

Henry Reaction between Benzaldehyde and Nitromethane over Solid Base Catalysts: A Green Protocol

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Abstract

The development of environmentally benign solid base catalysts instead of the soluble bases for C-C bond formation in organic reactions especially Henry reactions with nitroalkanes compounds is of intense research activity in the bulk and fine chemical chemistry in order to achieve the selectivity of the desired product and the reduction of the salts formed due to soluble bases neutralization. While using of LDHs catalysts in the synthesis of nitro alcohols is of great interest because LDHs (double layered hydroxides) is of unique properties and an excellent catalytic property. The nitroalcohols are obtained in a very good yield while using catalyst either by conventional at 90°C in liquid phase, microwave or sonoenergy without solvent methods, and the results yields are compared. A series of different nitro alcohols from (a - o) were prepared, the catalytic test reaction were carried out using benzaldehyde and their derivatives with nitromethane and their derivatives. A series of LDHs catalysts were prepared also and studying of the catalytic effect on the reactions was carried out. Properties of the compounds prepared were characterized by IR, MNR, and GC-MS.

Keywords

C-C Bond Formation, Henry Reaction, Base Catalyst

1. Introduction

The fine chemical industry has experienced remarkable interest over the past few years due to the high requirements for products like pharmaceuticals, pesticides, fragrances, flavorings and food additives [1].

The classical methods for the C-C coupling in Henry reaction using soluble bases such as alkali metal hydroxides, carbonates, bicarbonates, alkoxides, alkaline earth metal hydroxide, and aluminium ethoxides, complexes, and also organic bases such as primary, secondary and tertiary amines usually resulted in dehydrated products [2]. Therefore, careful control of the basic properties of the reaction medium is vital to obtain better yields of β -nitroalcohols. However, the efforts done by the researchers in the literature required longer reaction times and produced moderate yields [3] [4]. The stoichiometric organic synthesis largely applied so far resulted in large quantities of inorganic salts as byproducts; the disposal of such material causes a serious problem due to the important environmental issues [5].

The remarkable progress in the competition in the industry has pushed the researchers to develop more effective catalytic processes in the synthesis of fine chemicals.

The products of the Henry reaction, representing C-C bond formation, are important materials extensively used in many organic syntheses [6]. The greatest challenge in the selective synthesis of 2-nitroalkanols in the multiple product options such as aldol olefin and its polymer and Cannizzaro products is the selection of the right type of base [7].

Significant improvements to the Henry reaction have been achieved by using silyl nitronates in the presence of fluoride ion or alternatively α - α doubly deprotonated primary nitroalkanes [8].

Both of these procedures have proved to be useful for the stereo selective preparation of vicinal amino alcohols under drastic conditions, which reduced diastereoselectivity with aromatic aldehydes. In order to obtain better yields and diastereoselectivity of 2-nitroalcohols, it is necessary to develop new procedures employing heterogeneous catalysts with basic character [9].

The homogenous catalytic methodologies reported in the literature have many disadvantages, such as disposal of waste and difficulty to recover the catalyst from the products. In the last decade, there were notable improvements in the development of heterogeneous catalyst for Henry reaction [10].

Heterogeneous catalysis induced by solid catalysts such as basic alumina [11], alumina-KF [12] and homogeneous phase transfer catalysis with surfactants [13] in bi-phase system, the two divergent approaches being explored are aimed at achieving higher atom selectivity. The solid base catalysts provide an alternative to the classical soluble bases with emphasize to avoid the environmental problems caused by salt formation and hazardous conditions [14]. Previous work in the synthesis of fine chemicals using layered double hydroxides revealed the importance of such materials and discovered its environmentally favorable routes in comparison to the other catalysts [15]-[20].

2. Results and Discussion

Henry reaction is a base-catalyzed C-C bond-forming reaction between nitroal-

kanes and aldehydes or ketones. It is similar to the Aldol Addition, and also referred to as the Nitro Aldol Reaction.

If acidic protons are available (H), the products tend to eliminate water to give nitroalkenes. Therefore, only small amounts of base should be used if the isolation of the β -hydroxy nitro-compounds is desired, **Scheme 1**.

