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Waste Sea Sand Catalyzed a Microwave-Promoted Solvent-Free Biginelli Reaction for the One-Pot Synthesis of Dihydropyrimidin-2-(1H)-ones

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Abstract: *By cyclocondensing a variety of betaketoesters, a substituted urea, and an aromatic aldehyde, the Biginelli method generated functionalized 3,4-dihydro-2(H)-pyrimidinones (DHPM), as well as their byproducts and derivatives. Three steps are involved in the synthesis of dihydropyrimidinones and their derivatives. Due to the ecologically friendly manufacture of DHPM with increased good yields, because of its numerous advantages over the standard process, and due to the requirement for supportable chemistry of many examples, there has been resurgence in interest in this reaction. The synthesis of 3,4-dihydropyrimidinones (DHPMS) from aldehyde, substituted betaketoesters, substituted urea, and thiourea was said to be possible without the use of a solvent by using sea sand as a catalyst. The solvent-free, microwave-assisted green method provides advantages over conventional frying, including quicker reaction times, simpler processing, and higher yield.*

I. INTRODUCTION

In the Biginelli reaction, aldehydes and Betadicarbonyl compounds are condensed to yield 3,4-dihydropyrimidin2-(1H)-ones (DHPM) and its different thiones. Due to their numerous pharmacophoric properties, dihydropyrimidinones and their derivatives have become more significant in chemical, synthetic, and medicinal chemistry. This is due to the diverse range of biological roles that simple supported compounds exhibit, including antagonist, antagonist, and modular calcium channel. This simple reaction was initially described in 1893 by the Italian chemist Pietro Biginelli. Many mineral acids or other acids catalyzed the reaction.

A one-pot condensation of an aldehyde, beta ester, and substituted urea under extremely acidic conditions is Biginelli first recorded reaction. Product yields, with an emphasis on various substituted aromatic aldehydes, were frequently painfully low. Thus, prepare 3,4-dihydropyrimidin-2(1H)ones over different types of acid catalysts such as H2SO4 (sulfuric acid) [5], BF3•EtOH/CuCl as a Lewis acid [6], LaCl3•7H2O with catalytic concentrated HCl concentrated [7], CeCl3•H2O[8], InCl3 [9], heteropolyacids [10], BiCl3 [11], Cu(OTf)2 [12], TMSCl [13], LiClO4[14], LiBr [15] InBr3[16], FeCl3.6H20/HCl acid [17], TMSI [18] and CdCl2 [19-20] have been widely used. Numerous of the catalysts previously described have risky environmental implications and challenging disposal procedures.

In addition, the manufacture of 3,4-dihydropyrimidin-2(1H)-one necessitates long reaction periods, an atmosphere that is extremely acidic, aggressive reaction conditions (high temperature), and difficult scaling up. Current research has shown that sulfuric and silicosulfuric acids can be used in this process in place of acidic catalytic materials. [20-25] Nowadays, sulfuric and silicic acids serve as catalysts for other chemical reactions as well as the production of 3,4-dihydropyrimidin-2(1H)ones. Our project's and study's main goal was to contrast the methods used to synthesise 3,4-dihydropyrimidin-2(1H) ones and thiones using microwave heating and conventional heating without the use of a solvent.

II. EXPERIMENTAL

The uncorrected melting points of the compounds in a paraffin bath were measured in an open capillary. Chemical shift values were measured in units of 5 (ppm) with a Perkin-Elmer FT 1H NMR spectrophotometer, a 300 MHz FT-

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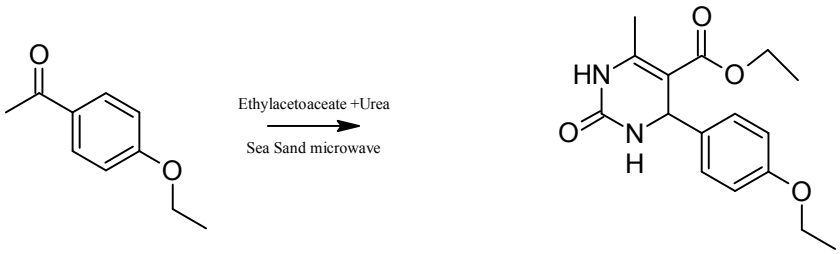
NMR spectrometer, and CDCl3 as the solvent, [26-27] in relation to the internal standard tetramethyl silane (Me4Si). This is an illustration of a typical microwave experiment that uses radiation rather than solvents: Aldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea or thiourea (15 mmol), and sea sand (20 mol %) were put in a 100 mL beaker and microwave-radiated for however long the technique called for without the use of any solvents. TLC reaction (TLC). Put the filtered output into an ice-filled container after you are done. It is then further dried at a specific temperature in an oven.

