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Catalytic effect of green zinc oxide nanoparticles on multi –component reactions

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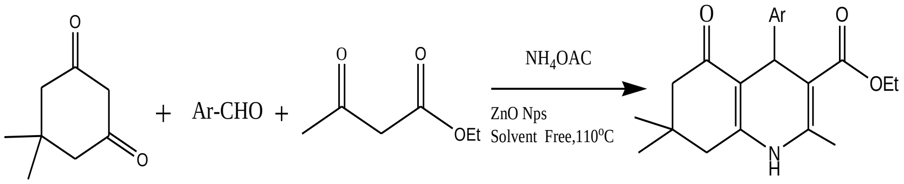
Abstract- In this study, multi component Hantzsch reaction was carried out between various Aromatic Aldehyde with Dimedone,Ethyl acetateand ammonium acetate to produce polyhydroquinolinederivatives under solvent-free conditions at 110°C by a (Zinc oxide nanocatalyst) as effective Lewis acid. The remarkable advantages offered by this method compared with other methods are a green catalyst, simple work-up procedures, fast reactions, a long high yields.

Keywords: Zinc oxide nanocatalyst, solvent free, Polyhydroquinolin derivatives, multi –component reaction, green synthesis

Introduction

Multicomponent reactions discovered a promising field and is considered a great success in chemistry. There is always something new on the old topic of the Hantzsch reaction since Arthur Hantzsch first reported it in 1882.[1] 1,4-Dihydropyridines (1,4-DHPs) are an important class of bioactive molecules, well-known for their role as calcium channel modulators and used extensively for the treatment of hypertension.2–4 The derivatives of 1,4-DHP have shown a variety of biological activities such as vasodilator, bronchodilator, antitumour, hepatoprotective and geroprotective activities.5,6 Commercial drugs such as Nifedipine which are a prototype of the1,4-DHP structure have been used extensively in both antianginal and antihypertensive treatment [7]. The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive nanocatalysts. Although metal oxide surface exhibits both Lewis acid and base properties, the nature of metal cation and surface area of the metal oxides have extensively amplify their catalytic properties. Zinc oxide is a low-priced metal oxide which has been used in both industrial and nano type as a professional catalyst in various organic transformations[8-12].However many of these methods suffer disadvantages such as harsh reaction conditions, longer reaction times, low yields and use of excessive organic solvents or expensive catalysts. Hence it is required to develop an efficient and versatile method for the synthesis of these compounds. Recently, several methods for the synthesis of polyhydroquinolines have been demonstrated by using molecular. VDDAP[13], PEG[14],ZnO beta Zeolit[15],P-TSA[16] and … .Organic reactions under green solvents have attracted much interest from chemists particularly from the viewpoints of green chemistry. Green chemistry approaches are significant due to the reduction in by-products and waste produced, and lowering of energy costs. Thepossibility of performing multi-component reactions under green solvent conditions with a heterogeneous catalyst could enhance their efficiency from an economic as well as ecological point of view [17-20].

In addition, any report based on a library named as the catalyst is not mixed use .Herein, We report a rapid method for Hantzsch condensation in the presence of a heterogeneous catalyst under solvent-free conditions, using substituted aldehydes, dimedone, ethyl acetoacetate and ammonium acetate to produce the polyhydroquinolinederivativesin excellent yields.



Scheme 1.Synthesis of polyhydroquinoline by nano zinc oxide

Experimental

Materials

All the chemicals required were purchased from Merck Company and used without further purification**.**

Apparatus

IR spectra were recorded using KBr pellets on a Perkin-Elmer spectrophotometer.^{1}H NMR spectra on(model)at 250 MHz respectively in $CDCl_3$. X-ray diffraction pattern was studied on (model X'pert Pro-Philips).

Synthesis of ZnO nanoparticles

In order to prepare the nano ZnO powder, 5 g ofpotato starch was dissolved in 150 mL of boiling deionized water. and the mixture was stirred at 80^{0}C for 10 min. Then filtered out,and 0.01 mol of $Zn(NO_3)_2 . 6H_2O$ was added to the resulting clear starch solution, The pH of the mixture solution was then adjusted to 7-8 by gradual addition of ammonium hydroxide Added drop by drop, and a milklike solution was formed. The solution was stirred for an additional 20 min at 85^{0}C, and the resulting precipitate was centrifuged, washed with deionized water, and dried at 50^{0}C. After several mills, the powder calcined up to two hours at a temperature of 500 ° C was placed in a furnace. The advantage of this method is that the materials used in this research work does not use any solvents or masking agent. And pure ZnO nanocrystals produced.

