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Animal Bone Meal: A Novel and Efficient Green Catalyst for Accelerated Oxidation of Hantzsch 1,4-Dihydropyridines

R. Azzallou[1,2], M. Ait Taleb[2], R. Mamouni[2]*, A. Benlhachemi[3], B. Bakiz[3], S. Villain[4], S. Lazar[1]*

[1]*Laboratoire de Biochimie, Environnement & Agroalimentaire, URAC 36, Université Hassan II-Casablanca, BP 146, 20650 Mohammedia, Morocco.*
[2]*Equipe de Matériaux, Catalyse & Valorisation des Ressources Naturelles,* [3]*Laboratoire Matériaux et Environnement, Université Ibn Zohr, BP 8106, 80000 Agadir, Morocco.*
[4]*Institut Matériaux Microélectronique & Nanosciences de Provence, Aix Marseille Université, CNRS, Université de Toulon, IM2NP UMR 7334, 83957 La Garde, France.*

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R. Mamouni, S. Lazar
rachidmamouni1@gmail.com
lazar_said@yahoo.fr
+212 523314705 /+212662048422

Abstract

Animal Bone Meal extract is an efficient reagent for the aromatization of 1,4-dihydropyridines to pyridines under mild, environmentally benign and heterogeneous conditions. Our method accurately identifies all the salient features including simplicity, rapidity, cost-effectiveness, selectivity and its extensive applications. Furthermore, this method could be a valuable addition to the existing methods for the oxidation of 1,4-dihydropyridines.

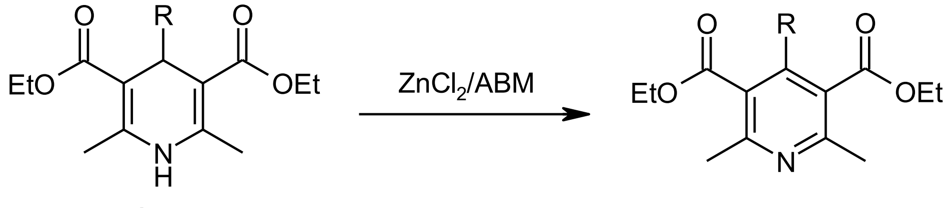
1. Introduction

The oxidation of Hantzsch 1,4-dihydropyridines (1,4-DHPs) to pyridines has been extensively studied in view of the pertinence of the reaction to the metabolism of Hantzsch esters and the calcium channel blocking drugs used in the treatment of various cardiovascular disorders [1-3]. Consequently, this aromatization reaction continues to attract the attention of researchers for the discovery of milder and general protocols applicable to a wide range of 1,4-dihydropyridines.

The oxidation of Hantzsch 1,4-dihydropyridines is one of the ubiquitous reactions in organic chemistry. In the last years, numerous catalysts and procedures have been recommended for this purpose such as: peroxydisulfate-cobalt (II) [4], sodium chlorite [5], nitric oxide [6], bismuth nitrate pentahydrate [7], 4-phenyl-1,2,4-triazole-3,5-dione [8], $Zr(NO_3)_4$ [9], selenium dioxide [10], H_2O_2/V_2O_5 [11], ferric perchlorate [12], $FeCl_3/KMnO_4$ [13], Dess-Martin periodinane with molecular iodine [14], MnO_2 or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [15] and 2,6-dicarboxypyridinum chlorochromate (2,6-DCPCC) [16]. However, most of these reactions require an extended period for completion, excessive use of strong oxidants, and afford only low to modest yields. Therefore, the development of an effective method for the aromatization of 1,4-DHP's under milder conditions is required. Microwave irradiation has several advantages compared to conventional thermal heating of reactants. Recently, it has been used widely in organic chemistry for the optimization of the reaction conditions and shortening the reaction times [17].

Actually, the use of solid supported reagents has received vital role in organic synthesis due to its ease of handling, improved reaction time, larger selectivity, simple workup and recoverability of catalysts.

