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Synthesis of 3-Phenyl Coumarins by Using Ionic Liquid as Green Solvent

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ABSTRACT

Coumarins occupy an important place in the realm of natural products and synthetic organic chemistry. A highly efficient green process for synthesis of 3-Phenyl Coumarin from salicylaldehyde and phenyl acetyl chloride in presence of N-methyl imidazole is developed. The method is simple giving high yield of pure product. The N-methyl imidazole form N-methyl imidazole hydrochloride which can be deprotonated to get N-methyl imidazole which can be recycled for the next reaction of 3-Phenyl Coumarin .N-methyl imidazole hydrochloride is also useful ionic liquid. This method also applies to ultrasonic bath to synthesis of same molecule and some other derivatives. Due to the recycle of reagents the process is green.

Keywords : 3-Phenyl Coumarin, salicylaldehyde, N-methyl imidazole, phenyl acetyl chloride, Sodium Hydroxide,Automatic Hot plat with heating, stirring, control of temperature and stirring speed arrangement [Heidolph MR Hei-Standard], Ultrasonic bath [Life care Instrument co.]

I. INTRODUCTION

Green Chemistry addresses not only safety but also development of technology to ensure that the chemical reaction produce less waste and pollution. Increased local and global concern for environmental pollution offers incentive to explore new green materials for safeguarding the environment. Green methods have been applied in the design of Coumarins synthesis. Coumarins are aromatic heterocyclic compounds possessing a wide variety of biological activities such antimicrobial, anti HIV, anti-coagulants, anti-hyper proliferative, anti-tubercular, antihistamic, anti-inflammatory, rodenticides and photodynamic activity etc. In many methods there is use of $POCl_3$, Phosphotungstic acids, $ZnCl_2$, $AlCl_3$, H_2SO_4 ,PPh_3 ,NaH, anhydrous condition , Sodium Carbonate, Solid Amberlyst 15 ,Ultrasonic irradiation, microwave oven .Green chemistry also known as sustainable chemistry is an umbrella concept that has grown sustainably since it has fully emerged a decade ago. In continuation of our research work on the synthesis of 3- Phenyl Coumarins via green processes. We report a new method involving reaction of salicylaldehyde in N-methyl imidazole with phenyl acetyl chloride in presence of excess N- methyl imidazole. Same reagents are used in Ultrasonic bath technique.

II. METHODS AND MATERIAL

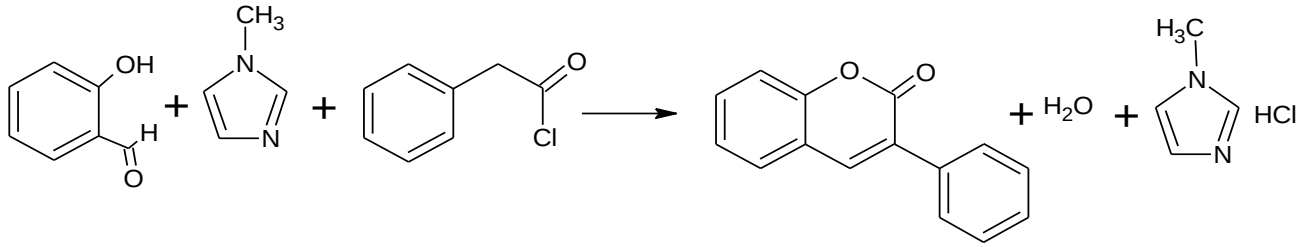
All chemicals, reagents and solvents used were purchased from M\S - S. D. Fine Chemicals Ltd, Mumbai. Phenyl acetyl chloride was prepared in the laboratory by the procedure reported in the literature [2] .Chemito 1000 Gas Chromatograph with HP-1 as capillary column [30 meter length],FID detector and N_2 carrier gas 2.5 ml/min. flow rate over temperature

80 ^{0}c -3 min./10 ^{0} c- 240^0 c was used for the analysis of final product .

