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An efficient and simple method for synthesis of aldazines using Eggshell waste as environmentally friendly catalyst

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Abstract: A convenient, direct and green method for synthesis of azines from aldehyde and hydrazine hydrate, our approach catalyzed by powder eggshell. The reaction was progress under visible light conditions and dissolved in mixture of water and ethanol. The method offers several advantages including high yield of products during short time period and using nontoxic, non-expensive and stable catalyst.

Keywords: Azines, Hydrazine hydrate, Visible light, Eggshell.

Introduction

Azines, $R_1R_2C=N–N=CR_1R_2$, are considered one of the most compounds significance in organic synthesis.[1,2] Recently, synthesis of azine has attracted the attention of many chemist researches as that azines compounds are good starting materials for synthesis a lot of bioactive heterocyclic compounds including as pyrazoles, purines and pyrimidines.[3] These compounds can be used also for preparation various useful synthetic transformations,[4]and possess some unexpected biological activities in many of fields.[5] Azines compounds have demonstrated antibacterial, antimalarial, antiviral, antitumor, and anti-inflammatory properties. [6-9]

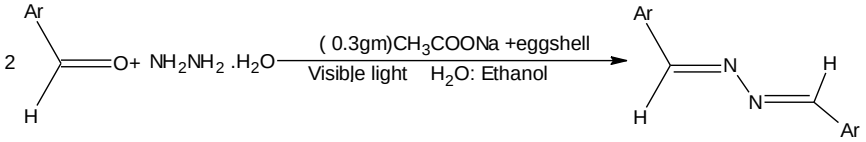
The traditional method for the preparation of azines involves treatment of carbonyl compounds and hydrazine hydrate with acetic acid in ethanol as solvent. [10-11] However, this method undergoes from many drawbacks with low yield and leads to produce of many products, long reaction time, and the difficulty to separation and recrystallizing of product.

Because of the problem using catalysts, which are difficult to use due to their high toxicity in addition to their high cost. It was necessary to use environmentally friendly catalysts, and it could be reused in same chemical reaction for several times without losing its catalytic value even if its weight decreased because of the number of the times consumed, but its catalytic activity remains the same in finished the reaction. These points made many researches to focus on the use of natural catalysts that are friendly to the environment.

Eggshell is one of the waste food factories in addition to being domestic kitchen, generally eggshell consist by high percentage 95% of calcium carbonate, little percentage of phosphate calcium 2%, magnesium carbonate 2% in addition to presence small amount of proteins and tract of elements such as iron, zinc, manganese, phosphorus … etc) and water.[12].

Eggshell waste has been used as heterogenous, high active, reusable solid catalyst in a wide range of industrial applications such as biodiesel production, immobilization of cadmium and lead in contaminated soil, as coating pigments for ink-jet

printing paper, and for removal of trace metals. [13-15]. Lactulose can be obtained from lactose by isomerization by using eggshell as catalyst. eggshell wastes have been also used to synthetize various biological active compounds having important in medicinal, pharmaceutical and agricultures fields such as chromenones, pyranes, 1,4-dihydropyridine and polyhydroquinolines, Benzothiazoles ….etc.[16-21] An attractive area in organic synthesis involves photochemical reactions particularly using visible light in environment friendly solvent like water or aqueous ethanol and is generally considered as a clean and green procedure. This type of photo-activation of substrate very often minimizing the formation of byproducts and requires much lesser time corresponds to thermal methods [22-25].



Scheme 1: synthesis of aldazines using Eggshell waste.

Herein, we report the first time the use of egg shell as ecofriendly and domestic catalyst for synthesis of aldazine compounds under visible light irritations.

Results and discussion

An efficient synthesis of azines derivatives was achieved via condensation reaction betwwen aromatic aldehyde, hydrazine hydrate and sodium acetoacetate using eggshell as catalyst under visible light conditions. In the beginning, the reaction benzaldehyde and hydrazine hydrate was chosen as a model reaction in order to study the optimum conditions of the reaction. Firstly, to investigate the influence of the solvent on the synthesis of *azines*, the reaction was carried out in various solvents such as water, ethanol, mixture of water and ethanol, THF, and CH_3CN. Table 1 shows that using mixture of water and ethanol was the best solvent with higher yield of 90 % obtained in 60 minutes whereas with the other solvents, the yields were from 2 to 50 % were during long time period. Next, we investigate the required amount of eggshell catalyst in the synthesis of azine, the best amount of catalyst was 0.3gm (higher yield). However, when the amount of catalyst was less than 0.3gm the yields of products were trace to less. While, when the amount of catalyst increased up to 0.3g, the yield of product was not better as shown in Table **1**.