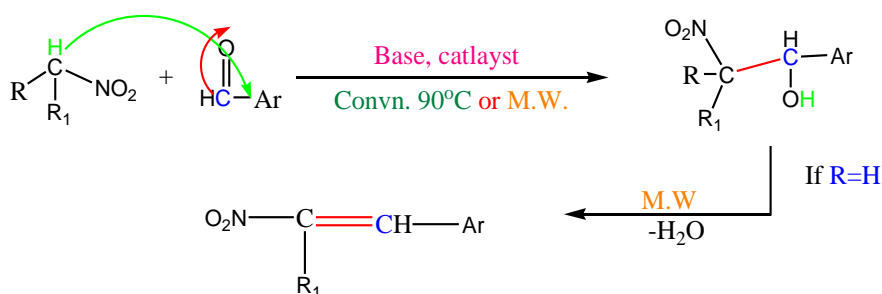
To generalize this reaction methodology three experiments were carried out using different LDHs catalysts which may also be called hydrotalcite, and their thermally activated form (calcined) were very active and very useful in many different organic synthesis reactions. Henry reaction was carried out under three conditions by these catalysts, by conventional method, and microwave method [21].

Cu LDHs series was used in this research which were: uncalcined HT-Solgel Cu:Mg:Al (1:2:1), calcined Cu:Mg:Al (1:2:1), calcined Cu:Mg:Al (2:1:1) and finally calcined Cu:Al (3:1). **Table 1** represents the nitroalkanes and the aldehydes used.

To compare the three types of this condensation reaction yield, it should be taken in consideration from literature the most optimum temperature for this reaction by conventional method was 90°C. While in this research temperature in conventional method decreased by using catalysts, **Table 1** represented the yield of this nitro aldol condensation reaction using three methods.

The use of uncalcined HT was not efficient enough like the other catalyst used and the reaction yields and time were near to the reaction yield and time in the absence of any catalyst and solvents in spite of temperature change and decreased to 60°C, as shown in **Table 4**. Using of different calcined catalysts at fixed weight 0.5 g, temperature 50°C for conventional method, fixed microwave temperature many different results but in a good and acceptable yield % for all of the catalysts used as illustrated in **Tables 5-7**. These good results directed us to make a comparison between the catalysts themselves and their activities toward the nitroaldol reaction.

The higher activity of LDHs catalysts were observed because of their structure flexibility as a host compound during the formation of final nitroalcohol. It was observed also at fixed amount of catalyst used, fixed temperature, and fixed M.W conditions, changing of the catalyst type led to decrease in time of the reaction required to be finished and increase of the reaction yield.



Scheme 1. Henry reaction and its mechanism.

Table 1. Compounds Structures.

Compound	R	R1	Ar
A	H	H	4-cholorobenzaldehyde
B	CH ₃	H	4-cholorobenzaldehyde
c	CH ₃	CH ₃	4-cholorobenzaldehyde
D	H	H	3, 5 Dibromo benzaldehyde
E	CH ₃	H	3, 5 Dibromo benzaldehyde
F	CH ₃	CH ₃	3, 5 Dibromo benzaldehyde
G	H	H	5-Bromo-3-nitro, Salicylaldehyde
H	CH ₃	H	5-Bromo-3-nitro, Salicylaldehyde
I	CH ₃	CH ₃	5-Bromo-3-nitro, Salicylaldehyde
J	H	H	2-Nitro-benzaldehyde
K	CH ₃	H	2-Nitro-benzaldehyde
L	CH ₃	CH ₃	2-Nitro-benzaldehyde
M	H	H	4-methoxy benzaldehyde
N	CH ₃	H	4-methoxy benzaldehyde
O	CH ₃	CH ₃	4-methoxy benzaldehyde

Table 2. Comparison between different methods time and yield without any catalysts.

Compound	Conventional at 90°C		Microwave	
	Time Min.	Yield %	Time Min.	Yield %
a	480	62	6.5	80
b	360	66	6.5	82
c	480	65	5.5	86
d	420	61	6	80
e	360	59	4.5	84
f	360	67	4.5	83
g	360	66	5.5	83
h	300	58	5.5	87
i	420	63	5	87
j	360	70	4.5	81
k	420	64	5	81
l	360	61	4.5	82
m	360	66	4	84
n	360	66	6	82
o	480	66	4.5	83

Table 3. Comparison between different methods time and yield using uncalcined HT-Solgel (0.5 g).

Compound	Conventional 60°C		Microwave	
	Time min.	Yield %	Time Min.	Yield %
a	300	61	4.5	90
b	360	64	4.5	88
c	360	48	3.5	88
d	270	60	4	92
e	300	58	4.5	90
f	360	56	3.5	88
g	360	63	3.5	84
h	300	59	3.5	90
i	240	65	3.5	90
j	270	70	3.3	80
k	300	64	3	83
l	300	69	4	93
m	300	71	3	94
n	300	68	4	90
o	300	72	3	92

Table 4. Comparison between different methods time and yield using Cu:Mg:Al (1:2:1) (0.5 g).

