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A Green One-Pot Three-Component Synthesis of α- Aminophosphonates using (PANI-Mn) Nano-catalyst

Kamalakar K.Wavhal[1], Deepak M. Nagrik[2]

[1]Department of chemistry, Late Ku. Durga K. Banmeru Science College Lonar Dist- Buldana (M.S) India-443302.

[2]Department of Chemistry, G.S. Science, Arts and Commerce College Khamgaon Dist- Buldana (M.S) India-443303.

Abstract

The one-pot three-component condensation process is a efficient and environment friendly procedure for synthesis of α-Aminophosphonates. It involves the condensation of aldehyde, amines and diethyl phosphite. The α-Aminophosphonates possess a broad range of applications ranging from agro chemistry to medicine. The Kabachnik-Fields reaction is the easiest route among all procedure to synthesize α-Aminophosphonates. The PANI-Mn Nano-catalyst as an eco-friendly catalyst at room temperature under solvent free conditions. The metal Nano-catalyst has high surface area, which can increase catalytical activity, It is easily separable and recycled. The advantages of this methods are high product yield, short reaction time, easy to do and facile to purification.

A new and highly flexible method is described here for the synthesis of α-Aminophosphonates. The novel PANI-Mn Nano-catalyst is synthesized and used in Kabachnik-Fields reaction for the synthesis of α-Aminophosphonates.

Keyword: KFR, Eco-friendly, Condensation, MnCl2, Polyaniline.

1. Introduction:

The one-pot three-components (Kabachnik-Fields Reaction) involving the condensation of primary or secondary animes, oxo compound aldehyde or ketones and especially diethyl phosphite. It shows the good choice for synthesis of α-Aminophosphonates. The researchers uses the lot of Nano-catalyst for the synthesis of α-Aminophosphonates. The Kabachnik-Fields Reaction: Mechanism and synthetic use for α-Aminophosphonates [1] Synthesis of α-Aminophosphonates and Related Derivatives; the Last Decade of the Kabachnik-Fields Reaction[2]The synthesis of α-Aminophosphonates by the Kabachnik-Fields Reaction under solvent free, catalyst free reaction condition[3]Researchers are synthesize α-Aminophosphonates using H6P2W18O62.14H2O as an efficient catalyst from amino acids[4] These α-Aminophosphonates shows promising antioxidant, antimicrobial, anticancer activity.

In recent development on the synthesis of biologically active α-Aminophosphonates. Recently the Nano-catalyst is used to synthesize Aminophosphonates because its Physical properties like specific surface area, size, solubility, surface morphology, defect structure and chemical properties, molecular structure, Phase identity, surface chemistry, purity, hydrophilicity. all these properties are helpful for Yield and Purity of the α-Aminophosphonates. In addition to this it reduce waste volumes and improving the economy of the process, improve the energy efficiency and reduce the carbon footprint of a process[5]

The polyaniline polymers having poly conjugated structures and they possess poor electrical conductivity but oxidized polymers shows excellent electrical conductivity. For the preparation of Nano catalyst polyaniline is the base compound. The polyaniline is unique properties among all polymers. Polyaniline having various application in Polymer electronics.[6] The unique properties such as electrical, optical and photoelectrical as well as easy to synthesis with great environment stability therefore its very useful in catalytical field.[7-8] The doping of polyaniline increase the conductivity. The synthesis of α-Aminophosphonates functionalized ZnO/polystyrene-butadiene Nano-composite[9] Controllable synthesis of MnO2/polyaniline Nano-composite and its electrochemical capacitive property and the capacitance of the composite achieves 207 F g−1, and the results suggest that the MnO2/PANI composites show superior performance over pure PANI or MnO2[10] The study focuses on green synthesis of α-Aminophosphonates by using PANI-Mn Nano-catalyst through one-pot three-component i.e. Kabachnik-Fields reaction.

2. Materials and Methods:

The chemicals used such as Ammonia, aniline, ammonium persulphate, manganese dichloride, ethanol, concentrated HCl, aldehyde, dethyl phosphite are of analytical grade, The Distilled water used for experimental work.