Among other heterogeneous catalysts, Animal Bone Meal (ABM) doped with zinc chloride has an attractive option for organic synthesis due to its various chemical transformations. These catalysts may change the catalytic activity, influence selectivity, give superior yields and, simplify purification and characterization procedures for new compounds. Our group has recently developed the preparation and use of ABM as a natural catalyst for C-S bond formation by thia-Michael addition [18], crossed-aldol condensation [19], synthesis of benzimidazoles, benzoxazoles, and benzothiazoles [20], synthesis of various chalcones by Claisen-Schmidt condensation and aza-Michael addition [21], synthesis of 3-cyanopyridine derivatives [22]. Our group is interested in improving oxidation processes. For this reason, we have developed a practical approach for the oxidative conversion of 1,4-dihydropyridines (**1a-n**) to pyridines (**2a-n**) using $ZnCl_2$/ABM as a green catalyst in CH_2Cl_2 under reflux condition and performed under microwave irradiation (Scheme 1).



1a-n **2a-n**

Scheme 1: Oxidative aromatization of 1,4-DHPs by $ZnCl_2$/ABM.

2. Experimental details

The structures of all compounds were identified by their spectral data. Silica gel 60 F254 (percolated aluminum plates) from Merck were used to monitor reaction progress. Melting points were determined on IA9300 Digital Melting Point Apparatus and are uncorrected. IR (KBr) spectra were recorded on buck scientific IR M-500 spectrophotometer and the values are expressed as ν_{max} (cm^{-1}). The ^1H NMR spectra were scanned on a Bruker (300 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. The chemical shift values are recorded on δ scale and the coupling constants (J) are in Hz. Mass spectral data were recorded on a Waters micromass spectrometer running under Mass Lynex version 4.0 software and equipped with an ESI source. The microwave irradiation was effected using the domestic microwave ovens (Westbend, Model EM915AJW-P2, WI, USA).

2.1. *General procedure for the aromatization of 1,4-DHPs*

In a 50 mL round-bottom-flask, the 1,4-dihydropyridines (1 mmol) and $ZnCl_2$/ABM (50 mg) were stirred in presence of dichloromethane (5 mL). The reaction mixture was refluxed for the specified time (Table 2). The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was concentrated under reduced pressure. The residue was diluted with 10% of $NaHCO_3$ (5 mL) and extracted with EtOAc. The organic layer was washed with iced water and brine (2 x 15 mL), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The crude products were crystallized from EtOH or EtOH/H_2O or chromatographed on silica gel column to obtain pure products.

2.2. *A typical procedure for aromatization of 1,4-dihydropyridines with $ZnCl_2$/ABM under microwave irradiation*

In a typical experimental procedure, a mixture of $ZnCl_2$/ABM (50 mg) and 1,4-dihydropyridine (1 mmol) was added to dichloromethane (5 mL). The reaction solution was thoroughly mixed at room temperature. The air-dried adsorbed material (in a small beaker) was placed inside the microwave oven and irradiated for the time indicated in the Table 2. The progress of reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and the reaction mixture was extracted with chloroform (2 × 25 mL), washed with 10% of $NaHCO_3$ solution. The organic layer with brine (2 × 15 mL), dried over Na_2SO_4 and concentrated under vacuum to give the crude product which was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane mixture as eluent to afford pure pyridine derivatives.

2.3. *Preparation of ABM and his doped analogs $ZnCl_2$/ABM*

Animal bones were collected from nearby butcher shops. All of the attached meat and fat were removed and cleaned from the bones. The bones were then washed several times with tap water at room temperature and left in open air for several days to get rid of odors. Later, they were transferred to the oven at 80°C for drying. The dried bones were crushed and milled into different particle sizes in the range 45-200 μm then calcined for 2 h at 800°C. The residue was washed with water and used after drying for 24 h at 80°C. The residue was washed with water and dried overnight at 100°C in a conventional drying oven, and then calcined at a heating rate of 2°C/min to 400°C, and kept at this temperature for 4 h. The modified bones $ZnCl_2$/ABM was prepared by impregnating the bones with an aqueous solution of zinc chloride. The weight ratio used was $ZnCl_2$/ABM =1/2. The mixture was stirred vigorously at room temperature, evaporated, dried, and calcined at 800ºC for 2 h. The obtained catalysts were characterized by Differential Scanning Calorimetric (DSC) coupled with Thermogravimetric

Analysis (TGA) (Fig. 1), X-ray diffraction (Fig. 2 and Fig. 3), Scanning Electron Microscopy with Energy Dispersive (SEM/EDS) (Fig. 4).