Compound	Conventional 60°C		Microwave	
	Time min.	Yield %	Time min.	Yield %
a	270	70	3.5	95
b	270	73	3.5	94
c	240	72	3.5	92
d	240	75	3	94
e	240	79	3.5	93
f	180	77	2.5	93
g	210	76	2.8	94
h	210	68	3.5	93
i	210	69	3	92
j	240	76	2.6	91
k	270	75	3	91
l	240	78	3	89
m	240	76	2.4	94
n	210	78	3	93
o	210	76	2.6	94

Table 5. Comparison between different methods time and yield using calcined Cu:Mg:Al (1:2:1) (0.5 g).

Compound	Conventional 60°C		Microwave	
	Time min.	Yield %	Time min.	Yield %
a	180	70	3	95
b	180	73	3.5	95
c	210	72	3.5	96
d	210	75	2.6	94
e	210	79	2.5	93
f	210	77	2.5	96
g	180	76	2.5	96
h	220	68	2.5	95
i	230	69	2.5	94
j	230	76	2.3	95
k	280	75	3	94
l	180	78	2.5	95
m	250	76	2	94
n	200	78	2.5	96
o	200	76	2.5	94

Table 6. Comparison between different methods time and yield using calcined Cu:Mg:Al (2:1:1) (0.5 g).

Compound	Conventional 60°C		Microwave	
	Time min.	Yield %	Time min.	Yield %
a	65	82	2.8	95
b	60	83	2	95
c	60	84	2.5	96.5
d	55	83	2.5	95
e	55	83	2	94.5
f	55	85	2	96
g	58	86	2.2	98
h	60	85	2	97.5
i	60	85	2.5	97
j	62	88	2	96
k	66	84	2	95
l	65	86	2	96
m	65	85	2	96
n	63	90	2	94.5
o	63	92	2	96.5

Table 7. Comparison between different methods time and yield using clacined Cu:Al (3:1) (0.5 g).

Compound	Conventional 60°C		Microwave	
	Time min.	Yield %	Time min.	Yield %
a	55	92	2.2	98.9
b	55	91	2	99
c	58	92	2.2	98.5
d	50	93.5	1.8	99
e	48	92.6	1.5	98.5
f	48	94.8	1.5	98.3
g	46	92	1.5	97.8
h	46	91	1.5	97.5
i	50	88	1.5	98
j	54	89	1.3	99
k	45	91	1.5	99
l	50	89	1.3	99
m	45	88.8	1.1	99
n	40	93	1	98.6
o	40	94	1	98.8

For Cu:Al 3:1 and Cu:Mg:Al 2:1:1 the reaction tended to be completed in a short time. This can be explained by the catalyst which has higher copper content was more active in this serious. One also could observe that aldehyde which has little electron withdrawing group influence and enhance the reaction activity. By the way microwave yields are the highest every time.

By the way from **Table 3** the reaction tented to be finished between 4 - 6.5 min using M.W and 300 - 480 min using conventional method by maximum yield 87% and 63% respectively. While using solvated catalyst reaction **Table 2** completed at 3 - 4 min M.W and 300 min. by using conventional method in a max. Yield % 94% and 71% respectively. The 99% yield percentage obtained by using clacined Cu:Al 3:1, using M.W at 1.5 - 2 min. But using of calcined Cu:Mg:Al (2:1:1) gave 98% yield as a highest yield percentage this may attributed to the crystalline structure of Cu:Al 3:1 [22]. The difference in reaction catalysts, yield and time was illustrated in **Figures 1-5**.

Where:

Figure 1: Compare between different methods time and yield without any catalysts.

Figure 2: Compare the yield % change during use of different catalysts, by MW irradiation method.

Figure 3: Compare the time change during use of different catalysts, MW irradiation method.

Figure 4: Compare time change during use of different catalysts, by conventional method.

Figure 5: Compare the yield % change during use of different catalysts, conventional method.

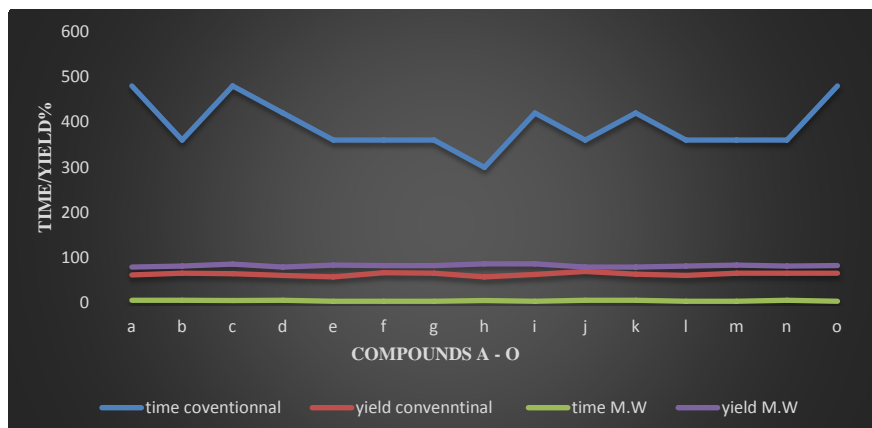


Figure 1. Comparison between different methods time and yield without any catalysts.

