Research article
International Journal of Heterocyclic Chemistry,
Vol. 7, No. 3, pp. 58-65 (Summer 2017)

http://ijhc.iauahvaz.ac.ir

Synthesis of imidazole derivatives using nano-La0.5Pb0.5MnO3 perovskite-type oxide

Ali Javid

Department of chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

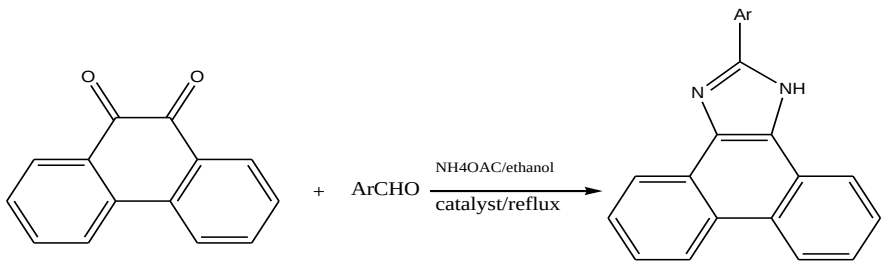
Abstract:

In this work,three component condensation of [9,10]-phenanthraquinone with benzaldehyde and ammonium acetate and nano Perovskites catalyst La0.5Pb0.5MnO_3(NP-LPMO) was evaluated using a multicomponent reaction of phenanthroquinone,aromatic aldehydes and ammonium acetate for preparation of imidazole derivatives. This reaction done under reflux conditions and compare with reaction with reaction in solvent-free reaction.

Introduction:

imidazoles are an important group of heterocyclic compounds.they have important role in heterocyclic chemistry also they have biological properties [1 - 2] . Now a days this compounds were used in pharmacology.they have capacity different such as anti-bacterial,anti viral,and anti-cancer, anti-inflammatory , [3 -5] In this work imidazole derivatives were synthesized with NP-LPMO catalyst. Perovskite oxides have caused great interests and have been wiedely studied for their various properties and application in the recent decades .[6]physical properties among superconductivity and perfect ionic conductivity nano proviskites put under consideration in

chemistry[7].this catalyst has enhance specific surface area, therefore increasing the contact between the catalyst and reactant[8].in this method were employed one-pot three component reaction .imidazole derivations were synthesized with [9,10]phenanthraquinone , benzaldehydes and ammonium acetate in presence of NP-LPMO catalyst (scheme1).Then, was compared with reaction in solvent-free reaction. On the other work diverses methods were reported for synthesis of tri substituted imidazoles by condensation reaction between 1,2-diketone , aldehydes ,ammonium acetate ,using FHS/SiO2[9], I2 [10] , TiCl4.SiO2[11], ZrOCl2.8H2O[12].some of this methods have fault such as low yield , hard separation, use toxic catalyst , protract reaction.in this work product was organized with high yield , catalyst separation is easily and catalyst recovery further ,reaction condition is cushy. These goals was proceeded in this work.



Scheme1.One-pot reaction for the preparation of imidazole derivatives in the presence of NP-LPMO

Experimental:

All materials and reagents were purchased from Merck and Aldrich and used without further purification. Melting points were determined on an Electro thermal type 9100 melting point apparatus and are uncorrected. The IR spectra were recorded on a Thermo Nicolet AVATAR-370 FT-IR spectrophotometer and 1H NMR spectra were obtained on a Bruker DRX400 spectrometer.

Preparation of nano La0.5Pb0.5MnO$_3$ Perovskite

reagents of La$(NO_3)_{3.6}$H2O,$C_6H_9MnO_6.2H_2O$,$Pb(NO_3)_2$ and citric acid (99.5%) were used as starting materials. Then aqueous solutions of metal Nitrates with nominal atomic ratios La:Pb:Mn=0.5:0.5:1(LPMO)were mixed together in deionized water .the solution was concentrated by evaporation at 50 0c with stirring for 1 h to convert them to stable (La,Pb)/CA complexes. The solution while being stirred was heated to 75 0c to remove excess water then dry

gel was obtained by letting the sol into an oven and heated to 120 0c .the gel pieces were ground to form a powder. Finally La0.5Pb0.5MnO_3 nanoparticles were gained by thermal treatment of the precursor at 650 oc for 9 h in air. Then SEM analysis was carried to determine the morphology of catalyst. Figure 1 shows the micrograph of the catalyst. According to the SEM image porosity of the surface is evident and it appear that the particles have developed with uniform size.