General procedure for synthesis of derivatives

A mixture of aromatic aldehyde (1mmol), ethyl acetoacetate (1 mmol),ammonium acetate (1.5 mmol), dimedone (1 mmol), and ZnO NPs 0.01g was heated in the oil bath at 110 °C . the reaction mixture was stirred until the reaction was completed. The progress of reaction was monitored by TLC (hexane:ethyl acetate, 2:1). After completion of the reaction as monitored by TLC, Add the To product (10mL) ethyl acetate, then is heated , the catalyst was separatedby filtration. the resulting product was crystallized by ethanol and water and the product was obtained with a yield of 61-94 percent.

Results and discussion

The XRD pattern of the ZnO NPs is shown in Figure1Nano-structure of this compound by comparing it with the reference XRD pattern were approved [21].The crystalline nature of the synthesized ZnO nanoparticles was further verified by XRD.XRD spectra compared with standard cards represents the wurtzite structure (hexagonal). The size of ZnO nanoparticles using Debye Scherrer formula calculated about 32 nm.

$$D = \frac{K\lambda}{\beta cos\theta}$$

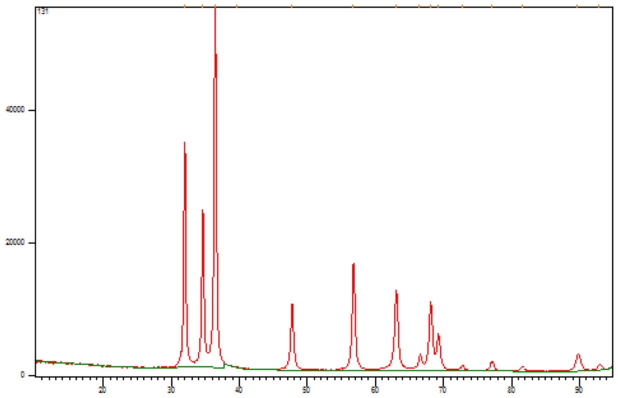


Figure 1. XRD pattern of the ZnO nanoparticle.

The results of FT-IR spectrum of ZnO NPs (Figure 2) the band from 464 cm^{-1} is assigned to the stretching vibrations of (Zn–O)bond. The results corresponded with the reference sample [21].

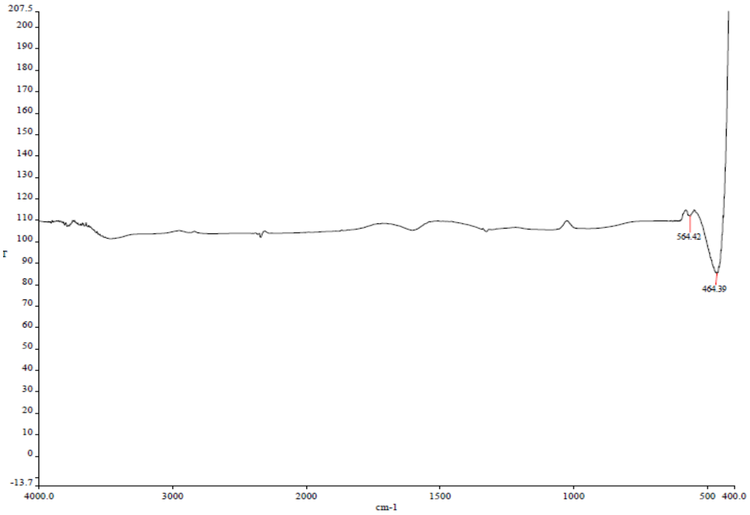


Figure 2. FTIR spectra of the ZnO nanoparticle

The reaction condition was then optimized by conducting the reaction in different temperatures(Table 2) and employing different catalyst(Table 1) loadings. The results showed that in the presence of 0/01gand Temperature 110 ^{0}C of catalyst, short reaction was created with a higher efficiency.

Table 1. Optimization of catalyst at temperatures of 90

Entry	Nanocatalyst (g)	Time (min)	Yield (%)
1	0.01	40	61
2	0.03	55	56
3	0.05	80	53