2.4. *Characterization of ABM and $ZnCl_2$/ABM*

2.4.1. *Thermal analysis (TGA and DSC)*

The thermal gravimetric analysis was carried out on a TGA Shimadzu DTG-60 Thermogravimetric analyzer in an alumina crucible at a heating rate of 10°C/min under air atmosphere. The mass of the sample was 12 mg. The sample pan was placed in the balance system equipment and the temperature was raised from 16 to 900°C.

2.4.2. *XRD analysis*

It provides information on the purity, crystallinity and crystallographic parameters. The analysis by X-ray diffraction was performed on the powder in ambient conditions of temperature and pressure. The X-ray diffractometer used was a Panalytical diffractometer, equipped with a copper X-ray (wavelength $\lambda = 1.54 \times 10^{-10}$ m; tension V = 45 kV, intensity I = 35 mA), and with a monochromator eliminating Kβ radiation. The analyses were carried out using the classical θ–2θ configuration, with 2θ angle steps of 0.02° and counting times of 20 sec per step.

2.4.3. *SEM-EDS analysis*

The scanning electron microscope (SEM) was used to obtain images of the surface of substantially solid materials at scales ranging from that of the lens (x 10) of the transmission electron microscope to (x 500000), its principle of operation is the interaction between the material and electron beam. The instrument used is ZEISS Supra 40VP with GEMINI® column coupled to an analyzer (Oxford Instruments X-Max 20 mm^2) with EDXS detector (Energy Dispersive X-rays Spectroscopy) to determine the local quantitative of elemental composition sample with a maximum resolution of 1 micron at voltages ranging from 10 to 25 kV.

2.4.4. *FTIR analysis*

Fourier Transformed Infrared (FTIR) spectrum of the sample was recorded by Fourier transform infrared (Nicolet 6700 FT-IR, Thermo Scientific) spectrophotometer. The FTIR spectrum ranged from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} by making an ATR mode.

3. Results and Discussion

3.1. *Thermal analysis*

The curves of Thermogravimetric analysis (TGA) and flow profiles of heat from 16.25°C to 900°C. The thermogram samples generally show three successive stages of the weight loss. The first stage is below 200°C, the second is between 200°C to 600°C, the third is between 600°C to 800°C and the last stage is above 800°C where the weight change is not significant [23, 24]. The results of DSC showed an endothermic peak at 67.8°C related to loss of surface and structural of water. It is then followed by two exothermic peaks with a maximum value around 359.66°C which is related to loss of both collagen and shoulder, while the loss of collagen and organic matter is around 535.31°C [25]. At the end, one single small endothermic peak at 693.2°C occurs due to loss of mineral CO_2 (Fig. 1).

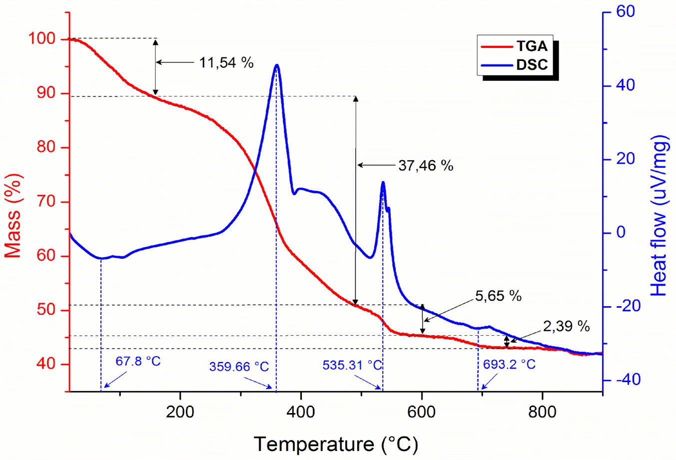


Figure 1: TGA and DSC plots of the control samples (non calcined bovine bone) in the 16.25–1000°C temperature range.

