
ABSTRACT

Bismuth(III)chloride is used as an efficient catalyst in the Von-Pachmann condensation of phenol with derivative of phenols with B-ketoesters leading to the formation of coumarin and their derivative with good yields, high purity and eco-friendly synthesis.

KEYWORDS: Coumarin, Von-Pachmann reaction, B-ketoesters, Substituted phenol, Bismuth (III) chloride.

INTRODUCTION

Coumarins are naturally occurring compound and found in various plants in large quantities, coumarins are biologically active compound used in various aspects of cosmetics, medicines & pharmaceutical industries (1) recently used in anti-tuberculosis and anti-HIV and active drugs (2).

Coumarin is the best known aromatic lactone (3) the isolation of coumarin was first reported by Vogel in Munich is 1820 (4) The IUPAC nomenclature of the coumarin ring system is 2H – 1 benzopyran – 2– one (5).

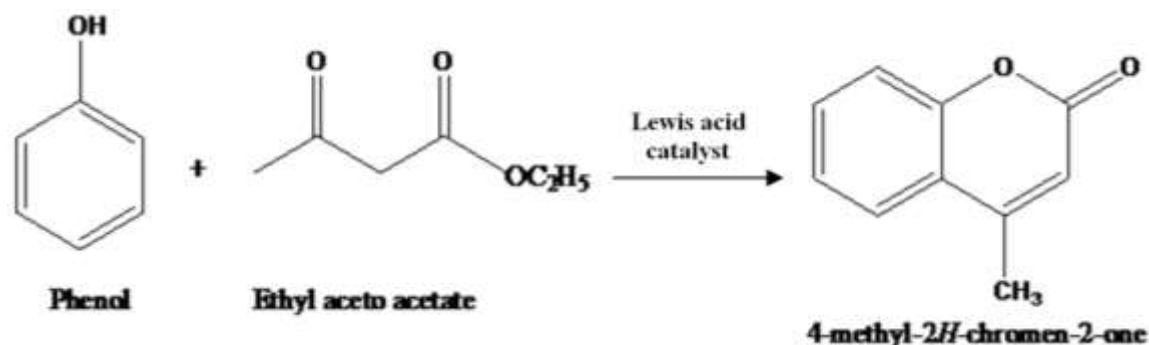
The synthesis of coumarins and their derivatives has attracted considerable attention from the organic and medicinal chemist for many years as a large number of natural products contain this heterocyclic nucleus. The Von – Pechmann reaction is a venerable reaction and it is one of the most simple & straightforward methods used to produce coumarins classically, the process consists of the condensation of phenols with B- ketoesters in the presence of a variety of reagents and gives a good yield of G- substituted coumarin(6).Several acid catalysts have been used in the Von-Pechmann reaction including sulfuric acid, aluminum chloride (7). Phosphorus pentoxide (8) This catalyst used as excess.

Chloroaluminate ionic liquids have been used in Friedel–crafts and other reaction in which they play the dual role of lewis acid catalyst and solvent (9), Coumarins have been synthesized by several routes including Von-Pechmann (10), Perkin (11), knoevenagel (12), Reformatsky (13)and by flask vacuum pyrolysis.

Thimons et al (14) have also reported the synthesis of substituted coumarins from substituted phenols and ethyl acetoacetate via Pechmann condensation, Using toluene as a solvent in the presence of acidic catalysts. Such as Amberlyst IR 120 or Nafion 417.

Variety of reagents have been used for this condensation and the reaction has been studied thoroughly using Lewis acid (15) ionic liquids (16), CAN (17), SiO₂ (18), FeCl₃ (19), oxalic acid (20) etc.

