Synthesis of New Knoevenagel Derivative using Fe$_3$O$_4$ Magnetic Nanoparticals

PRAVINSING S. GIRASE[1], DEEPAK V. NAGARALE[2], BHIKAN J. KHAIRNAR[3] and BHATA R. CHAUDHARI[4]*

[1]Department of Chemistry, Jaihind Educational Trusts's Z. B. Patil College, Dhule-424002, India.
[2]Department of Chemistry, VVM's S. G. Patil Arts, Science and Commerce College, Sakri 424101,India.
[3]SSVPS's Arts, Commerce and Science College, Shindkheda, MH SH 11, Chimthane Road, Sindkheda, Maharashtra 425406, India.
[4]Department of Chemistry, SSVPS's L. K. Dr. P.R, Ghogrey Science College, Dhule, Vidyanagri, Deopur, Dhule, Maharashtra 424005, India.
*Corresponding authors E-mail: brc155@gmail.com, psgirase65@gmail.com

ABSTRACT

Heterogeneous catalysts mediated reaction system should compensate some of drawbacks observed in previously reported reactions. We have obtained magnetic nanoparticles (MNPs) were using a reduction–precipitation method and characterized for nano particle verification. This method is very easy and extremely efficient for the Knoevenagel reaction. We have used aromatic aldehydes with various active methylene containing compounds. It give Knoevenagel products in good to excellent yields at refluxed temperature and work with elevated temperature condition.

Keywords: Magnetite nanoparticles, Knoevenagel condensation, Active methylene compounds, Heterogeneous catalysts.

INTRODUCTION

Today organic synthesis based on magnetic nanomaterial's are found a major role in many fields including industrial procedure, biotechnology, environmental remediation, biomedicine, and particularly catalysis[1-2a-d]. Reactions were generally and mostly carried out in organic solvents, some time with aqueous[3]. Some case water also act as environmentally benign solvent[4]. The use of environmentally benign solvents like water[5] and absent of organic[6] methods from inexpensive as well as importance in synthetic point of view[7]. This methods improve the rate of many organic reactions. Thus carry out the Knoevenagel condensation in water medium[8]. Application of Knoevenagel condensation reaction of in water aromatic aldehydes with ethyl cyanoacetate or malononitrile[9]. The separation and recycling of the catalyst is highly favorable because catalysts are very expensive.

Surface reform i. e. immobilization of

functional group has been extensively studied[10] formation of new covalent bond on the targeted structure[11]. There are wide reports[12-13] immobilization also different kind like chelate forming organic reagents, some on polymers, naturally found compounds, metal salts and carbon and highly dispersed silica. Immobilization of compounds depend on substitution reaction between the surface of the supporting material[14]. Among the different adsorbents, silica gel particularly restrained with various organic compounds[15-19] Conducting same reactions by using heterogeneous catalyst had reduced many drawbacks found in previously reported reactions. In this type of reactions, the catalyst can be recovered by filtration and it can be reuse for the next cycle. However, it is worthy to mention in spite of several advantages experienced practically in using of heterogeneous catalysts, due to the nanosized particles used, few limitations to the sustainability are observed[20-24].

EXPERIMENTAL

^{1}H NMR Spectra and ^{13}C NMR spectra were recorded as δ values in ppm on instrument Brucker FT AC-400 MHz and 100 MHz (TMS Internal standard). IR spectra on a Perkin-Elmer 1605 FT-IR and absorptions recored in cm^{-1} unit. Thermo Scientific Q-Exactive, Accela 1250 pump use for LCMS data.