3.2. *XRD analysis*

The XRD pattern of the ABM phase thermally calcined at 900°C are reported in Fig. 2. First, these results confirm that the amorphous organic material was removed after calcination. Second, it should be recalled that the XRD analyses for ABM in the range 2θ = 10-80° clearly showed that the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ powder was in a major structured form by comparison with the standard JCPDS data (96-901-0052) [26]. This identification allowed attributing Miller indices (hkl) to Bragg peaks, in conformity with the approximate parameters of a compact hexagonal a = b = 9.4148 Å, c = 6.8791 Å, α = β = 90°, γ = 120° [27] which was characterized with $P_{63/m}$ space group (N° 176).

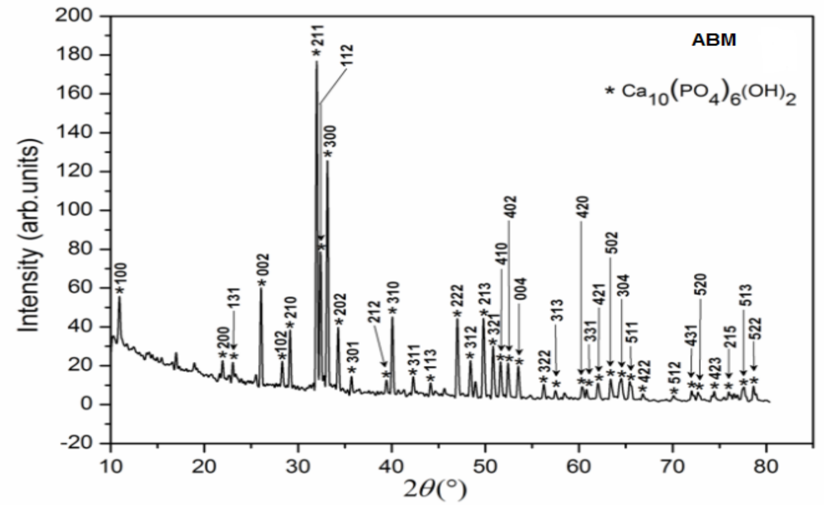


Figure 2: X-Ray diffraction patterns of ABM.