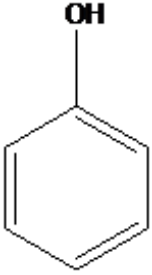
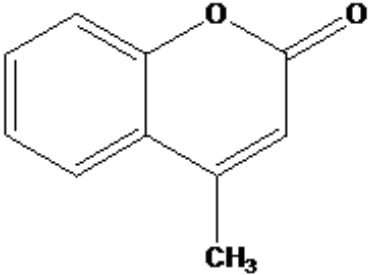
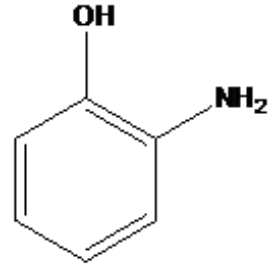
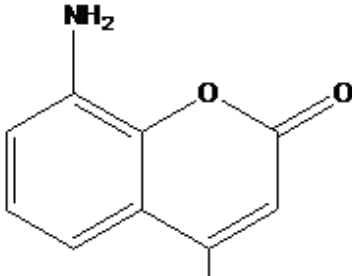
BiCl₃ is a pale yellow crystalline compound of bismuth and chloride, it is hygroscopic solid found to be white to the yellow crystal. BiCl₃ is Lewis acid catalyst highly soluble in acetone and methanol. It is hydrolyzed and decomposes readily to bismuth oxychloride (BiOCl). It is an oxidizing agent being readily reduced to metallic bismuth by reducing agent.

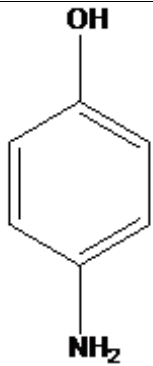
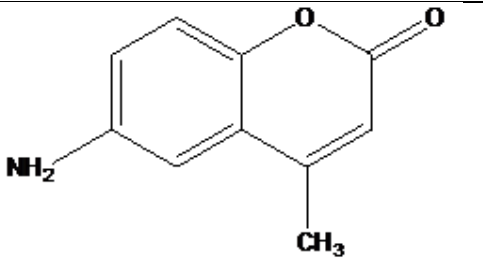
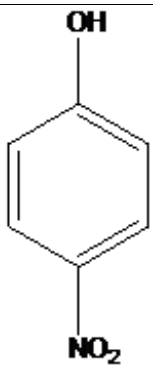
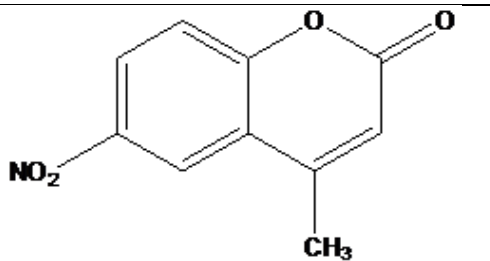
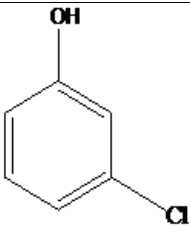
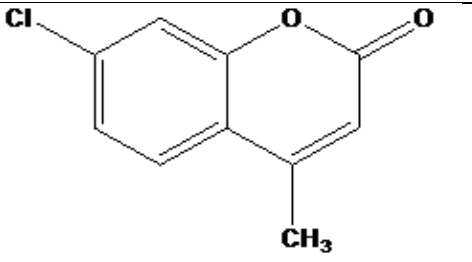
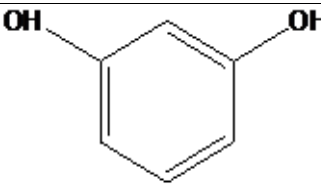
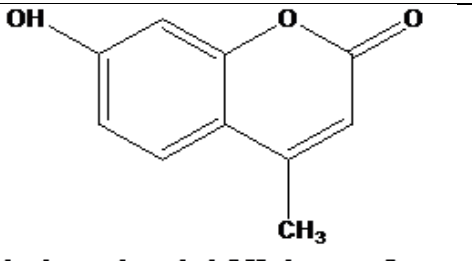


Scheme-1

A mixture of Ethyl aceto acetate & bismuth chloride as catalyst and ethanol as a solvent were taken in an iodine flask. It was stirred for 12 hours on the Magnetic stirrer. The reaction mixture was poured into crushed ice precipitate separated out which is then filtered, dried and recrystallised by ethanol the reaction was monitored by TLC. The melting point of recrystallized sample was determined.