Table 1: The effect of reaction conditions on condensations of benzaldehyde and hydrazine hydrate.

Entry	Catalyst (gm)	Solvent	Conditions	Time (min)	Yield (%)[b]
1	0.1	H_2O:Ethanol	V.L	60	40
2	0.2	H_2O:Ethanol	V.L	60	65
3	0.3	H_2O:Ethanol	V.L	60	95
4	0.4	H_2O:Ethanol	V.L	60	80
5	0.5	H_2O:Ethanol	V.L	60	85
6	0.3	H_2O	V.L	60	70
7	0.3	Ethanol	V.L	60	80
8	0.3	Methanol	V.L	60	45
9	0.3	THF	V.L	60	30
10	0.3	Acetonitrile	V.L	60	50
11	0.3	H_2O:Ethanol	RT	60	NR
12	0.3	H_2O:Ethanol	Reflex	60	50

All the reactions were carried out using benzaldehyde (1mmol) 1a, phenyl hydrazine (2mmol) 2a , eggshell catalyst 0.1, 0.2, 0.3, 0.4 and 0.5 mg, in solvents(H_2O:Ethanol, H_2O, Ethanol, Methanol, THF and Acetonitrile. [b] isolated yield , Time 3hrs conditions of reactions visible light , room temperature and reflux.

NR: no reaction

After optimizing the conditions of the reaction, different aromatic aldehydes having electron

donating groups and electron withdrawing groups were treated with hydrazine hydrate in the presence of 0.3gm % of eggshell dissolving in mixture water and ethanol under visible light conditions . It was concluded that all the aromatic aldehyde having electron donating groups or electron withdrawing groups reacted fast to give products in excellent yields. When the same reaction progress with Acetophenone,Benzylacetone and Benzophenon , it noticed the azines not formed by using same conditions employed to synthesis aldazine compounds.

Table 2: Eggshell catalyzed synthesis of azines from aromatic aldehyde, hydrazine hydrate.

Entry	R	Time(min)	Yield %	Mp(° C)
1	C_6H_5-	60	95	92- 93
2	3-$NO_2C_6H_4$	45	98	194-196
3	4-$NO_2C_6H_4$	30	95	332-334
4	4-ClC_6H_4	50	90	204-206
5	4-OHC_6H_4	90	97	264-266
6	4-$Me_2NC_6H_4$	50	96	210-212
7	4-MeC_6H_4	120	98	152-154
8	4-$MeOC_6H_4$	45	94	172-174
9	$(C_6H_5)_2CO$	-	-	-
10	C_6H_5 $CH_2CH_2COCH_3$	-	-	-
11	$C_6H_5OCH_3$	-	-	-

Conclusions

In the present work, we have successfully developed a simple, green assisted one- pot multicomponent synthesis of azines compounds by reaction of carbonyl compound and hydrazine hydrate in the presence of eggshell as catalyst using ethanol as solvent under visible light conditions. The salient feature of this work are higher yield 90-98% of products, short reaction time 20-90 minutes, using eggshell as green solvent and wide scope of substrate and operational simplicity, simple work up and purification of product without using chromatographic method.

Materials and Methods:

All solvents and reagents were purchased from commercial sources with the best quality and they were used without further purification.IR spectra were recorded on a Shimadzu –IR spectrophotometer.

1HNMR, spectra were recorded on 300 MHz Bruker Avance and Chemical shifts are expressed in ppm using TMS as internal standard. All products were characterized by their spectral data. Yields refer to isolated pure products. Thin layer chromatography (TLC) was applied for monitoring of the TLC and performed on 200 μm thick aluminum TLC plates.

General Procedures for the Synthesis of azines:

A mixture of aldehyde (2mmol), hydrazine hydrate (1mmol), and 0.3g of eggshell catalyst + 0.3 g sodium acetate were dissolved by mixture 5 ml of water and ethanol .The mixture was stirred for 10 minutes, the reaction mixture was subjected to irradiation with 200 W tungsten lamp till the completion of the reaction (monitored by TLC). Then, the reaction mixture was cooled and the crystalline product so obtained was filtered. The filtrate was evaporated to remove water and leavening the catalyst. The products were re-crystallized by hot ethanol to produce pure products. All products were identified by melting point and compared with the authentic samples. In addition, all the isolated products were characterized by IR, and ^{1}HNMR spectrums.

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