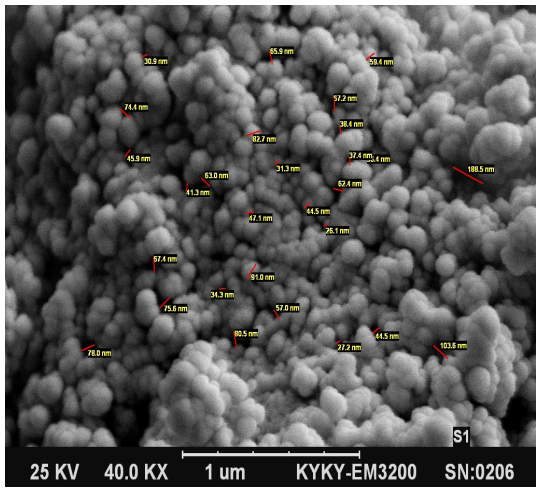


Figure 1:SEM image of nano-Perovskite LPMO

General Procedure for the Synthesis of imidazole derivatives in reflux condition

A mixture of benzaldehyde(1mmol), [9,10]-phenanthraquinone(1mmol), ammonium acetate (2.5mmol) and LPMO nanoperovskite (0.15mmol) in ethanol (10 ml) was stirred. The mixture was refluxed for described time. After completion of the reaction (the reaction progress was monitored by TLC using *n*-hexane: ethyl acetate as eluent)the catalyst was separation with filtering, and solid Perovskite catalyst was isolated and could be reused. The organic phase was evaporated and the resulting solid product washed with cold water (3 × 20 cm^3), and recrystallized in ethanol to give pure product.

General procedure for the synthesis of imidazole derivative in free-solvent

A mixture of benzaldehyde(1mmol) , [9,10]- phenanthraquinone(1mmol), ammonium acetate (2.5mmol) and LMPO nanoperovskite (0.15mmol) in ethanol (1 cc) was stirred. Then mixture was heated to 100 °c for described time. After completion of the reaction (the reaction progress was monitored by TLC using *n*-hexan: ethylacetate as eluent) after cooling the mixture was

filtered and washed with ethanol to separated catalyst.then to obtain pure products the solid residue was recrystallized from ethanol-water 9:1(v/v)

Analytical Data for Selected Compounds:

2-**(4-Nitro-phenyl)-1H-phenanthro[9,10-d]imidazole(2):**

m.p.316°c. IR(KBr):ῡ=3195 , 1615 , 1531 , 1511, 1347 cm^{-1} . HNMR (100MHz, DMSO-d6) : δ =7.63-8.83(12 H , Ar-H) , 9.11(2H , Ar-H) , 13.8 (1H , NH)ppm

2-p – Tolyl-1H-phenanthro[9,10-d] imidazole(8):

m.p.290°c. IR(KBr):ῡ = 3420, 2922,1606 , 1463 , 1416 cm^{-1}.HNMR (100MHz, DMSO-d6):δ=2.38(3H) , 7.28-8.82(12 H , ArH) , 13.36(1H, NH)ppm

N-[4-(1-Hphenanthro[9,10-d]imidazol-2-yl)-phenyl]acetamid(10):

m.p.247°c. IR(KBr):ῡ=3461 ,2480 , 1673 , 1593 cm^{-1}. HNMR (100MHz, DMSO-d6):δ=2.08(3H) , 7.28-8.82(12H , ArH) , 10.17(1H , NH),13.40(1H , NH) ppm

2-2(chloro-phenyl)-1H-phenanthro[9,10-d]imidazole(6):

m.p.233-234°c.IR. IR(KBr):ῡ=3584, 1674,1592,1451 cm^{-1}. HNMR (100MHz, DMSO- d6):δ= 7.37-8.88(12H , ArH) , 13.57(1H , NH)ppm