Preparation of Ferrite (Fe$_3$O$_4$) magnetic nanoparticles

FeCl$_3$.6H$_2$O (Ferric chloride hexahydrate) (5.8 g, 0.022 mol) and FeCl$_2$.4H$_2$O (Ferrous chloride tetra hydrate) (2.1 g, 0.011 mol) were were dissolved in 150 mL of deionized H$_2$O in a round bottom flask (250 mL) at R.T. under constant stirring. Thereafter, 10 mL of aq. NH$_3$ solution (32%) was then added into mixture within 40 min with stirring. Finally the black precipitate solid was collected by magnetic decantation, washed with distilled water until solution becomes neutral, and then washed with ethanol two times. After the performed of procedure the magnetic nano materials have been characterized using an Infrared spectroscopy and the structure of magnetic catalysts was determined by X-ray diffraction (XRD) study. Scanning electron microscope (SEM) use for determine crystal size of catalyst.
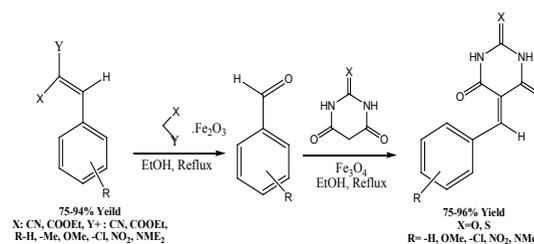
General procedure

We have carried out reaction of various substituted benzaldehyde with active methylene compounds active (acyclic) and (cyclic) active methylene compounds (e.g. barbituric acid and thiobarbituric acid) in presence of ferrite heterogeneous catalyst as shown in Scheme 1.

Knoevenagel reactions of substituted benzaldehydes with active methylene compounds using nano-ferrite as catalyst

We have carried out Knoevenagel condensation reactions. In this various substituted benzaldehyde with active methylene compounds (cyclic and acyclic) use ferrite catalyst (Scheme 1).


75-94% Yeild
X: CN, COOEt, Y+ : CN, COOEt,
R-H, -Me, OMe, -Cl, NO$_2$, NME$_2$

75-96% Yield
X=O, S
R= -H, OMe, -Cl, NO$_2$, NMe$_2$

Scheme 1 Nano-ferrite catalysed Knoevenagel condensation

RESULTS AND DISCUSSION

We have made efforts to improve a catalytic system that would overcome the limitations of the earlier reported Knoevenagel reactions. When initial study held, benzaldehyde (1a) and malononitrile (2a) used as a represented system. optimization was done by Sequences of the experiments performed with a variety of reaction parameters, like type of catalyst, catalyst quantity, solvent, temperature and time (Table 1). Initially we have synthesized the paramount magnetically distinguishable catalysts, all MFe$_2$O$_4$ (M=Fe^{2+}, Zn^{2+}, Mn^{2+} and Ni^{2+}) by screened for sample reaction. Apart from catalysts examined, Fe$_3$O$_4$ found to be the best, providing very good yields of the targeted product 3a (Table , entries 1-5). Then catalysts concentration study performed having rang 10 to 20 mol% rises the yield of product 3a up to 94%, Further increase of catalyst concentration to 25 mol% did not improve the yield of 3a (Table 1, entries 5-8). As the solvent have an impact on the overall process, the effect of various solvents (Table 1, entries 5, 9-13,15) were examined; the best results was obtained with C$_2$H$_5$OH which afforded 3a in 94% yield (Table 1, entry 5). We have also made temperature study data 3a obtained good yield at reflux temperature for complete consumption of aldehyde (Table 1,entries 5,14). Reaction conditions optimized and we have explore the substrate scope of the ferrite catalyzed Knoevenagel condensation of substituted aldehydes with acyclic active methylene compounds

(malononitrile, ethyl cyanoacetate, ethyl acetoacetate) and cyclic active methylene compounds (barbituric acid and thiobarbituric acid) for the synthesis of styrene derivatives having different functional groups. Thus, we have observed that electron good yield of products. Satisfyingly this protocol endured a range of common functional groups such as alkyl, ether, halogen and nitro groups irrespective of the place. Results of these reactions listed in Table 2.