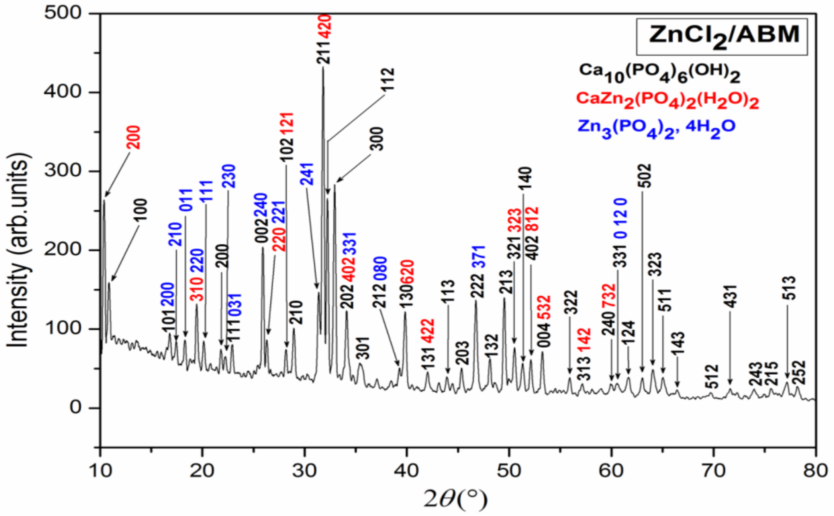


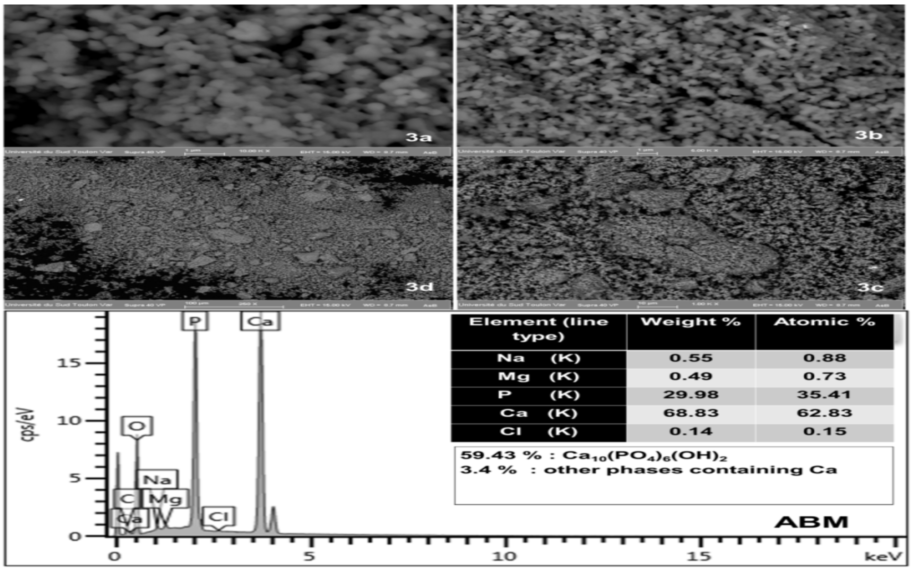
Figure 3: X-Ray diffraction patterns of $ZnCl_2$/ABM.

The XRD pattern of $ZnCl_2$/ABM sample is shown in Fig. 3. The diffraction rays characteristics of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ are identified clearly. These rays are consistent with standard JCPDS (01-074-0566). This identification allowed attributing Miller indices (hkl) to Bragg peaks in conformity with the approximate parameters of a compact hexagonal a = b = 9.4240 Å, c = 6.8790 Å, α = β = 90°, γ = 120° [28] which was characterized with $P_{63/m}$ space group (N° 176). In addition, the corresponding rays of calcium zinc phosphate hydrate $CaZn_2(PO_4)_2(H_2O)_2$ (standard JCPDS file 01-071-0889) is comparable with orthorhombic structure a = 17,1490 Å, b = 7,4120 Å, c = 6,6670 Å, α = β = γ = 90° [29], which is characterized by P_{bcn} space group (N° 60). Furthermore, the corresponding rays of zinc phosphate hydrate $Zn_3(PO_4)_2(H_2O)_4$ (standard JCPDS file 00-037-0465) is comparable with orthorhombic structure a = b = 10,6067 Å, c = 5,0284 Å, α = β = γ = 90° [30], characterized by Pnma space group (N° 62).

3.3. *SEM-EDX analysis*

The scanning electron analysis of ABM (Fig. 4) shows that its spherical morphology is characterized by small particles whose average size is between 0.2 to 1 µm (image **3a** and **3b**). The image **3c** and **3d** show that these particles form agglomerates (size 10 and 50 µm). These shapes showed the presence of a significant percentage of cavities (in all images) which will be interesting for the catalysis. EDX analysis was performed on a large perspective of ABM sample including small and large grains.

The results of this analysis showed that the mean experimental atom fractions of the Ca and P heavy atoms were successively about 63 at% and 35 at % respectively (ignoring light atoms such as C, H and O). The ratio of Ca/P is equal to 1.8 higher than that which characterizes the stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (1.67) and other minor phases which contain calcium.



Element (line type)	Weight %	Atomic %
Na (K)	0.55	0.88
Mg (K)	0.49	0.73
P (K)	29.98	35.41
Ca (K)	68.83	62.83
Cl (K)	0.14	0.15

59.43 % : $Ca_{10}(PO_4)_6(OH)_2$
3.4 % : other phases containing Ca

Figure 4: SEM images and EDX of ABM

3.4. *Application ABM and $ZnCl_2$/ABM for aromatization of 1,4-dihydropyridines*

