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The LiFe_5O_8 an efficient catalyst for one pot synthesis of β -amino ketones under microwave irradiation

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Abstract

The LiFe_5O_8 catalyzed one pot three component Mannich type reaction of Acetophenone, aromatic aldehydes and aniline done by using ethylene glycol as a solvent in microwave irradiation. This reaction gives good yield of β -amino ketones.

Keywords: Lithium ferrite, Mannich reaction, aniline, aromatic aldehydes and acetophenone.

Introduction

The Mannich type reactions are very important carbon-carbon bond forming reactions in organic synthesis and one of the most widely utilized chemical transformations for the formation of β -amino ketones and other amino carbonyl compounds, which are important synthetic intermediates for various pharmaceutical and natural products [1, 2]. Therefore, the development of new synthetic methods leading to β -amino carbonyl compounds or their derivatives has attracted much attention. However, the classic Mannich reaction has limited applications. To overcome the drawbacks of the classic method, numerous modern versions of the Mannich reaction using performed electrophiles, such as imines and stable nucleophiles, such as enolates, enol ethers, and enamines [3] have been developed. Conventional catalysts for the classical Mannich reaction of aldehydes, ketones and amines involve mainly Lewis acids [4-5], Bronsted acids [6-7] and Lewis base catalysts [8]. However, sulfonated poly (4-vinylpyridine) heteropolyacid salts [9], GuHCl [10], $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ [11], sulfated MCM-41 [12] ionic liquids [13] have been found to catalyze this reaction. These catalysts suffer mainly from the drawbacks of long reaction time, toxicity and their use as in stoichiometric amounts. While searching for economical, cheap and better catalysts, we thought it worthwhile to perform a controlled reaction condition for the Mannich reaction using solid acid catalyst.

Lithium ferrite and mixed lithium ferrites have very high potential for microwave applications, especially as replacements for garnets, due to their low cost. The squareness of the hysteresis loop and superior temperature performance are other prominent advantages that have made them very promising candidates for application in microwave devices.

Microwave promoted reactions are well known as environmentally benign methods that also usually provide enhanced reaction rates, cleaner products and manipulative simplicity. However, these procedures are practically limited as the solvents in microwave oven at elevated temperature create high pressure, which may cause explosion. To circumvent these problems there is need for the development of newer methods which proceed under mild condition.

2. Material and Methods**2.1 The synthesis of β -amino ketones**

A mixture of Benzaldehyde (1.0 mmole), Acetophenone (1.0 mmole) and Aniline (1.0 mmole) and (10 mole %) lithium ferrite and ethylene glycol as a solvent were taken in beaker. The reaction mixture was irradiated in microwave oven at 80 °C temperatures for the pre-cised time shown in (Table 1). The progress of the reaction was monitored by TLC. After completion, the reaction mass was cooled and poured over crushed ice and solid was obtained, purified by recrystallization. The products were confirmed by melting point comparisons with authentic samples.

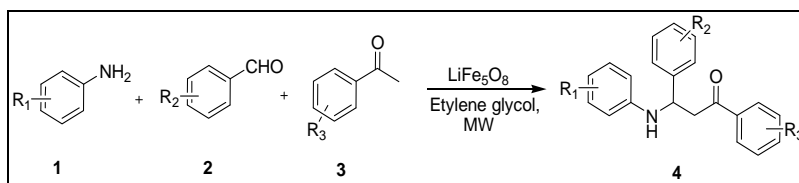


Table 1: Synthesis of β -amino ketones catalyzed by LiFe_5O_8

Entry	R_1	R_2	R_3	% of Yield	Time (Min)	M. P. ($^{\circ}\text{C}$)	
						Found	Reported
4a	H	H	H	72	8	168-171	169-170
4b	H	4-Cl	H	77	3	113-115	114-115
4c	H	4- NO_2	H	76	8	106-108	107-110
4d	H	4- OCH_3	H	80	9	146-148	147-149
4e	H	4- CH_3	H	77	5	129-130	131-132
4f	H	4-Br	H	73	7	123-126	123-127
4g	H	4-OH	H	70	6	171-173	172-173
4h	4- NO_2	H	H	72	10	178-180	179-180
4i	4-Cl	H	H	79	11	167-171	170-171

