



Polyethylene glycol (PEG 400): A recyclable Catalyst system for the Synthesis and characterization of some 2-acetyl-5-methyl furan chalcones

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ABSTRACT

In an effort to develop, a series of chalcones were prepared by Claisen-Schmidt condensation. In the present study some new chalcones (a-h) have been synthesized by the reaction of 2-acetyl-5-methyl furan with different aromatic aldehydes in the presence of aqueous solution of sodium hydroxide, ethanol and PEG 400 used as a catalyst at room temperature. The structures of the various synthesized compounds are assigned on the basis of elemental analysis, IR, ¹HNMR and mass spectral data.

Keywords: Chalcones, 2-acetyl-5-methyl furan, Aromatic aldehydes, Aqueous NaOH, PEG 400.

INTRODUCTION

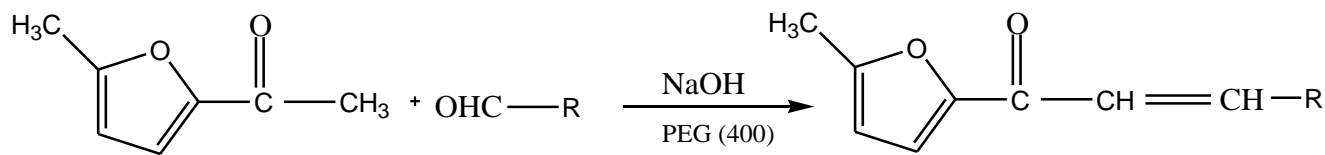
Survival of the fittest is the basis for life and the human beings also. The biggest threats for human beings are the various diseases and scientists and doctors are still fighting to find solutions with various forms of medications. Today's developed medicines are results of relentless effort made by human civilization time to time. When the era of synthetic drugs began, it opened thousand doors for the development of various synthetic molecules with potential action. Chalcones are natural compounds belonging to the flavonoid family. The compounds with the backbone of chalcones have been reported to possess various biological activities such as antimicrobial[1], anti-inflammatory[2], analgesic[3], antipalelet [4], antiulcerative[5], antimalarial[6], anticancer[7], antiviral[8], antileishmanial[9], antioxidant, antitubercular, antihyperglycemic[10]. The presence of a reactive α , β - unsaturated keto function in chalcones is found to be responsible for their antimicrobial activity. A number of recent reviews have also covered PEG chemistry and its applications in biotechnology and medicine [11, 12], PEG and PEG-supported catalysis [13]. PEG is a hydrophilic polymer, easily soluble in water and many organic solvents including: dichloromethane, alcohol and acetone, but it is not soluble in aliphatic hydrocarbons such as hexane, cyclohexane or diethyl ether [14]. In addition, PEG may be recovered from aqueous solution by extraction with a suitable solvent or by direct distillation of water or solvent [15]. PEG 400 used as a catalyst in addition, clean, low cost, recyclable solvent system and ready availability of catalyst, an environmentally benign.

MATERIALS AND METHODS

2-acetyl-5-methyl furan and all aromatic aldehydes were purchased from Sigma Aldrich. PEG 400 used was of Thomas baker. Ethanol and other chemicals of A.R. grade were used as received.

Experimental

General procedure for the synthesis of chalcones(a-h): A mixture of 2- acetyl-5-methyl furan (0.01 mol) and appropriate aldehyde (R) (0.01 mol) was stirred in ethanol and then aqueous solution of NaOH (40%, 10 ml) was added to it and in this solution 2 ml PEG 400 was added as a catalyst with continuous stirring. The mixture was kept at room temperature for two hours. The sodium salt of chalcone separated was decomposed by ice-cold HCl (30%). The separated chalcone was filtered, washed with water (50 ml) and dried and recrystallized from absolute ethanol.



Scheme 1: Synthesis of some new chalcones of 2-acetyl-5-methyl furan (a-h).

Furan chalcones (a-h) were prepared by carrying out the reactions of 2-acetyl-5-methyl furan with 2-chloro-6-fluro benzaldehyde, 2-hydroxy-5-bromo benzaldehyde, 4- fluro benzaldehyde, furfuraldehyde, 3-methoxy-4-hydroxy benzaldehyde, 2,4-dihydroxy benzaldehyde, 4-chloro benzaldehyde, 2-nitro benzaldehyde in ethanol using aqueous sodium hydroxide and PEG 400 as a catalyst.

Synthesis of chalcone is a single step method. The synthesized compounds were undergone physiochemical characterization and the obtained results are given. The yield of the synthesized compounds was found to be significant because of PEG 400 use as a catalyst. Elemental analysis showed that the percentage of carbon, hydrogen and oxygen was found experimentally is equivalent to the calculated values in all compounds.