Table 1: Optimization of Reaction Parameters[a]
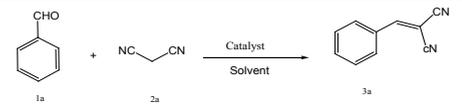
Sr. No	Catalyst	Catalyst (mol%)	Solvent	Temp (°C)	Time (min)	Yield (%)[b]
1	--	--	EtOH	Reflux	120	19
2	$ZnFe_2O_4$	20	EtOH	Reflux	30	85
3	$MnFe_2O_4$	20	EtOH	Reflux	30	88
4	$NiFe_2O_4$	20	EtOH	Reflux	30	86
5	Fe_3O_4	20	EtOH	Reflux	30	94
6	Fe_3O_4	10	EtOH	Reflux	30	60
7	Fe_3O_4	15	EtOH	Reflux	30	82
8	Fe_3O_4	25	EtOH	Reflux	30	94
9	Fe_3O_4	20	ACN	Reflux	30	78
10	Fe_3O_4	20	H_2O	Reflux	30	46
11	Fe_3O_4	20	MeOH	Reflux	30	64
12	Fe_3O_4	20	$CHCl_3$	Reflux	30	26
13	Fe_3O_4	20	PEG-400	80	30	43
14	Fe_3O_4	20	EtOH	60	30	81
15[c]	Fe_3O_4	20	--	80	30	59

[a]Reaction conditions: Benzaldehyde (1mmol), Malononitrile (1 mmol), Solvent (5 mL),[b]Isolated yield, [c]neat reaction

Table 2: Substrate Study of Knoevenagel Product[a] **(Acyclic Active Methylene Compound)**
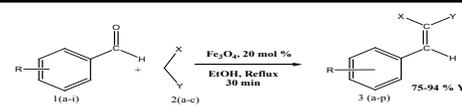
Sr. No	Aldehyde (-R)	X	Y	Product	Yield (%)[b]	m.p. (°C) Found	m.p. (°C) Lit. [Ref.]
1	H	CN	CN	3a	94	82-84	82[49]
2	H	CN	COOEt	3b	91	47-49	49-50[49]
3	H	COOEt	COOEt	3c	90	Oil	N.A.
4	4-Cl	CN	CN	3d	89	162-164	164-165[49]
5	4-Cl	COOEt	COOEt	3e	90	84-86	87[53]
6	2-Cl	CN	CN	3f	82	96-98	96-97[49]
7	2-Cl	CN	COOEt	3g	86	50-52	53[52]
8	4-NMe₂	CN	CN	3h	84	186-188	160[50]
9	4-NMe₂	CN	COOEt	3i	86	124-126	125[51]
10	4-NO₂	CN	CN	3j	94	158-169	162-163[49]
11	4-NO₂	CN	COOEt	3k	93	168-170	173-174[49]
12	3-NO₂	CN	CN	3l	90	104-106	104-106[49]
13	2-NO₂	CN	CN	3m	90	140-142	141-142[54]
14	3-OMe	COOEt	COOEt	3n	80	240-242	N.R
15	3,4-di OMe	CN	CN	3o	86	142-144	N.R
16	3,4-di OMe	CN	COOEt	3p	82	156-158	N.R

[a]Reaction conditions: Aldehyde (1mmol), acyclic active methylene compound (1 mmol), Ethanol (5 mL), [b]Isolated yield, N.R.= Not Reported, N.A.= Not Applicable

Table 3: Substrate Study of Knoevenagel Product[a] **(Cyclic Active Methylene Compound)**
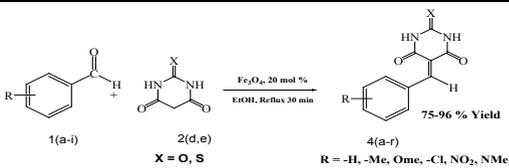
Sr. No	Aldehyde (-R)	Active methylene Compound	Product (%)[b]	Yield	m.p. (°C) Found	m.p. (°C) Calcu.
1	H	Barbituric acid	4a	96	270-272	248-249[47]
2	2-Cl	Barbituric acid	4b	90	220-222	250-252[57]
3	4-Cl	Barbituric acid	4c	93	232-234	271-272[47]
4	4-NMe₂	Barbituric acid	4d	88	276-278	260-267[47]
5	4-NO₂	Barbituric acid	4e	96	278-280	272-274[55]
6	3-NO₂	Barbituric acid	4f	92	256-258	256-258[48]
7	2-NO₂	Barbituric acid	4g	92	238-240	231-234[55]
8	3-OMe	Barbituric acid	4h	93	>290	295-297[55]
9	3,4-di -OMe	Barbituric acid	4i	90	>290	N.R.
10	H	Thiobarbituric acid	4j	96	271-272	>290[59]
11	2-Cl	Thiobarbituric acid	4k	90	234-236	234–236[59]
12	4-Cl	Thiobarbituric acid	4l	94	288-290	291-293[59]
13	4-NMe₂	Thiobarbituric acid	4m	90	254-256	255[56]
14	4-NO₂	Thiobarbituric acid	4n	96	240-242	N.R.
15	3-NO₂	Thiobarbituric acid	4o	92	264-266	261–263[59]
16	2-NO₂	Thiobarbituric acid	4p	93	240-242	247–248[59]
17	3-OMe	Thiobarbituric acid	4q	90	236-238	204[58]
18	3,4-di -OMe	Thiobarbituric acid	4r	89	>290	>300[59]