2.2 Selected spectral data

1, 3-diphenyl-3-(phenylamino) propan-1-one (Entry 4a)

IR (KBr): 3381, 1665 cm^{-1} . ^1H NMR (CDCl_3 , δ ppm): 7.92–7.95 (m, 2H), 7.58–7.63 (m, 1H), 7.41–7.53 (m, 4H), 7.33–7.37 (m, 2H), 7.23–7.28 (m, 1H), 7.03–7.06 (m, 2H), 6.71 (t, 1H, $J=6.74\text{ Hz}$), 6.60 (d, 2H, $J=7.83\text{ Hz}$), 5.01 (m, 1H, $J=7.41\text{ Hz}$), 4.52 (s, 1H), 3.56 (m, 1H, $J=16.13\text{ Hz}$), 3.50 (m, 1H, $J=16.15\text{ Hz}$).

3-(4-nitrophenyl)-1-phenyl-3-(phenylamino) propan-1-one (Entry 4c)

IR (KBr): 3370, 1666 cm^{-1} . ^1H NMR (CDCl_3 , δ ppm): 7.87 (m, 2H), 7.60 (m, 1H), 7.37–7.45 (m, 4H), 7.33 (m, 2H), 7.25 (m, 1H), 7.06 (m, 2H), 6.38 (d, 2H, $J=7.50\text{ Hz}$), 4.91 (m, 1H, $J=7.4\text{ Hz}$), 4.51 (s, 1H), 3.53 (m, 1H, $J=15.9\text{ Hz}$), 3.44 (m, 1H, $J=15.8\text{ Hz}$).

3-(4-methoxyphenyl)-1-phenyl-3-(phenylamino) propan-1-one (Entry 4d)

IR (KBr): 3370, 1667 cm^{-1} . ^1H NMR (CDCl_3 , δ ppm): 7.25 (d, 2H, $J=8.2\text{ Hz}$), 7.31–7.27 (m, 2H), 7.44–7.41 (m, 2H), 7.52–7.50 (m, 1H), 7.88 (d, 2H, $J=7.5\text{ Hz}$), 3.45–3.38 (m, 2H), 3.60 (s, 3H), 4.94 (t, 1H), 6.44 (d, 2H, $J=8.1\text{ Hz}$), 6.51 (t, 1H), 6.87–6.85 (m, 2H).

3-(4-nitrophenylamino)-1, 3-diphenylpropan-1-one (Entry 4h)

IR (KBr): 3375, 1672 cm^{-1} . ^1H NMR (CDCl_3 , δ ppm): 7.11 (d, 2H, $J=7.6\text{ Hz}$), 7.22–7.26 (m, 1H), 7.30–7.34 (m, 2H), 7.60 (d, 2H, $J=6.3\text{ Hz}$); 7.91 (d, 2H, $J=7.2\text{ Hz}$), 3.42–3.55 (m, 2H), 5.09 (t, 1H), 6.45 (d, 2H, $J=6.2\text{ Hz}$), 6.66–6.62 (m, 2H), 6.79–6.81 (m, 1H)

3. Results and Discussion

In this method, we selected LiFe_5O_8 for their capability to catalyze the three-component Mannich reaction and acetophenone, benzaldehyde and aniline and the results are summarized in Table 1. To investigate the scope and general idea of the present method, different aldehydes and amines were tested for the Mannich reactions with acetophenone in ethylene glycol under microwave irradiation at 80 $^{\circ}\text{C}$ as shown in Table 1. The three-component Mannich reaction proceed efficiently in short time in the presence of 10 mol %

of lithium ferrite under microwave irradiation to give the corresponding products (Table 1, entries 4a– 4i).