traditional heating technique in a 100 mL round-bottom flask with a reflux condenser, a mixture of an aromatic aldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea or thiourea (15 mmol), and sea sand (20% mol%) were taken up in ethyl alcohol as a solvent. The aggregate was heated to eight degrees Celsius over a period of time in an oil bath. As soon as the filtering process is complete, pour the filtrate into ice water.



Observation Table 1 (Microwave Reaction)

Sr. No	Aldehyde	Microwave Method			Conventional Method		
		Time in sec.	Yield	Physical constant in 0C	Time in Min.	Yield	Physical constant in 0C
1	P-Nitrobenzaldehyde	50	98	202	90	77	208
2	P-chlorobenzaldehyde	60	90	206	95	66	207
3	P-methyl Benzaldehyde	45	92	211	98	78	211
4	P-Methoxy Benzaldehyde	70	94	195	100	78	196
5	furfuraldehyde	55	88	196	95	87	196
6	Benzaldehyde	70	85	188	98	55	188
7	cinnaldehyde	55	80	227	98	67	226
8	M-methyl Benzaldehyde	88	90	242	95	56	246
9	M-chlorobenzaldehyde	65	85	216	97	67	218

III. RESULTS AND DISCUSSION

Aldehydes, ethyl acetoacetate, urea or thiourea, and sea sand were contrasted in the 1-pot synthesis of dihydropyrimidines. When applied to a catalyst at 80 degrees Celsius with ethyl alcohol as a solvent and in solvent-free circumstances, microwave assisted response significantly decreased reaction time from hours to a few seconds. Recognized substances share the same physical and spectral characteristics as described in the literature. Several aromatic and heterocyclic aldehydes with different structural characteristics were employed in this condensation.

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Unsaturated aldehydes primarily interact with the aldehyde functional group, in contrast to acid-sensitive heterocyclic aldehydes, which entirely generated dihydropyrimidine.

IV. CONCLUSION

In comparison to traditional heating techniques, microwave assisted dihydropyrimidine synthesis using sea sand catalyst provides a number of benefits, including faster reaction times, higher harvests, and easier experimental diagnosis procedures. Given that it doesn't require any harmful compounds and doesn't produce any pollution, this solvent-free technique qualifies as a green Biginelli response approach. Microwave-assisted synthesis, which is risk-free, ecologically friendly, and economical for the Biginelli reaction with three components, should be successful overall due to the method's softness and simplicity.