[a]Reaction conditions: Aldehyde (1mmol), cyclic active methylene compound (1 mmol), Ethanol(5 mL), [b]Isolated yield, N.R = Not Reported

Table 3: Catalyst Recycle Study[a]

Sr.No.	Run No.	Yield(%)[b]
1	1st	94
2	2nd	88
3	3rd	76

[a]Reaction conditions: Benzaldehyde (1mmol), malononitrile (1mmol), ethanol (5 mL), [b]Isolated yield

Our aim is to make catalytic system more cheap, we have focused on the reusability of nano-Fe_3O_4 catalyst in this condensation reaction as shown in Table 3, the catalyst shown extraordinary activity in all three cycles. Reaction was monitored by TLC. Followed by touching the external magnet to wall of the round bottom flask and reaction mixture was decant in the small beaker. The catalyst was washed with ethanol (3×5 mL) and dried it for 1 h at 120°C in oven, it is ready for next cycle. Catalyst were recycled three times without significant loss of catalytical activities.
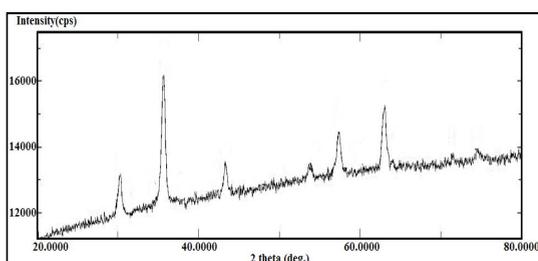

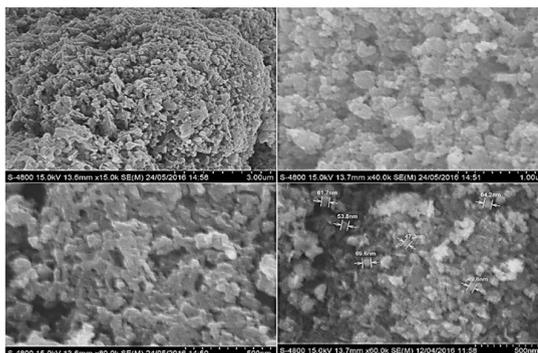**Fig. 1. X-ray diffraction study of nano-ferrite catalyst**

Fig. 2. Scanning Electron Microscope (SEM) images of nano-ferrite catalyst

Synthesis of styrene compounds

Benzaldehyde (1 mmol), malononitrile (1 mmol), Fe_3O_4 (20 mol %) in ethanol (5 mL) heated at reflux for 30 minute. Reaction was monitored by Thin Layer Chromatography. The catalyst was recovered by simple magnetically decantation of reaction mixture by pouring in cold H_2O and the product were filtered and purified in aqueous ethanol. Recovered catalyst was washed with ethanol and dried in oven. The catalyst is ready for next cycle of the reaction.

Spectral Data of Selected Compounds

1)2-(4-chlorobenzylidene)malononitrile (3d)

FT-IR(KBr): 3030, 2227, 1955, 1558, 779, 617 cm⁻¹. ¹H-NMR(CDCl₃,400MHz)δ: 7.880(d, *J*=8.4Hz, 2H), 7.760(s,1H), 7.545(d, *J*=8.4Hz, 2H). ¹³C NMR(CDCl₃,100MHz)δ: 158.30, 141.18, 131.86, 130.09, 129.28, 113.45, 112.35, 83.37.