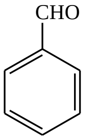
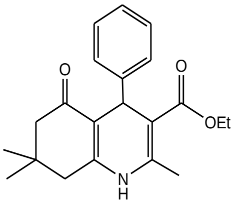
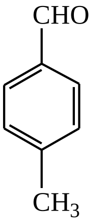
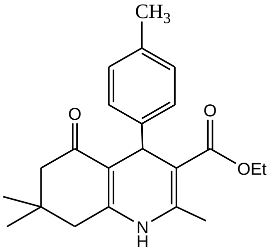
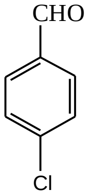
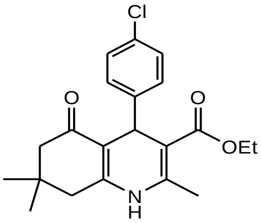
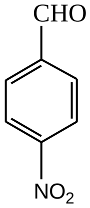
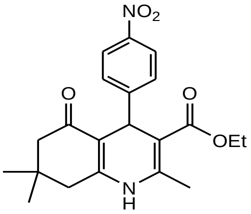
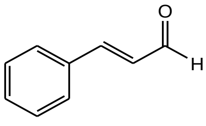
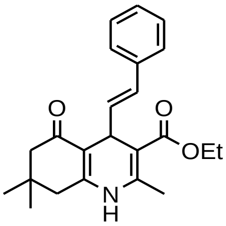
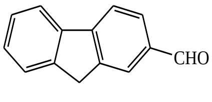
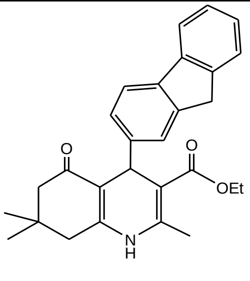
Table2. Optimization of reaction temperatu

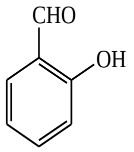
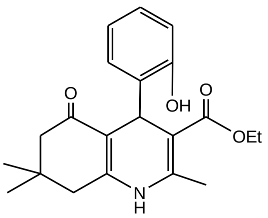
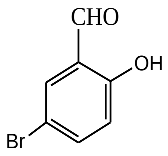
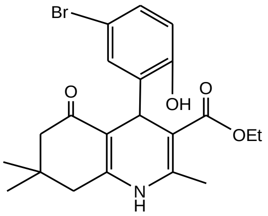
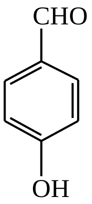
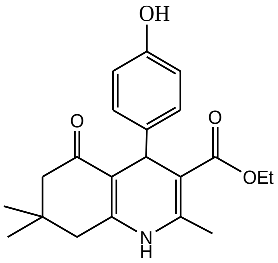
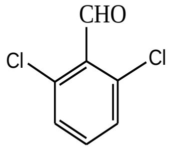
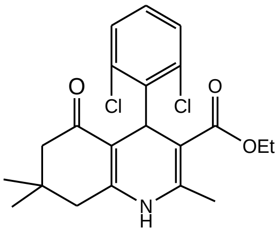
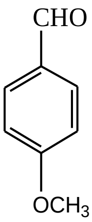
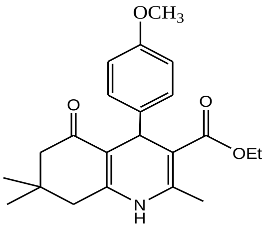
Entry	Reaction temperature (^{0}C)	Time (min)	Yield (%)
1	Room temperature	24 h	No reaction
2	70 ^{0}C	55	47
3	90 ^{0}C	40	61
4	100 ^{0}C	25	72
5	110 ^{0}C	15	76

The resulting of table 3 shows Various aldehydes with electron -withdrawing grope such as NO_2, CL, on para position in shorter reaction times and higher yields. All products are identified by their spectral properties such as melting point and IR.

Table 3 .Hantzsch condensation of polyhydroquinioline derivativesunder solvent free conditions in Temperature 110 0C

Entry	Aldehyde	Product	Time (min)	Yield (%)	M.P.(°C)	M.P.(°C) Reported

a			15	76	192-198	200-202 (12)
b			15	72	242-244	252-255 (13)
c			10	92	226-228	230-232 (14)
d			10	94	222-227	239-241 (15)
e			20	78	186-190	205-206 (14)
f			15	85	206-210	210-215

g			20	83	176-182	110-111 (16)
h			30	61	193-197	…………….
i			10	90	224-226	230-231 (17)
j			25	65	230-231	241-244 (13)
k			15	89	254-255	254-255 (14)

Spectroscopic data

Ethyl 1,4,5,6,7,8-hexahydro-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate

IR(KBr in cm^{-1}):3227,3077,2961,1699,1605,1489,1381,^{1}H NMR ($CDCl_3$, 250 MHz): δ: 0.9 (s, 3H),1.08 (s, 3H), 1.2 (t, 3H),2-2.3 (m, 4H), 4 (q, 2H), 5 (s, 1H) , 6.0(s, 1H, NH),6.5-7 (dd, $1H_{arom}$)

Conclusions

The survey results showed that the green zinc oxide nanocatalyst as effective Lewis acid for the Synthesis of 1,4-DHPs and Polyhydroquinolins.Thismethod offers several advantages including high yield,short reaction time, a simple work-up procedure with solvent-free conditions, Avoid the formation of side products, follow the principles of green chemistry.

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