2.1 Synthesis of Polyaniline:

The 0.5 M aniline monomer (99%) and 0.5 M ammonium persulphate (APS) was prepared in 0.5M Cons. HCl solution, In a round bottom flask. These are mixed slowly with constant stirring on magnetic stirrer. This mixture was kept in ice bath maintaining the temp below 0-4ºC for 8-10 hours. The reaction mixture was poured into 200 ml water to complete the precipitation, washed with distilled water and HCl solution to remove un-reacted monomers.[11] After some time polymerization take place and the dark suspension becomes green in color. The green colored residue like paste was obtained. The final product was washed 2-3 times with D.W. and ethanol. Finally the dark-green powder is dried at 80^{o}C for 6-8 Hours in Oven[12] The final product was grinded to form a green powder is known as conducting PANI (ES).

2.2 Synthesis of PANI-Mn Nano-catalyst:

After formation of Polyaniline Emeraldine Salt (ES) the accurate amount of 0.2 M solution of Manganese chloride ($MnCl_2$) slowly and carefully dissolved in polyaniline. The Polyaniline Manganese chloride solution was kept in R. B. flask and kept for vigorous stirring with the help of hot plate with

magnetic stirrer (700 RPM) is adjusted, about 3-5 hours. The dark green suspension is formation in the R. B. flask after that this R B flask was kept in Ice bath for 12 Hours. After filtration, The product were washed with 2 times with distilled water and 3 times with ethanol. The prepared Nano catalyst was kept in hot air oven for 7 hours at 70^0C. [13]In this method the Nano particle of Mn is uniformly distributed in Polyaniline. There is formation of Nano- catalyst having dark green color, as shown in **Fig-3**

Fig-1. PANI-Mn Nano-catalyst In Icebath

Fig-2. Filtered Product

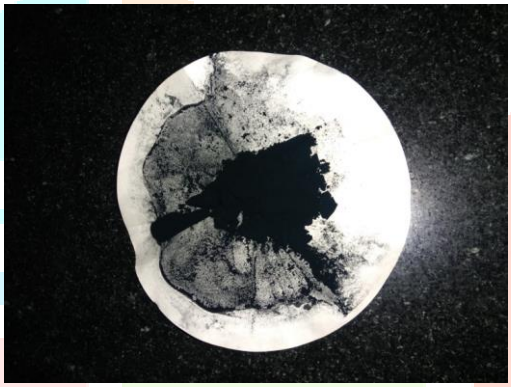


Fig-3. PANI-Mn Nanocatalyst

2.3 A Green One-pot Three–components synthesis of α-Aminophosphonates

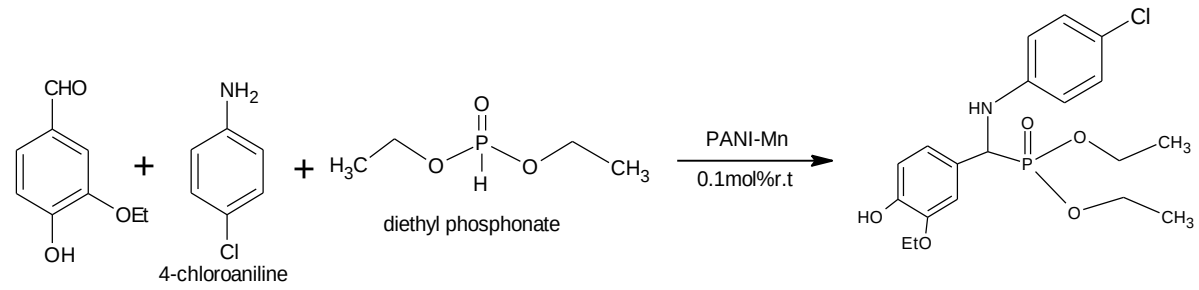
α- Aminophosphonates are prepared with the help of one-pot three components Reaction i.e. Kabachnik-Fields reaction. An equimolar quantity of substituted aldehyde (10 m mol), substituted aromatic amine (10mmol) and diethyl phosphate (10mmol) and PANI-Mn Nano-catalyst (0.1mol%) was mixed together in one round bottom flask. The stirring was done properly with help of magnetic stirrer for proper collision at room temperature. The reaction was carried out Under solvent free condition. [14]The catalyst was separated by centrifugation. It gives the crude product. The completion of reaction is indicated by TLC [15-16] The reaction mixture quenched with water (10 mL) and extracted with ethyl acetate, after drying, the pure α- Aminophosphonates are formed.