3. Results and discussion

Initially we were executed various amount catalyst in presense ethanol solvent.and best amount of catalyst was obtained for model reaction.(4-choloro benzaldehyde (1mmol) , [9,10]phenanthraquinone (1mmol), ammonium acetate (2.5 mmol) and catalyst (0.15mmol) in ethanol .)for establish effectiveness of nano Perovskite LPMO ,a test reaction was did without catalyst at room temperature .we were performed trace amount product in absence catalyst(entry 1).we increased temperature up to 100 °c but final product wasn't appreciable.(entry 2).we did model reaction with different amount of catalyst. results are listed in Table1.best amount of catalyst was 0.15 mmol(0.041gr)

Table1.Condensation reaction for synthesis imidazole in the presence of different loading of the catalyst under reflux condition.

Entry	Catalyst loading	Temperature(°c)	Time(h)	Yield(%)
1	-	Room temprature	12	trace
2	-	100	12	<25
3	0.01	T-reflux	2	45
4	0.02	T-reflux	2	63
5	0.03	T-reflux	2	77
6	0.04	T-reflux	2	94
7	0.05	T-reflux	2	94

Reaction conditions:4-choloro benzaldehyde (1mmol) , [9,10]phenanthraquinone (1mmol), ammonium acetate (2.5 mmol) in ethanol .

Considering solvent has important role in reactions,we did model reaction in presence different solvent. Results are listed in Table 2.we observed protic solvent such as ethanol and methanol have higher yield in this method. When achieved best result that we used ethanol for solvent. This reaction had proper result in free solvent condition. Thus this reaction was considered in free solvent reaction similary.

Table2.Condensation reaction for synthesis imidazole in presence of distinct solvents and 0.15 mmol catalyst

Entry	solvent	Time(h)	Yield(%)
1	CHCl3	3	64
2	MeOH	2	78
3	EtOH	2	94
4	DMF	4	42
5	Solvent free	4	80

Reaction conditions:benzaldehyde (1mmol) , [9,10]phenanthraquinone (1mmol), ammonium acetate(2.5 mmol) and catalyst (0.15mmol) at reflux temperature.

In next step we offered model reaction for determine best temperature in free solvent condition in presence NP-LPMO catalyst.(benzaldehyde (1mmol) , [9,10]phenanthraquinone (1mmol), ammonium acetate(2.5 mmol) and catalyst (0.15mmol) at free solvent).results are listed in table 3.when temperature was 100°c ,higher yield was determined

Table3: Condensation reaction for synthesis imidazole in temperatures different

entry	Temp(°c)	Time (h)	Yield (%)
1	Room temprature	12	trace
2	40	4	47
3	80	4	70
4	100	4	80
5	110	4	80

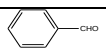
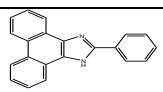
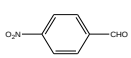
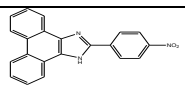
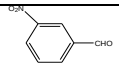
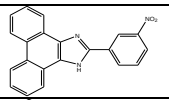
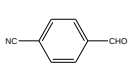
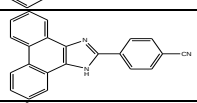
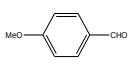
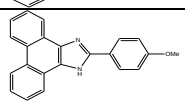
Reaction conditions:benzaldehyde (1mmol) , [9,10]phenanthraquinone (1mmol), ammonium acetate(2.5 mmol) and catalyst (0.15 mmol) at free solvent condition

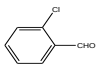
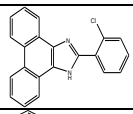
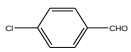
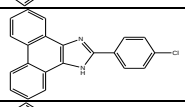
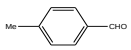
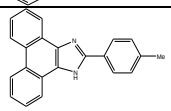
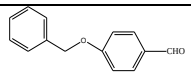
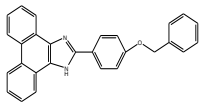
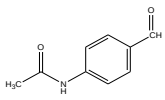
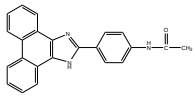
We synthesized imidazole derivatives *via* a one-pot reaction of [9,10]-phenanthraquinone aromaticaldehyde and ammonium acetate in presence of NP-LPMO catalyst and reflux conditions in ethanol as solvent in excellent yields in this work(Scheme 1).