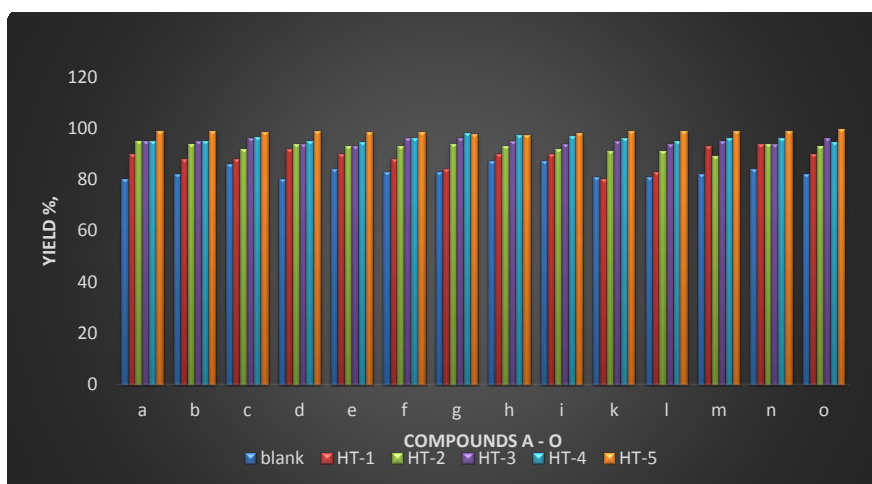


Figure 2. % Yield change during use of different catalysts, MW.

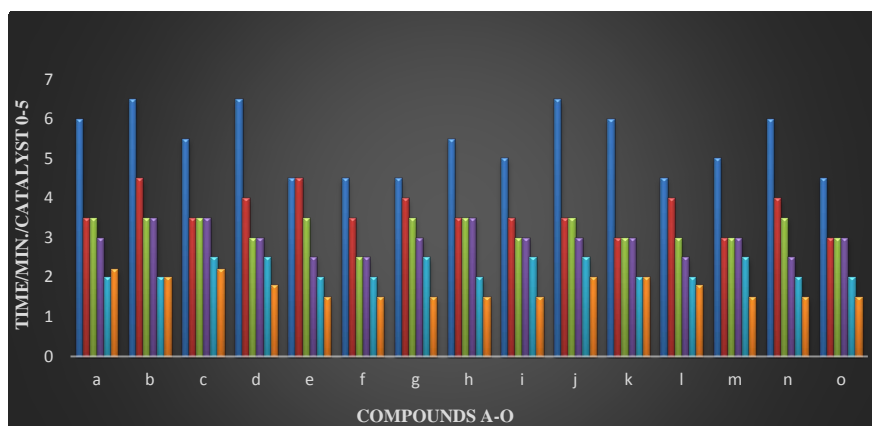


Figure 3. Time change during use of different catalysts, MW.

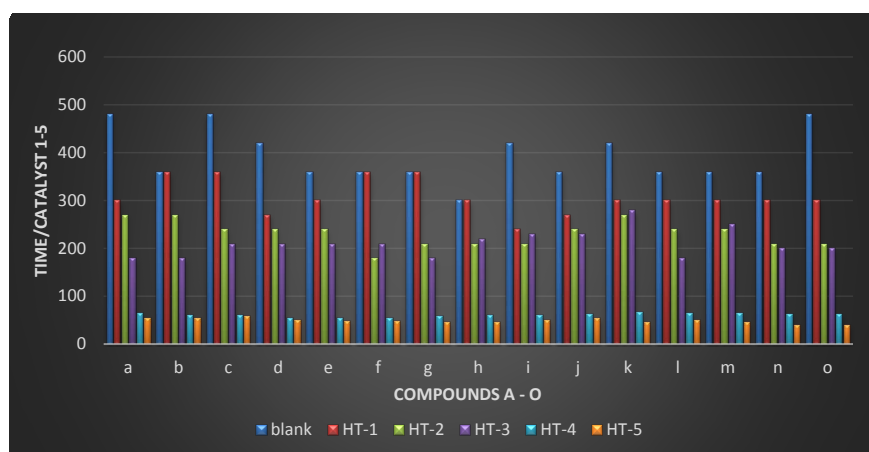


Figure 4. Time change during use of different catalysts, conventional.

