediated Ortho-Specific Formylation and Formaldoximation of Phenols, J.of Chem.Soc.Perkin. Trans., 1823-1831 (1994).
- [5] Z.Pouramini; Synthesis and Purification of Salicylaldehyde and Determination of the Optimum Formulation for the Selective Extractor of Coppe, M.Sc.Thesis, (2010).
- [6] L.Weisse, R.Neunteufel, H.Strutz, Process for the Selective Preparation of Hydrobenzaldehydes, US Pat. 5, 395, 978 (1995).
- [7] H.Eynberg, E.W.Meijer; Reimer-Tiemann Reaction, Nettrland, (2005).
- [8] F.Charles, Albright; Process for the Selective Synthesis of Salicylaldehyde, US Pat. 3, 972, 945 (1976).
- [9] Paul B. Budde; Process for the Preparation of Salicylaldehyde, US Pat. 3, 206, 513, (1965).
- [10] U.Nini Hofsløkken, L.Skattebol; Convenient Method for the Ortho-Formylation of Phenols, Acta Chemica Scandinavica, **53**, 258-162 (1999).
- [11] M.Dennis, W.Godek, M.Synder, M.Andrew Stewart; Formylation Process for Aromatic Aldehydes, US Pat. 5, 294, 744, (1994).
- [12] R.Aldred, R.Johnston, D.Levin, J.Neilan; Magnesium-Mediated Ortho-Specific Formylation and Formaldoximation of Phenols, J.Chem.Soc.Perkin. Trans., 1823 (1994).

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- [13] G.Casanti, M.Crisafulli, A.Ricca; A New Method for the Selective Ortho-Formylation of Phenols, *Tetrahedron Letters* No. 4, 243-245 (1965).
- [14] A.I.Kochnev, I.I.Oleynik, I.V.Oleynik, S.S.Ivanchev, B, G.A.Tolstikovà; Synthesis of Salicylaldehydes Bearing Bulky Substituents In the Positions 3 and 5, *Russian Chemical Bulletin, International Edition*, **56**, 1125-1129 (2007).
- [15] M.R.Razmirad, A.Moradi; Characterization and structural study of chlorinated polyethylene production in suspension phase, *Chem.Technology an Indian J.*, **7(1)**, 1-8 (2012).