The mechanism of the reaction was proposed in Scheme 2. As can be seen, reaction proceeds via one-pot condensation of benzaldehyde with carbonyl compound, and cyclodehydration.We think that NP-LPMO as Lewis acid might promote the reaction byaccelerating the formation of imidazole from the aldehydes and also 1,2-dicarbonyl compounds such as [9,10]phenanthraquinone, in the rate determining step (Scheme 2) in excellent yields in this work

To investigate generality of this method we was extended reaction to different diverse of benzaldehyde .the results are in table 4. Product yield was influenced by electeronic and steric effects of substituted.when we used benzaldehyds with electron donate groups products had lower yield . ortho substituted benzaldehydes had lower yields compare to their para substituted.easy separation and recovery of catalyst is one of best result of our method. ,high performance of catalyst even after four runs.

Table4.Synthesis of tri substituted imidazoles in presence of nano Perovskite La0.5Pb0.5MnO3

Entry	aldehyde	product	Time (h)		Yield(%)		m.p(°c)		ref
			Ref	free-solvent	Reflux	free-solvent	found	reported	
1			2	4	89	78	286-288	288-289	13
2			2	4	92	77	316	<300	14
3			2	4	89	75	269-270	271-272	14
4			2.5	4	86	71	301	-	-
5			2	4.5	83	76	260-261	254-255	14

6			2.5	4.5	87	79	233-234	235	14
7			2	4	94	80	268-270	275-276	15
8			2.5	4	84	82	290	290-292	16
9			3	4.5	68	60	228-230	-	-
10			3	4	74	66	247	-	-

4. Conclusions

In this work, we benefit of one-pot reaction procedure for the synthesis of imidazole derivatives by reaction of [9,10]-phenanthroquinone , benzaldehyde , ammoniumacetat and NanoPerovskite

La0.5Pb0.5MnO3 catalyst in ethanol solvent under reflux condition.and in next stop being used NanoPerovskite La0.5Pb0.5MnO3 catalyst for synthesis imidazole derivatives in free solvent condition.and obtained desired products with high yields.therfore this method is simple , efficient , easy separation, and high performance of catalyst even after four runs.

5. Refrences

1-S.H.Mashraqui , M.B.Patil , H.D.Mistry , chem . let , 2004 , 33 , 1058

2- Y.B.Kim , Y.H.Kim , J.Y.Park , S.K.Kim , bioorg.med.chem.lett.14, 2004 , 541-544

3-I.Devi,P.J.Bhuyan , Tetrahedron Lett , 2004 , 45 , 8625

4- N .S .Gunay , G . Capan, N . Ulosoy, C N. Ergen,G.Otuk, D.Kaya , I L.Farmaco, 54,1999 , 826-831

5- P .Gupta, S .Hameed, R.Jain, Eur.J . Med . Chem. , 39,2004 , 805 – 814

6-H.Tavakkoli, T.Moayedipour,journal nano struct chem.,2004,33,1058

7-L. Micheal ,Cation ordering and octahedral in provskites , actacrystallographica , B60 ,2004, 10-20

8-H.Sanaeishoar,H.Tavakkoli,M.Asareh,Iranian journal of catalysis6(3), 2016 , 213-219

9- M.Bakavoli , H.Eshghi , A.Mohammadi, H.Moradi ,Iranian journal of catalysis 5(3) , 2015 , 237-243

10-H.Behmadi , M.Roshani , Chinese chemical let , 20 ,2009 , 5-8

11- L.Zamani, F.Mirjalili , M.Namazian, CHEMIJA,24 , 2013,312-319

12- N.Jaiprakash.sangshetti,Nagnnath D.Kokare,Chinese chemical let, 19(7) , 2008,762-766

13- W.Lin , L.Long , L.Yuan , B.Chen,org .lett , 10, 2008, 55-77

14- A.S.Edgar , R.D.Allan , J.Am.chem.soc , 68,1946,771

15- S.Damavandi , Heterocycl . commun , 17 , 2011 , 79

16- H.Bemadi , M.Roshani , Chinese chemical let , 2009 , 5-8