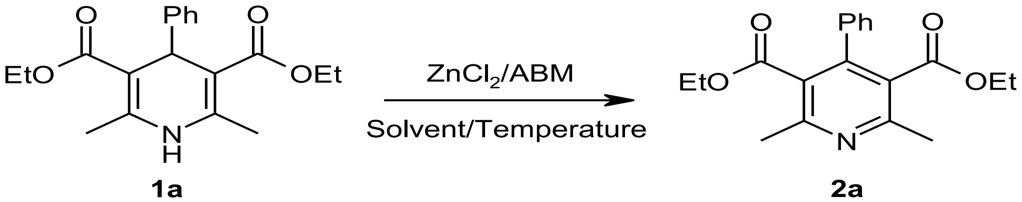
In continuation of our application to develop an efficient and environmentally benign methodology for the aromatization of 1,4-dihydropyridine derivatives, we initiated our studies by subjecting catalytic of $ZnCl_2$/ABM with diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**) in various solvents at room temperature. Unfortunately, the resulted yield was very poor even after 2 h of stirring. Therefore, various solvent systems were screened at different temperatures to yield high. We were pleased to see that the synthesis of pyridines was efficiently catalyzed by $ZnCl_2$/ABM in solvent free condition at elevated temperature leading to high yield. The reaction condition was then, optimized by conducting the reaction in different temperatures and employing different catalyst loadings. The results are summarized in Table 1.

The influence of the various solvents on the yield of the reaction was investigated using compound (**1a**) as the substrate. The obtained results show that dichloromethane is the best choice for the oxidation reaction. This can be attributed to enhance soluble power of the solvent for the oxidant as well as the substrate.

All previous reactions were carried out in dichloromethane, but in the absence of catalyst. We were unable to isolate any desired product (**2a**) from the reactants present in the reaction mixture (Table 1, Entry 18). For this reason, we went further to determine the optimum catalyst loading; we performed the same reaction using 50, 100 and 150 mg of $ZnCl_2$/ABM respectively. The product (**2a**) is obtained with a good yield. However, an increase in the amount of catalyst is accompanied with a significant decrease in yield. Indeed, in the same reaction the product (**2a**) is obtained with a yield of 97% using 100 mg of $ZnCl_2$/ABM, but the yield does not exceed 87% with 150 mg of $ZnCl_2$/ABM.

This result is explained by the use of a high concentration of $ZnCl_2$/ABM (150 mg), which seems to cause either the chlorination of the 1,4-dihydropyridine or the formation of pyridinium salts associated with the desired product (**2a**). This study also showed that the reactivity of the reaction is highly dependent on the load of the catalyst present in the medium reaction.

From these results we conclude that the reactivity is significantly higher in the presence of $ZnCl_2$/ABM because the yield of the product (**2a**) reaches 92% only after 30 minute of the reflux. However, the observed yield of the product (**2a**) is approximately 67% when the catalyst ABM is used alone for three hours of stirring at reflux condition. Several side reactions were observed in the reaction medium due to utilization of ABM alone which lead to incomplete reaction. At room temperature, the obtained yield for the product (**2a**) is modest 72% even if the reaction was performed in the presence of $ZnCl_2$/ABM in dichloromethane for two hours (Table 1, Entry 1). It seems that reflux gives high yield and short reaction time compare to room temperature. For this reason, we have conducted all reactions using reflux method in order to isolate the desired product **2a** in excellent yield (Table 1, Entry 6).



1a **2a**

Table 1: Aromatization of 1,4-DHPs catalyzed by ZnCl$_2$/ABM under different catalyst loadings, temperature and solvent systems.

Entry	Catalyst load (mg)	Solvents	Temperature (°C)	Time (min)	Conversion (%)	Yield (%)
1	50	CH_2Cl_2	RT	120	74	72
2	50	CH_3CN	RT	120	70	68
3	50	EtOH	RT	120	79	74
4	50	H_2O	RT	120	80	73
5	50	Neat	RT	120	40	35
6	50	CH_2Cl_2	Reflux	30	93	92
7	50	CH_3CN	Reflux	60	84	82
8	50	EtOH	Reflux	60	88	87
9	50	H_2O	Reflux	60	86	84
10	100	CH_2Cl_2	Reflux	30	98	97
11	100	CH_3CN	Reflux	60	93	90
12	100	EtOH	Reflux	60	94	91
13	100	H_2O	Reflux	60	90	89
14	100	THF	Reflux	60	54	48
15	150	CH_3CN	Reflux	60	95	92
16	150	EtOH	Reflux	60	97	93
17	150	CH_2Cl_2	Reflux	30	90	87
18	Neat	CH_2Cl_2	Reflux	120	0	N.R

Yield refers to isolated yield. Conversions determined by ^{1}H NMR spectroscopy.