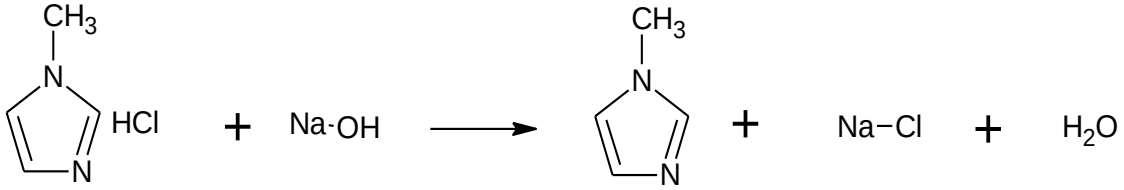
III. RESULTS AND DISCUSSION

In a 50 ml RB flask fitted with reflux condenser with heating ,stirring,refux mode condenser set up programme as shown in Figure. Charge salicylaldehyde and N-methyl imidazole under stirring to make a homogeneous mass .Then add phenyl acetyl chloride and continue stirring. The exotherm occours and temperature reach up to 40 ^{0} c .Heat the reaction mixture to 80 ^{0} c and maintain for 8 hours .The maximum product conversion got in 8 hours times that was confirmed by doing kinetic study of reaction. Reaction was monitored by TLC every hour .After completion of reaction mass cool to room temperature. The reaction mass solidifies to white paste. Add ice cold dilute HCl under stirring. Decand the aqueous layer preserve it and crystallise the solid remained in RBF with 80 % ethanol. Heat reaction mass to get clear solution and cool gradually under slow stirring to 15^0 c .Filter mass under released vacuum and dry in an oven at 100 ^{0} c. Check the weight, M.P. and GC. The same method used for Ultrasonic Bath. The parameters such as reagents,temperature,time,yields for various derivatives are given in Table.
The aqueous layer collected after the separation of 3-Phenyl Coumarin is treated with NaOH to deprotonate N-methyl imidazole .HCl formed during the reaction. The separated N-methyl imidazole is dehydrate by treating with anhydrous Na_2SO_4 and vacuum distil to get pure N-methyl imidazole, Checked by GC.The N-methyl imidazole hydrochloride formed during the reaction of 3-phenyl coumarin reacts with NaOH to deprotonate to produce N-methyl imidazole.

Basic reaction :-



Protonation of N-Methyl imidazole



This N-methyl imidazole after separation and vacuum distillation is used for the synthesis of 3-Phenyl Coumarin by the above process. The product 3-Phenyl Coumarin obtained was 98% yield. The melting point was found to be 141 0 C. The FTIR spectrum of the product. The sharp peaks at 3039 and 3056 cm-1 are due to aromatic C – H stretching; the peaks at1600.8 cm-1, 1572.8 cm-1 , 1488 cm-1 are due to C = C stretching , the peaks between 728.1 to 913.2 cm-1 are due to C –H deformation. The sharp peak at 1717.5 cm-1 is due to aromatic C = O group.The PMR spectrum of the. The chemical shift of C - H protons are between 7.2 to 7.8 ppm which are characteristic to the phenyl protons. The peak obtained at 1.6 ppm is due to the moisture absorbed by deuterated chloroform solvent and is not due any protons from the compound.The mass spectrum of the product.The fragmentation peak of the product at m+1, m / z value

is 223.1 indicates that the molecular weight of the product is 222. Considering the structure of 3- phenyl coumarin its molecular formula becomes C15H10O2 which gives molecular formula 222 .These results corresponds to the results of the earlier work reported by the workers by other methods.

Ultrasonic Bath reaction Process and Table.

In clean, dry 50 Mls RBF with water bath heating ,mechanical stirring and sonication with reflux mode condenser Set up.

Charge Salicylaldehyde and N-methyl imidazole stirred to make a homogeneous solution or slurry. Add phenyl acetyl chloride temperature increase to 40 ^{0} c and make programme of Ultrasonic bath with temperature, sonication and hours .The reaction mass digest at 50 ^{0} c for 3 hours with heating, mechanical stirring and sonication.Every hours reaction was monitored by TLC. The reaction kinetic study shows that at 3 Hours digestion it gives maximum product. By this method we prepared 4 different derivatives.

After completion of reaction, cool reaction mass to room temperature add dilute cold hydrochloric acid Under stirring,decand the aqueous layer which contains N-methyl imidazolium hydrochloride. Add sodium hydroxide and separate organic layer dry it on sodium sulphate.That dry organic layer distilled under vacuum to get N-methyl Imidazole.Solid remains in bottom was crystallise in ethanol. Heat this mass to clear liquid at 60 ^{0} c.Reaction mass cool gradually to 15 ^{0} c under stirring and filter at reduced pressure and dry in oven. The product was characterised by MP, IR and Gas Chromatography.

Table 1

Sr.No.	Name of Products	Reagents used	Time Minutes	Yield %	Melting Point ^{0} c
1	3-Phenyl Coumarin	Salicylaldehyde & Phenyl Acetyl chloride	180	98	141
2	6-Nitro-3-Phenyl Coumarin	5-Nitro Salicylaldehyde & Phenyl Acetyl chloride	180	75	122-124
3	6-Bromo-3-Phenyl Coumarin	5 Bromo Salicylaldehyde & Phenyl Acetyl chloride	180	25	185-186
4	3-(4-Nitro Phenyl) Coumarin.	Salicylaldehyde & 4-Nitro Phenyl Acetyl Chloride	180	12	189-190
5	6-Bromo-3-(4-Nitro Phenyl) Coumarin	5-Bromo Salicylaldehyde & 4-Nitro Phenyl Acetyl Chloride	180	15	201-202

Figure Experimental Setup:-

Salicylaldehyde reacts with Phenyl Acetyl Chloride in presence of N-methyl imidazole to form 3- Phenyl Coumarin. The N-methyl imidazole absorbs the liberated HCl to forms the N-methyl imidazole.HCl during the formation of 3- Phenyl Coumarin. Variation of various parameters to get high yield of 3-Phenyl Coumarins,found that salicylaldehyde , N-methyl imidazole and phenyl acetyl chloride when reacted in Mole ratio of 1:6:2.2 produces good yield of 3- phenyl Coumarin under stirring condition at 80 ^{0} c for 8 hours. RT value of the product is comparable with RT value of standard. M.P., FTIR, PMR and mass spectral data.

IV. CONCLUSION

This method of synthesis of 3-Phenyl Coumarins is simple and do not produce any hazardous waste. The N-methyl imidazole hydrochloride produce during the synthesis is a useful ionic liquid can be either used or to recover N-methyl imidazole for next reaction.Ultrasonic Bath completes reaction in 3 hours at 50 0 c due to effect of sonication.

V. ACKNOWLEGEMENT

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