4. Result and Discussion:

4.1 Following Four α- Aminophosphonates were prepared:

1) Diethyl (4-Chloro Phenylamino) (3-ethoxy- 4-hydroxy phenyl) methylphosphonates:

The equimolar quantity (10mmol) of 4-chloroaniline, 3-ethoxy-4-hydroxy benzaldehyde and diethyl Phosphonates was mixed together in R.B flask. The Nano-catalyst(0.1 mol%) adding in reaction mixture at r. t. to form α- Aminophosphonates.[17] MF- $C_{19}H_{25}ClNO_5P$ M W – 411 Color- Faint Yellowish M.P- 174-177^{0}C Yield- 93%



3-ethoxy-4-hydroxybenzaldehyde

diethyl (4-chlorophenyl)amino(4-methoxyphenyl)methylphosphonate

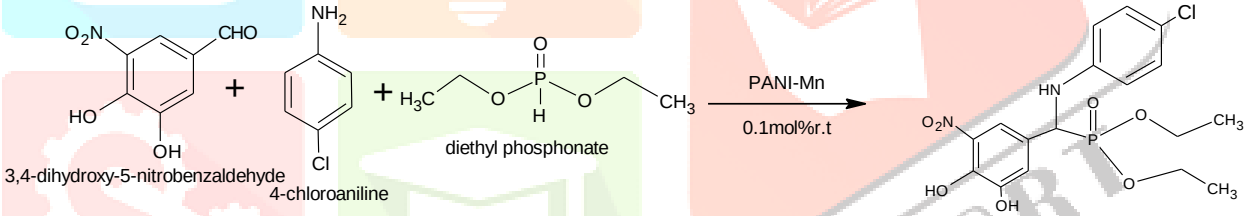
^{1}H- NMR- (300 MHz, DMSO-d_6 ppm)

Peak Observed in δ ppm	Multiplicity	Inference
10.2	s	1H,-OH
7.73-6.41	m	7H, Ar-H
5.40	m	1H,N-H
3.97	m	1H, P-CH
3.73	q	6H,-OCH_2
1.32	t	9H,O -CCH_3

^{31}P-NMR (161.8MHz, DMSO-d_6)δ 32.4.M/z:413 and 415 with 3:1 ratio.[18]

2) Diethyl (4-Chlorophenylamino)(3,4-dihydroxy-5-nitro-phenyl) methylphosphonate

The equimolar quantity (10mmol) of 4-chloroaniline, 3,4-dihydroxy-5-nitro benzaldehyde and diethyl Phosphonates was mixed together in R.B flask. The Nano-catalyst (0.1 mol%) [19] adding in reaction mixture at r. t. to form α- Aminophosphonates. MF- $C_{17}H_{20}ClN_2O_7P$ M W- 428 Color- Dark Brown M.P-177-180^{0}C Yield- 82%



3,4-dihydroxy-5-nitrobenzaldehyde 4-chloroaniline

diethyl (4-chlorophenyl)amino](3,4-dihydroxy-5-nitro phenyl) methylphosphonates

^{1}H- NMR- (300 MHz, DMSO-d_6 ppm)

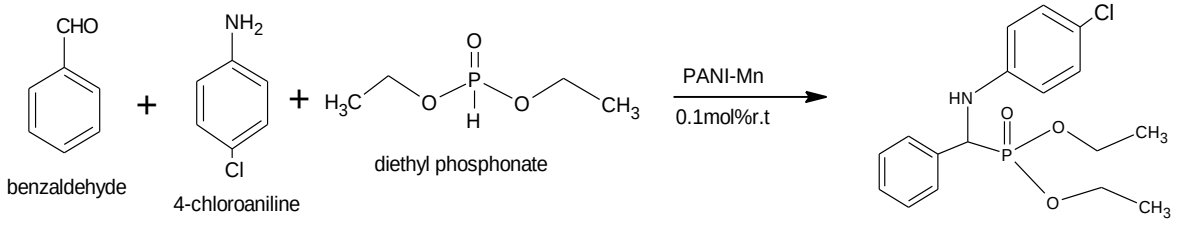
Peak Observed in δ ppm	Multiplicity	Inference
10.4	br	2H, -OH
7.91-6.78	m	6H,Ar-H
5.44	m	1H, N-H
4.15	m	1H, P-CH2
3.70	q	4H, -OCH_2
1.24	t	6H, P-CCH3

^{31}P-NMR(161.9MHz,DMSO-d6) δ31.6M/z:431and 433 with 3:1 ratio.[20]

3)Diethyl (Phenyl) –N-(4-chlorophenyl amino) methylphosphonate:

The equimolar quantity(10 mm mol) [21] of 4-chloroaniline, benzaldehyde and diethyl Phosphonates was mixed together in R.B flask. The Nano-catalyst(0.1 mol%) adding in reaction mixture at r. t. to form α- Aminophosphonates.