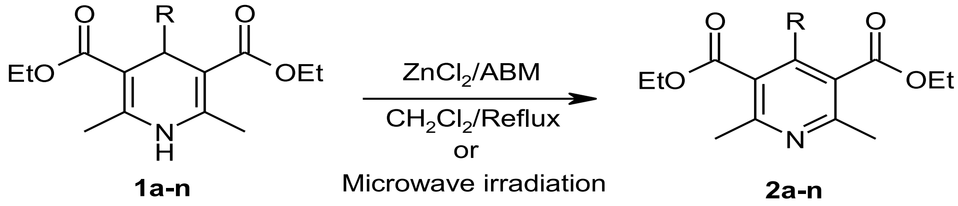
Another reason is that the reaction was complete and all side reactions were completely removed. According to the study of the various constituents of the reaction medium, it appears that the best optimum conditions to achieve oxidation of the derivatives of 1,4-dihydropyridine, are formed using dichloromethane as solvent in the presence of 50 mg of catalyst under reflux. The most interesting aspect of these conditions is that ZnCl$_2$/ABM responded very well and provided an excellent yield of the derivatives of pyridine within a short reaction. The results obtained with various 4-substituted 1,4-dihydropyridine are shown in Table 2.

In continuation, we have developed an effective approach using microwave irradiation for the oxidative conversion of 1,4-dihydropyridine derivatives to pyridines using ZnCl$_2$/ABM as a catalyst. Initially, 4-phenyl-1,4-dihydropyridine (**1a**) was used as a substrate to test the feasibility of ZnCl$_2$/ABM for the oxidation process. It was found that proceeding reaction for each 1 mmol of (**1a**) with 50 mg of ZnCl$_2$/ABM gave a high efficiency in terms of yield and reaction time. This approach confirmed that a wide variety of 1,4-dihydropyridines having alkyl, aryl and heterocyclic substituents were successfully oxidized to give an excellent yield of the derivatives of pyridines (Table 2). We found that ZnCl$_2$/ABM is an effective catalyst for the aromatization of 1,4-dihydropyridines to pyridines under mild and heterogeneous conditions. The resulted yields fall between 89% and 99% even though the variations of the substituents of arylbenzaldehyde were focused on both electron withdrawing and electron-donating. The nature of the electronic and steric factors of the substituents on 4-position had no significant influence on the reaction.

The results showed that the oxidation of 4-alkyl, aryl, and alkenyl 1,4-dihydropyridines containing methyl, phenyl and *p*-tolyle, substitutes produced exclusively pyridines in excellent yields. We also observed that the oxidation of 4-alkyl-dihydropyridine (**1d** and **1e**) leads to a small decrease in yield. This could possibly be explained by steric hindrance oxygen.

As a model reaction, the possibility of recycling the catalyst was then examined using compound (**1a**, 1 mmol), 50 mg of ZnCl$_2$/ABM and 5 mL of dichloromethane at reflux. After completion of the reaction (30 min), the catalyst was filtered and washed with water and then recycled four times after each use. In the first three runs, the activity was more or less maintained. However, after the three run it started decreasing, which may be due to the degradation of the catalyst under reflux conditions. The yields for the five runs were found to be 92%, 90%, 90%, 88% and 84% respectively (Fig.5).

Table 2: Oxidative aromatization of 1,4-dihydropyridines with $ZnCl_2$/ABM under refluxing conditions and microwave irradiation.