Physical measurements and analytical data: The melting points were determined in open capillaries on Electro thermal apparatus and are uncorrected. The purity of all compounds were checked by thin layer chromatography using percolated silica 60 F 254 plate using hexane, ethyl acetate, chloroform (6:2:2) as mobile phase. Microanalysis of carbon, hydrogen and oxygen of the compounds were carried on a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were recorded on a Perkin-Elmer RX-1 infrared spectrophotometer in the range 4000–400 cm⁻¹. ¹H NMR spectra of the compounds were recorded on a Bruker Avance 400 MHz. The ESI mass spectra were recorded on a JEOL-Accu TOF JMS-100LC Mass spectrometer.

RESULTS AND DISCUSSION

The data obtained of the synthesized compounds-

1(5-methyl furan-2-yl)-3-(2-chloro-6-fluro phenyl) prop-2ene-1-one (a): Shiny yellow solid; yield: 83%; m.p. 125°C; Anal. Calcd. for C₁₄H₁₀O₂ClF; C: 76.80; H: 5.50; O: 15.20 (%); Found: C: 76.78; H: 5.56; O: 15.16 (%); IR (cm⁻¹): 1724 (C=O), 1562 (C=C), 1330 (C-O-C); ¹H NMR (400 MHz, DMSO-d₆): δ(in ppm) = 2.50 (DMSO), 7.25-7.75 (m, 9H, Ar- H) 6.88 (s, 1H, CH), 8.98 (s, 1H, CH); MS m/z 168 (M+).

1(5-methyl furan-2-yl)-3-(2-hydroxy-5-bromo phenyl) prop-2-ene-1-one (b): Shiny yellow solid; yield: 92%; m.p.: 122°C; Anal. Calcd. for $C_{14}H_{11}O_3Br$; C: 54.25; H: 3.70; O: 15.46 (%); Found: C: 54.24; H: 3.78; O: 15.44 (%); IR (cm^{-1}): 1691 (C=O), 1569 (C=C), 1263 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 7.12-7.67 (m, 9H, Ar-H), 6.72 (s, 1H, CH), 8.92 (s, 1H, CH); MS m/z 306 (M+).

1(5-methyl furan-2-yl)-3-(4-fluoro phenyl) prop-2-ene-1-one (c): Shiny yellow solid; yield: 91%; m.p.: 148°C; Anal. Calcd. for $C_{14}H_{11}O_2F$; C: 76.45; H: 5.46; O: 14.80 (%); Found: C: 76.43; H: 5.40; O: 14.84 (%); IR (cm^{-1}): 1715 (C=O), 1555 (C=C), 1332 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 7.28-7.92 (m, 9H, Ar-H), 6.60 (s, 1H, CH), 8.20 (s, 1H, CH); MS m/z 220 (M+).

1(5-methyl furan-2-yl)-3-(furfuryl) prop-2-ene-1-one (d): Shiny yellow solid; yield: 93%; m.p.: 120°C; Anal. Calcd. for $C_{12}H_{10}O_3$; C: 71.48; H: 5.52; O: 23.96 (%); Found: C: 71.45; H: 5.55; O: 23.98 (%); IR (cm^{-1}): 1696 (C=O), 1537 (C=C), 1265 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 6.97-7.93 (m, 9H, Ar-H), 6.64 (s, 1H, CH), 8.05 (s, 1H, CH); MS m/z 202 (M+).

1(5-methyl furan-2-yl)-3-(3-methoxy-4-hydroxy phenyl) prop-2-ene-1-one (e): Shiny yellow solid; yield: 80%; m.p.: 105°C; Anal. Calcd. for $C_{15}H_{14}O_4$; C: 69.46; H: 5.85; O: 24.90 (%); Found: C: 69.47; H: 5.82; O: 24.86 (%); IR (cm^{-1}): 1700 (C=O), 1622 (C=C), 1250 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 6.95-7.57 (m, 9H, Ar-H), 6.82 (s, 1H, CH), 8.38 (s, 1H, CH); MS m/z 258 (M+).

1(5-methyl furan-2-yl)-3-(2,4-dihydroxyl phenyl) prop-2-ene-1-one (f): Shiny yellow solid; yield: 82%; m.p.: 122°C; Anal. Calcd. for $C_{14}H_{12}O_4$; C: 68.96; H: 5.20; O: 26.45 (%); Found: C: 68.95; H: 5.19; O: 26.42 (%); IR (cm^{-1}): 1714 (C=O), 1519 (C=C), 1285 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 7.06-7.43 (m, 9H, Ar-H), 6.37 (s, 1H, CH), 8.21 (s, 1H, CH); MS m/z 244 (M+).

1(5-methyl furan-2-yl)-3-(4-chloro phenyl) prop-2-ene-1-one (g): Shiny yellow solid; yield: 85%; m.p.: 110°C; Anal. Calcd. for $C_{14}H_{11}O_2Cl$; C: 68.80; H: 5.59; O: 13.46 (%); Found: C: 68.85; H: 5.56; O: 13.48 (%); IR (cm^{-1}): 1738 (C=O), 1679 (C=C), 1325 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 6.77-7.64 (m, 9H, Ar-H), 6.70 (s, 1H, CH), 8.42 (s, 1H, CH); MS m/z 246 (M+).