2) 2-(2-chlorobenzylidene) malononitrile (3f)

Colour: Pale yellow, m.p:96-98°C. FT-IR (KBr): 3055, 2222, 1907, 1587, 756, 619 cm⁻¹. ¹H NMR (Deuterated chloroform, 400MHz)δ: 8.295(s, 1H), 8.205(d, *J* = 8.0Hz, 1H,), 7.576 (d, *J*=3.6Hz, 2H), 7.495–7.435 (m, 1H).¹³CNMR (Deuterated chloroform, 100MHz)δ: 156.05, 136.35, 135.04, 130.72, 129.51, 129.07, 127.80, 113.22, 111.91, 85.81.

3) 2-(2-nitrobenzylidene) malononitrile (3m).

Colour: Yellow m.p.: 140-142°C FT-IR(KBr): 3047, 2239, 1975, 1591, 1523, 1440 cm⁻¹. ¹H NMR(Deuterated chloroform, 400MHz) δ: 8.474(s, 1H), 8.393-8.369(m, 1H), 7.931-7.891 (m, 1H), 7.855-7.816(m, 2H).¹³C NMR(Deuterated chloroform, 100MHz) δ: 158.83, 146.80, 134.98, 133.44, 130.49, 126.72, 125.88, 112.24, 110.98, 88.55.

4) 2-(3,4-dimethoxybenzylidene)malononitrile (3o)

Colour: Yellow, m.p: 142-144°C, FT-IR(KBr): 2933, 2833, 2218, 1909, 1467, 1251,1147 cm⁻¹, ¹H NMR(Deuterated chloroform, 400MHz) δ: 7.683 (t, *J* = 2.0 &12.0Hz, 2H,), 7.399 (q, *J* = 2.4 &6.0Hz, 1H), 7.283 (s,1H), 4.003 (s, 3H), 3.953 (s, 3H). ¹³C NMR(Deuterated chloroform, 100MHz)δ: 159.15, 154.28, 149.56, 128.22, 124.29, 114.42, 113.59, 111.10, 11, 0.78, 78.45, 56.34, 56.09.

5) (Z)-ethyl 2-cyano-3-(3,4-dimethoxybenzylidene) acrylate(3p).

Colour: Yellow, m.p: 156-158°C, FT-IR(KBr): 3003, 2845, 2222, 1928, 1710, 1512, 1159, 1097 cm⁻¹.¹H NMR(Deuterated chloroform, 400MHz) δ: 8.162 (s, 1H), 7.808 (s, 1H),7.482 (d, *J* = 7.6 Hz, 1H), 6.955 (d, *J* = 7.6 Hz, 1H), 4.377 (q, *J* = 7.2 Hz, 2H), 3.900(s,6H), 3.400(t, *J* = 7.2 Hz, 3H). ¹³C NMR(Deuterated chloroform, 100MHz) δ: 163.11, 154.70, 153.68, 149.28, 127.89, 124.61, 116.36, 111.65, 110.95, 99.38, 62.46, 56.15, 56.05, 14.21.

6) 5-benzylidenepyrimidine-2,4,6(1H,3H,5H)-trione(4a)

Colour: Yellow, m.p: 270-272°C,FT-IR(KBr): 3512, 3313,3074, 2845, 1880, 1701, 1581,1438. ¹H NMR(Dimethyl sulfoxide-d₆, 400MHz) δ: 11.735(bs,2H), 7.913(t, *J* = 6.8 &1.6 Hz, 1H), 7.615 (t, *J* = 6.8 &7.6Hz, 1H),7.180(t, *J* = 7.6 Hz,

1H), 7.075 (t, *J* = 7.2 Hz, 1H), 7.015(d, *J* = 8.0Hz, 2H), 5.946(s,1H).^{13}C NMR(Dimethyl sulfoxide-d$_6$, 100MHz)δ: 193.74, 173.30, 163.50,142.89, 136.64, 135.07, 133.89, 129.96, 129.63,128.61, 128.17, 126.99, 125.44, 96.35, 31.06.