Product[a]	R	Refluxing condition	Microwave irradiation	Mp (°C)
		Time (min) / Yield (%)[b]	Time (min) / Yield (%)[b]	found / reported
2a	C_6H_5	30 / 92	2 / 96	62-64 / 61-62 [16]
2b	H	10 / 96	1 / 94	69-71 / 68–70 [16]
2c	CH_3	10 / 97	1 / 98	Oil / Oil [16]
2d	n-C_3H_7	30 / 87	3 / 93	Oil / Oil [4]
2e	n-C_4H_9	30 / 78	3 / 90	Oil / Oil [4]
2f	4-$MeOC_6H_4$	20 / 96	2 / 93	56-59 / 56–58 [4]
2g	4-$O_2NC_6H_4$	15 / 94	2 / 94	113-114 / 112–114 [4]
2h	4-MeC_6H_4	30 / 95	3 / 96	70-72 / 72–73 [4]
2i	4-ClC_6H_4	40 / 92	3 /93	67–69 / 66–67 [16]
2j	3-$O_2NC_6H_4$	30 / 90	3 / 94	61–63 / 62–63 [16]
2k	$CH_3CH=CH$	25 / 90	3 / 92	Oil / Oil [4]
2l	PhCH=CH	25 / 90	3 / 90	160-162 / 162-165 [4]
2m	2-Furyl	30 / 82	3 / 86	Oil / Oil [5]
2n	2-Thienyl	35 / 85	3 / 86	74-76 / 76-79 [4]

[a] All known compounds were characterized by comparing their spectral data with those reported.

[b] Isolated yields.

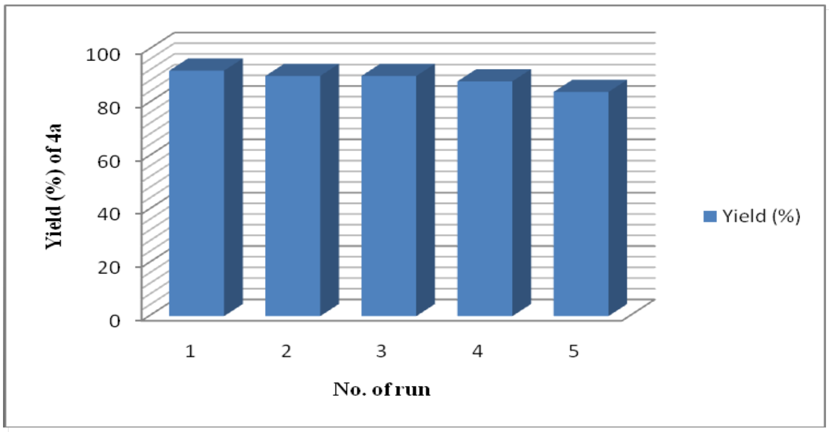


Figure 5: Reusability of $ZnCl_2$/ABM catalyst for the oxidation reaction of 1,4-DHPs.

In order to show the advantages of this reagent over some other oxidants, we have compared our results with those reported in Table 3. The results show that $ZnCl_2$/ABM promotes the reaction more effectively than other reagents. The reaction in the presence of those reagents which are listed in Table 3 requires longer reaction times.

Table 3: Comparison of $ZnCl_2$/ABM with some the other reagents for oxidation of Hantzsch 1,4-DHPs.

Reagent	Conditions	Time (h) / Yield (%)	Reference
$FeCl_3/KMnO_4$	H_2O_2, Reflux	3-6 / 45-78	[13]
DDQ	CH_2Cl_2, 20°C	1 / 73-90	[15]
$K_2S_2O_8$/ Cobalt-II	CH_3CN, Reflux	1-3 / 82-94	[4]
H_2O_2/V_2O_5	CH_3CN, RT	1-2 / 94-98	[11]
$Bi(NO_3)_3/5\ H_2O$	ACOH, RT	1-14 / 50-90	[7]
$ZnCl_2$/ABM	CH_2Cl_2, Reflux	10-45 (min) / 82-99	This work
$ZnCl_2$/ABM	Microwave	1-3 (min) / 86-98	This work

Finally, although the elimination of 4-substitution (R) and the formation of by-product have been observed in many other reported oxidation reaction, it is very notable that not by product was observed via this method.

Conclusion

We have introduced in this study the green catalyst ABM as a new highly effective, non-corrosive, heterogeneous and environmentally benign catalyst to accelerate oxidation of Hantzsch 1,4-dihydropyridine. The procedure offers several advantages including mild and efficient organic synthesis under solvent-free conditions, short reaction time, complete reaction, high isolated yields, cost effectiveness and excellent chemo selectivity.

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