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REFERENCES

[1]. Roy S R, Jadhavar P S, Seth K, Sharma K K and ChakrabortiA K 2011 Synthesis 2261;
[2]. Simon C, Constantieux T and Rodriguez J 2004 Eur. J. Org. Chem. 4957.
[3]. Biginelli P 1893 Gazz. Chim. Ital. 23 360
[4]. (a) P. Biginelli, Gazz. Chim. Ital., 23, 360 (1893); (b) C.O. Kappe, Tetrahedron, 49, 6937 (1998).
[5]. (a) T.U. Mayer, T.M. Kapoor, S.J. Haggarty, R.W. King, S.L. Schreiberand T.J. Mitchison, Science, 286, 971 (1999); (b) K.S. Atwal, G.C.Rovnyak, S.D. Kimball, D.M. Floyd, S. Moreland, B.N. Swanson, J.Z.Gougoutas, K.M. Smille and M.F. Malley, J. Med. Chem., 33, 2629 (1990).
[6]. K. Folkers and T.B. Johnson, J. Am. Chem. Soc., 55, 2886 (1933).
[7]. E.H. Hu, D.R. Sidler and U.H. Dolling, J. Org. Chem., 63, 3454 (1998).
[8]. J. Lu, Y. Bai, Z.Wang, Yang and H. Ma, Tetrahedron Lett., 41, 9075 (2000).
[9]. D.S. Bose, L. Fatima and H.B. Mereyala, J. Org. Chem., 68, 587 (2003).
[10]. B. C. Ranu, A. Hajara and U. Jana, J. Org. Chem., 65, 6270 (2000).
[11]. E. Rafiee and H. Jafari, Bioorg. Med. Chem. Lett., 16, 2463 (2006).
[12]. K. Ramalinga, P. Vijayalakshmi and T.N.B. Kaimala, Synlett, 863 (2001).
[13]. A. S. Paraskar, G.K. Dewkar and A. Sudalai, Tetrahedron Lett., 44, 3305 (2003).
[14]. Y.L. Zhu, S.L Huang and Y.J. Pan, Eur. J. Org. Chem., 2354 (2005).
[15]. J.S. Yadav, B.V.S. Reddy, R. Srinivas, C. Venugopal and T. Ramalingam,Synthesis, 1341 (2001).
[16]. G. Maiti, P. Kundua and C. Guin, Tetrahedron Lett., 44, 2757 (2003).
[17]. N.Y. Fu, Y.F. Yuan, Z. Cao, S.W. Wang, J.T. Wang and C. Peppe, Tetrahedron,58, 4801 (2002).
[18]. J. Lu and H. Ma, Synlett, 63 (2000).
[19]. G. Sabitha, G.S.K. Reddy, C.S. Reddy and J.S. Yadav, Synlett., 858 (2003).
[20]. A.V. Narsaiah, A.K. Basak and K. Nagaiah, Synthesis, 1253 (2004);
[21]. J.C. Rodriguez-Dominguez, D. Bernardi and G. Kirsch, Tetrahedron Lett., 48, 5777 (2007).
[22]. Gaikar, P. S., Shivankar, V. S., Patil, P. A., Chavan, A. U., &Wadhawa, G. C. (2021). Preliminary Phytochemical Analysis and Antioxidant, Anti-Inflammatory Activity of DiclipteraGhaticaSantapau. Int. J. of Aquatic Science, 12(2), 4973-4980.
[23]. N. A. Mirgane, A. Chandore, V. Shivankar, Y. Gaikwad and G. C. Wadhawa, "Phytochemical Study and Screening of Antioxidant, Anti-inflammatory TyphoniumFlagelliforme," Res. J. Pharm. Technol., 14(5), 2021, 2686–2690.
[24]. Patil, Dinanath D., Gurumeet C. Wadhava, and Arun K. Deshmukh. "One Pot Synthesis of Nitriles from Aldehydes and Hydroxylamine Hydrochloride Using Ferrous Sulphate in DMF Under Reflux Condition." Asian Journal of Chemistry 24.3 (2012): 1401.

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[25]. Patil DD, Mhaske DK, Wadhawa GC. Green Synthesis of 3,4dihydropyrimidinone using ferrous sulphate as recyclable catalyst, Journal of Pharmaceutical Research and Opinion, 2011; 1(6): 172–174.

[26]. Nayak, Shubhada S., et al. "Green synthesis of the plant assisted nanoparticles from Euphorbia neriifolia L. and its application in the degradation of dyes from industrial waste." Plant Science Today 8.2 (2021): 380-385.

[27]. Efficient catalyst. European journal of pharmaceutical and medical research, (ejpmr), 2016; 3(12): 556-558.

[28]. Procopio, A.; Das, G.; Nardi, M.; Oliverio, M.; Pasqua, L. A Mesoporous Er(III)-MCM-41 Catalyst for the Cyanosilylation of Aldehydes and Ketones under Solvent-free Conditions. Chem. Sus. Chem. 2008, 1, 916–919. [CrossRef]

[29]. Procopio, A.; Gaspari, M.; Nardi, M.; Oliverio, M.; Romeo, R. MW-assisted Er(OTf)3 -catalyzed mild cleavage of isopropylidene acetals in Tricky substrates. Tetrahedron Lett. 2008, 49, 1961–1964. [CrossRef]