Table 1 : Synthesis of coumarin via Von –Pachmann condensation of phenol with B– ketoesters induced by BiCl₃ catalyst

Sr. No.	Substrate	Time (hour)	^a Product	M.P.	^b % Yield
1	 Phenol	12	 4-methyl-2H-chromen-2-one	78 ^o C	86
2	 2-Aminophenol	12	 8-amino-4-methyl-2H-chromen-2-one	145-149 ^o C	71.57

3	 4-Aminophenol	12	 6-amino-4-methyl-2H-chromen-2-one	160°C	69.59
4	 P-nitrophenol	12	 4-methyl-6-nitro-2H-chromen-2-one	154°C	58.42
5	 m-chlorophenol	12	 7-chloro-4-methyl-2H-chromen-2-one	185°C	64.80
6	 Resorcinol	12	 7-hydroxy-4-methyl-2H-chromen-2-one	185°C	81.36

^aAll Products were characterized by comparison of their M.P. and IR spectra with those of samples.

^b Isolated yield

RESULT AND CONCLUSION

A variety of the method have been reported for the preparation of this class of compound coumarin were prepared in this work through a method on substituted phenol and ethyl acetoacetate by using BiCl₃, yield was coumarin found to be 50–84 %, the IR data confirmed their molecular structure melting point were determined by a capillary tube.

In conclusion, here we conclude comparative study for preparation of coumarin. This method has several advantages such as simple experimental work up, short reaction time, one pot synthesis, leading to a useful and attractive process for the preparation of coumarin.

REFERENCES

- [1] W.C.Muley, Kirk Othmer Encyclopedia of chemical Technology, 3rd Edition, John Wiley and sons New York, 1979.
- [2] Kirkiacharian S, Thuy Dt, SICSIC S Bakhchianian R., Kurkjian R. and Tonnaire T, Structure-Activity relationship of some 3 – sub, 4–hydroxy coumarins as HIV – I protease inhibitors II Farmaca, 2002, 57, 703.
- [3] Ahmed, S.K. James, Po Owen, K Patel (2002) Bio org& med. Chem. Lett, 12, 1343.
- [4] Abernethy, J.J. (1969), Chem. Edu. 46. 561.
- [5] O'Kennedy, R, Thornes, R.D. coumarins, Biology applications, and mode of Action ; John Wiley & sons, Chichester, (1997).
- [6] Sethna, S.M. Shah, N.M. Shah, R.C.J. Chem.Soc. 1938, 228.
- [7] Simmonis H. Remmert, P.Chem. Ber. 1914, 47, 2229, Robertson, A Sandrock, W.Fi Henry. C.B.J. Chem Soc. 1931, 2426.
- [8] Boon. J. A. Levisky, J.A. Pflug, J.liwilkes, J.S.J.org. Chem. 1986, 51, 480 , Adams, C.J. Earle, M.J. Roberts, Gisseddon, K.R.J. Chem. Soc. Chem. Commun 1998, 2097.
- [9] Von Pechmann, Hi duisberg, C. Chem. Ber. 1884, 17, 929.
- [10] Johnson, J.R. org. React 1942, 1, 210.
- [11] Cal Jones, G.org. react 1967, 15, 203, B) Brufola, G I Fringuelli, Fi Piermatti, oiPizzo, F Heterocycles 1996, 43, 1257.
- [12] Shirner, R.L.org. React 1942, 1, 1.
- [13] O.M.Singh and N.S. Devi, J.org. Chem. Vol. 74, 3141, 2009.
- [14] H. Pechmann Ber, 17, 929, 1884.
- [15] M.K.Potdar, M.S.Rasalkar, S.S. Mohile, M.M.Salunkhe, J.Mol cat A Chem. 235, 249 (2005).
- [16] Y. T. Reddy, V.N.Sonar, P.A. crooks, P.k. Dasar, P.N.Reddy, Commun, 38, 2082 (2008).
- [17] M. Maheshwara, V. Siddiah, G.LV. Damu, Y.K. Rao, C.V. Rao J.mol, cat a Chem. 255, 49 (2006).
- [18] B. Tagi, M.K. Mishra. R.V. Jarsa.
- [19] B. Karimi, D Aareyee org, Lett 10 (18), 3989 (2008).
- [20] H. Valizadana, A Shockravi Tetrahedron Lett, 46, 3501, (2005).