7) 5-(3-methoxybenzylidene)pyrimidine-2,4,6 (1H,3H,5H)-trione(4h)

Colour: Brown, m.p: 268-270°C.FT-IR(KBr): 3518, 3458, 3007, 2828, 1938, 1660, 1570, 1444, 1163 cm^{-1}.^{1}H NMR (Dimethyl sulfoxide-d$_6$, 400 MHz)δ: 11.407 (s,1H), 11.256(s,1H), 8.259 (s, 1H),7.845 (t, *J* = 2.0Hz, 1H), 7.611(q, *J* = 0.8Hz&. 0.4Hz, 1H),7.395 (t, *J* = 8.0Hz, 1H), 7.142– 7.117 (m,1H,) 3.797(s,3H). ^{13}C NMR (Dimethyl sulfoxide-d$_6$, 100MHz) δ**:** 163.87, 162.09, 159.08, 154.98, 150.64, 134.31, 129.59, 126.55, 119.74, 118.91, 118.07,55.68.

8)5-(2-chlorobenzylidene)-dihydro-2-thioxopyri-midine-4,6(1H,5H) dione(4k)

Colour: Red, m.p: 234-236°C.FT-IR(KBr)**:** 3633, 3388, 3076, 1718, 1583, 1215, 1049,725, 642 cm^{-1}.^{1}H NMR(Dimethyl sulfoxide-d$_6$, 400MHz) δ: 11.491(s,1H), 11.272(s,1H), 8.292,(s, 1H), 7.747 (t, *J* = 6.8 & 0.8 Hz, 1H), 7.556, (q, *J* = 1.2Hz & 6.8Hz, 1H), 7.497–7.456, (m, 1H), 7.392-7.352, (m,1H). ^{13}CNMR(Dimethyl sulfoxide-d$_6$, 100MHz)δ: 163.12, 161.38, 150.69, 150.17, 133.64, 132.74, 132.44, 132.40, 129.35, 126.80, 122.26

9) 5-(3-methoxybenzylidene)-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione(4q)

Colour: Red, m.p: 236-238°C.FT-IR(KBr): 3485, 3070, 2904, 1944, 1701,1651, 1548, 1228, 1151, 1047 cm^{-1} ^{1}HNMR(Dimethyl sulfoxide-d$_6$, 400 MHz)δ: 12.477(s,1 H), 12.357 (s,1H), 8.271(s,1H), 7.892(s,1H), 7.676 -7.657(d,1H, *J* = 7.6Hz),7.430-7.390(m,1H, *J* = 8.0Hz), 7.172-7.147, (m,1H), 3.803 (s, 3H)., ^{13}C NMR(Dimethyl sulfoxide-d$_6$, 100MHz) δ: 179.02, 162.18, 159.94, 159.12, 155.88, 134.29, 129.68, 126.92, 119.80, 119.45, 118.31, 55.72.

10)5-(3,4-dimethoxybenzylidene)-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione (4r).

Colour: Red, m.p: >290°C,FT-IR(KBr):

3506, 3386, 3083, 1946, 1662, 1583, 1220, 1159 cm^{-1}, ^{1}H NMR (Dimethyl sulfoxide-d$_6$, 400MHz) δ: 12.403-12.300(d, 2H), 8.438(d, *J* = 1.6Hz, 1H), 8.275(s, 1H), 7.969 (t, *J* = 1.2 & 7.2 Hz, 1H), 7.157(q, *J* = 8.0 & 9.2 Hz, 1H), 3.830(s,6H), ^{13}C NMR (Dimethyl sulfoxide-d$_6$, 100 MHz) δ: 191.86, 178.65, 162.76, 160.60, 156.97, 154.70, 154.66, 149.63, 148.35, 132.84, 130.09, 126.60, 125.91, 117.43, 115.79, 111.74, 111.69, 109.87, 56.42, 56.35, 55.98, 55.93.

CONCLUSION

We have carried out Knoevenagel reactions of various substituted aromatic aldehydes with cyclic and acyclic active methylene compounds resulting compounds form with good to significant yields at refluxed temperature in presence of environmentally benign Fe_3O_4 as a nano catalyst. The ferrite catalyst was recycled upto three successive times. But not in considerable loss in action. The present method displaces all other methods that used various homogeneous catalysts and performed compare with elevated temperature. FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, characterized structures of the synthesized compounds.

Conflict of interest

The authors declare that there is no conflict of interests concerning the publication of this article.

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