4. Conclusion

In summary, we have introduced an efficient, clean and mild synthetic process for three components, One-pot method for the synthesis of β -amino carbonyl derivatives in the presence of Lithium ferrite highly efficient catalyst. This method is beneficial for the good yields, short reaction time, mild conditions, low catalyst loading and convenient operation.

5. References

- (a) Davis FA, Zhang Y, Anil Kumar G. *J Org Chem.* 2003; 68(21):8061-8064. (b) Even GB, Fureneaux RH, Tyler PC, Schramm VL. *Org. Lett.* 2003; 5:3639-3640. (c) Nartin SF. *Acc. Chem. Res.* 2002; 35(10):895-904. (d) Fujita T, Nagasawa H, Uto Y, Hashimoto T, Asakawa Y, Hori H. *Org. Lett.* 2004; 6(5):827-830. (e) Joshi NS, Whitaker LR, Francis MB. *J Am Chem Soc.* 2002; 124:12964. (f) Ishimaru K, Kojima T. *Tetrahedron Lett.* 2003; 44(29):5441-5444. (g) Cordova A. *Acc. Chem. Res.*, 2004; 37(2):102-112. (i) Cordova A. *Chemistry- A European Journal.* 2004; 10(8):1987-1997.
- (a) Blicke FF. *Organic Reactions.* 1942, I(303). (b) Leinmann EF. In *Comprehensive Organic Synthesis* Trost BM, Ed. Pergamon Press, New York, 1991, 2. Chapter 4.1. (c) Arend M, Westerman B, Risch N. *Angew. Chem. Int. Ed.* 1998; 37:1044. (d) Kabayashi S, Ishitani H. *Chem. Rev.* 1999; 99(5):1069-1094.
- (a) Trost BM, Terrell LR. *J Am Chem Soc.* 2003; 125:338-339. (b) Matsunaga S, Kumagai N, Harada S, Shibasaki M. *J Am Chem Soc.* 2003; 125:4712-4713. (c) Juhl K, Gathergood N, Jorgensen KA. *Angew. Chem.* 2001; 113:3083-3085. (d) List B. *Am. Chem. Soc.* 2000; 122:9336-9337. (e) List B, Pojarliev P, Biller WT, Martin HJ. *J Am Chem Soc.* 2002; 124:827-833. (f) Cordova A, Notz W, Zhong G, Betancort JM, Barbas CF. *J Am Chem Soc.* 2002; 124(9):1842-1843. (g) Kobayashi S, Hamada T, Manabe K. *J Am Chem Soc.* 2002; 124:5640-5641. (h) Hayashi Y, Tsuboi W, Ashimine I, Urushima T, Shoji M, Sakai K. *Angew.*

- Chem. 2003; 42:3677-3680. (i) Wenzel AG, Jacobsen EN. J Am Chem Soc. 2002; 124(44):12964-12965.
4. Kobayashi S, Hamada T, Manabe K. J Am Chem Soc. 2002; 124:5640-5641.
 5. Desai P, Schildknecht K, Agrios KA, Mossman C, Milligan GL, Aube J. J Am Chem Soc. 2000; 122:7226-7232.
 6. Akiyama T, Takaya J, Kagoshima H. Synlett. 1999; 9:1426-1428.
 7. Akiyama T, Matsuda K, Fuchibe K. Synlett. 2005; 2:322-324.
 8. Takahashi E, Fujisawa H, Mukaiyama T. Chemistry Letters. 2004; 33(7):936-937.
 9. Li WY, Zong YX, Wang JK, Niu YY. Chin. Chem. Lett. 2014; 25(4):575-578.
 10. Heravi MM, Zakeri M, Mohammadi N. Chin. Chem. Lett. 2011; 22:797-800.
 11. Dai Y, Li BD, Quan HD, Liu CX. Chin. Chem. Lett. 2010; 21:31-34.
 12. Vadivel P, Maheswari CS, Lalitha A. IJITEE. 2013; 2(5):267-270.
 13. Gong K, Fang D, Wang HL, Liu ZL. Monatsh. Chem. 2007; 138(11):1195-1198.