MF- $C_{17}H_{21}ClNO_3P$ MW- 351 Color-Brown M.P.-105-106^{0}C Yield- 88%



benzaldehyde 4-chloroaniline diethyl phosphonate

diethyl (4-chlorophenyl)amino methylphosphonates

^{1}H- NMR- ($CDCl_3$, TMS ppm)

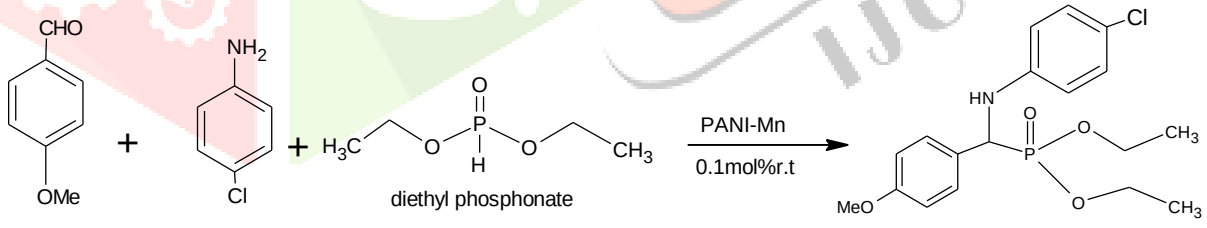
Peak Observed in δ ppm	Multiplicity	Inference
7.35-7.39	m	3H
7.21-7.25	m	2H
6.92-6.97	m	2H
6.40-6.44	m	2H
4.61	d	1H, $2J_{P,H}$=24.0Hz
4.01-4.02	m	P-CCH
3.80-4.00	m	1H
3.44-3.68	m	1H
1.18-1.23	m	3H
0.98-1.02	m	3H

^{31}P-NMR(161.9MHz,DMSO-d6) δ31.6M/z:431and 433 with 3:1 ratio.[22]

4)Diethyl(4-methoxyphenyl)-N- (4-chloro phenylamino) methylphosphonates:

The equimolar quantity(10 mm mol) of 4-chloroaniline,3-methoxy benzaldehyde and diethyl Phosphonates was mixed together in R.B flask. The Nano-catalyst (0.1 mol%)[23] adding in reaction mixture at r. t. to form α- Aminophosphonates.

MF-$C_{18}H_{25}ClNO_4P$ MW- 383 M.P-181-183^{0}C Color- Yellow Yield- 91%



4-chloroaniline diethyl phosphonate

diethyl (4-chlorophenyl)amino](4-methoxyphenyl)methyphosphonate

^{1}H- NMR- ($CDCl_3$,TMS ppm)

Peak Observed in δ ppm	Multiplicity	Inference
7.24-7.28	m	2H
6.98	dd	2H, $J_{H,H}$=6.6 Hz, $J_{H,H}$=2.0Hz
6.78	d	2H, $J_{H,H}$=8.4Hz
6.45	dd	2H, $J_{H,H}$=6.6 Hz, $J_{H,H}$=2.0Hz
4.49-4.60	m	2H
3.98-4.03	m	2H
3.80-3.85	m	1H
3.70	s	3H
3.40-3.71	m	1H
1.21	t	3H, $J_{H,H}$=7.1Hz, 3H
1.04	t	3H, $^3J_{H,H}$=7.0Hz

^{31}P-NMR(160.9MHz,DMSO-d6) δ31.6M/z:435and 444 with 3:1 ratio.[24]

5. Conclusion:

We have successfully synthesized pure polyaniline (ES) and with the help of doping methods synthesize PANI-Mn Nano catalyst. The four derivatives of α- Aminophosphonates were prepared with the help of green One-pot three-components i.e. Kabachnik-Fields Reaction. The novel PANI-Mn Nano-catalyst is used as catalyst for synthesis of α- Aminophosphonates derivatives. The study indicated that the synthesized Nano-catalyst had the potential to increase the yield of product at room temperature.

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