1(5-methyl furan-2-yl)-3-(2-nitro phenyl) prop-2-ene-1-one (h): Shiny yellow solid; yield: 96%; m.p.: 135°C; Anal. Calcd. for $C_{14}H_{11}O_4N$; C: 67.40; H: 5.46; O: 25.85 (%); Found: C: 67.43; H: 5.40; O: 25.84 (%); IR (cm^{-1}): 1711 (C=O), 1527 (C=C), 1295 (C-O-C); 1H NMR (400 MHz, DMSO- d_6): δ (in ppm) = 2.50 (DMSO), 6.85-7.82 (m, 9H, Ar-H), 6.46 (s, 1H, COCH), 8.31 (s, 1H, CH); MS m/z 250 (M+).

Infrared spectra of the chalcone compounds show significant peaks. In the IR spectra of the chalcones a sharp band observed at 1738-1691 cm^{-1} is assigned to the $\nu(C=O)$ mode of the aldehyde group. This is further substantiated by the presence of a new band at 1679-1519 cm^{-1} , assignable to $\nu(C=C)$. The bands at 1332-1263 cm^{-1} due to $\nu(C-O-C)$ were also observed in the chalcone compounds.

1H NMR spectra of the chalcones were recorded in DMSO- d_6 . The compounds exhibit a singlet at δ 6.88-6.37 ppm due to the -COCH proton. The chalcones show multiplets in the region δ 7.93-6.77 ppm attributable to the aromatic protons. The signals at δ 8.98-8.05 ppm are due to CH group.

In Mass spectra, the structure further confirmed by appearance of peak at m/z 168, 306, 220, 202, 258, 244, 246, 250 (M+) for a,b,c,d,e,f,g,h chalcone compounds respectively.

APPLICATIONS

This is an environmentally benign procedure and reduces the total reaction time and good to excellent yields of chalcones.

CONCLUSIONS

In conclusion, PEG 400 used as a catalyst, an environmentally benign procedure makes this methodology a useful contribution to the existing procedure available for the synthesis of chalcone derivatives. The synthesis of chalcones using PEG 400 as a catalyst results enhancements in the rate of reaction. The proposed method for the synthesis of chalcones reduces the total reaction time and good to excellent yields, also allows easy separation of the product.

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REFERENCES

- [1] S.S. Mokle, M.A. Sayeed, Kothawar, Chopde, *Int. J. Chem. Sci.*, **2004**, 2(1), 96.
- [2] H.K. Hsieh, L.T. Tsao, J.P. Wang, *J. Pharm. Pharmacol.*, **2000**, 52,163.
- [3] G.S. Viana, M.A. Bandeira, F. Matos, *J. Phytomedicine*, **2003**, 10, 189.
- [4] L.M. Zhao, H.S. Jin, L.P. Sun, H.R. Piao, Z.S. Quan, *Bioorg. Med. Chem. Lett.*, **2005**, 15, 5027.
- [5] S. Mukarami, M. Muramatsu, H. Aihara, S. Otomo, *Biochem, Pharmacol*, **1991**, 42, 1447.
- [6] M. Liu, P. Wilairat, L.M. Go, *J. Med. Chem.*, **2001**, 44, 4443.
- [7] E. Francesco, G. Salvatore, M. Luigi, C. Massimo, *Phytochem*, **2007**, 68, 939.
- [8] J.C. Onyilagna, B. Malhotra, M. Elder, G.H.N. Towers, *Can. J. Plant Pathol*, **1997**, 19, 133.
- [9] S.F. Nielsen, M. Chen, T.G. Theander, A. Kharazmi, S.B. Christensen, *Bioorg. Med. Chem. Lett.*, **1995**, 5, 449.
- [10] M. Satyanarayana, P. Tiwari, K. Tripathi, A.K. Srivastava, R. Pratap, *Bioorg. Med. Chem*, **2004**, 12, 883.
- [11] J.M. Harris, *Poly (ethylene glycol) Chemistry: Biotechnical and Biomedical Applications*, Plenum Press, New York, **1992**.
- [12] J.M. Harris, S. Zalipsky, *Poly(ethylene glycol) Chemistry and Biological Applications*, American Chemical Society, Washington, DC, **1997**, ed., ACS Symposium Series 680.
- [13] C.M. Starks, C.L. Liotta, M. Halpern, *Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*, Chapman & Hall, New York, **1994**, p. 158.
- [14] E. Santaniello, A. Manzocchi, P. Sozzani, *Tetrahedron Lett.*, **1979**, 47, 4581.
- [15] F.E. Bailey, J.V. Koleske, *Poly (Ethylene Oxide)*, Academic Press, New York, **1976**.