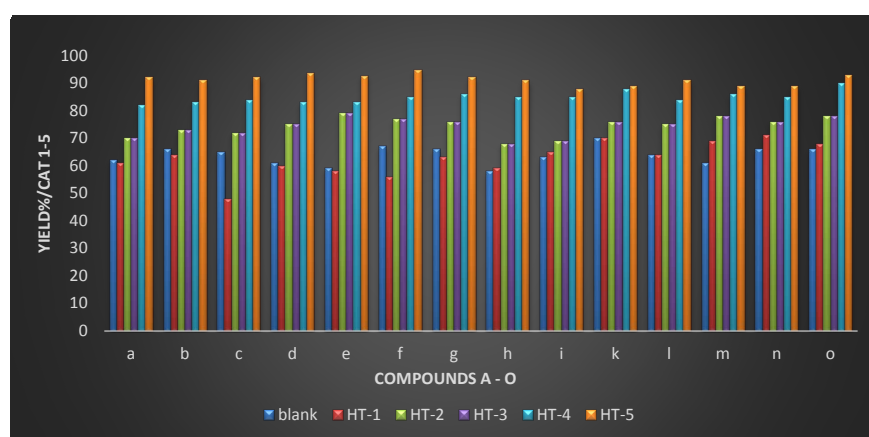


Figure 5. % Yield change during use of different catalysts, conventional.

XRD of the catalysts were represented in **Figure 6**, indicating the diffraction patterns of HT-1, HT-2, HT3, HT-4 and HT-5, which gave information about the crystalline nature of these five catalysts. Catalyst showed diffraction pattern at 2θ 35.6° , 38.8° , 48.8° , 53.6° , 58.5° , 61.5° , 66.3° , 68.1° and 75.4° . The catalyst was also analyzed after reuse by XRD and it showed no significant change. XRD patterns catalysts layered structure was obtained (Ref. Pattern 22-0700, JCPDS) [23].

FTIR (Fourier transform infrared spectroscopy) of HT catalyst series sample (**Figure 7**) showed a broad band at nearly 3500 cm^{-1} belonged to stretching vibration OH. This might be because of the water interlayer and hydroxyl groups in HT series [24]. Small weak band appeared at 1650-1700. This might be related to the bridging mode $\text{H}_2\text{O}-\text{CO}_3^{2-}$. Because of the vibrational mode of water a weak peak at 1590 cm^{-1} appeared in the infrared spectrum which might be related to interlayer of water [25]. The peak around 1340 cm^{-1} belonged to carbonate. All of carbonate bands of HT catalysts were removed completely during calcinations at 450°C [26]. This was as a result of complete thermal decomposition of hydrated catalysts phase into mixed metal oxides, which gave a good indication of the XRD data [27] [28].

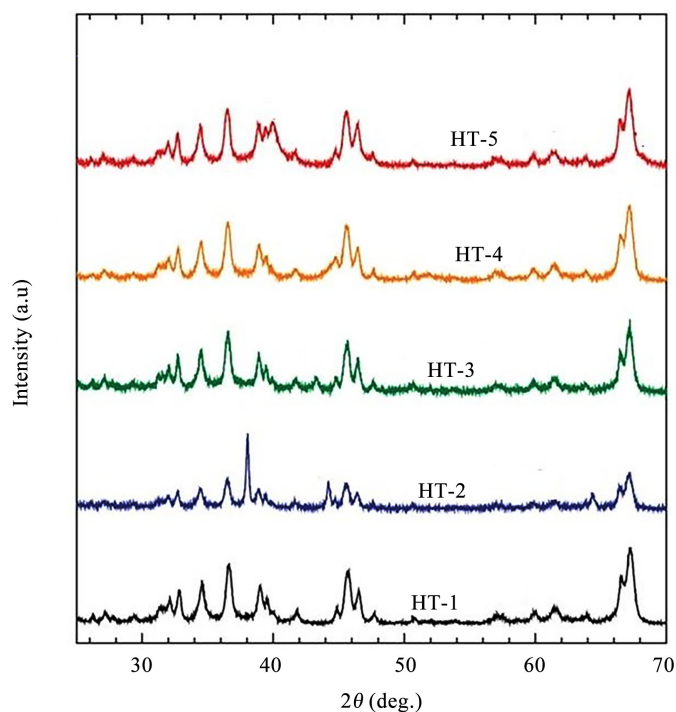


Figure 6. XRD for HT catalysts series.

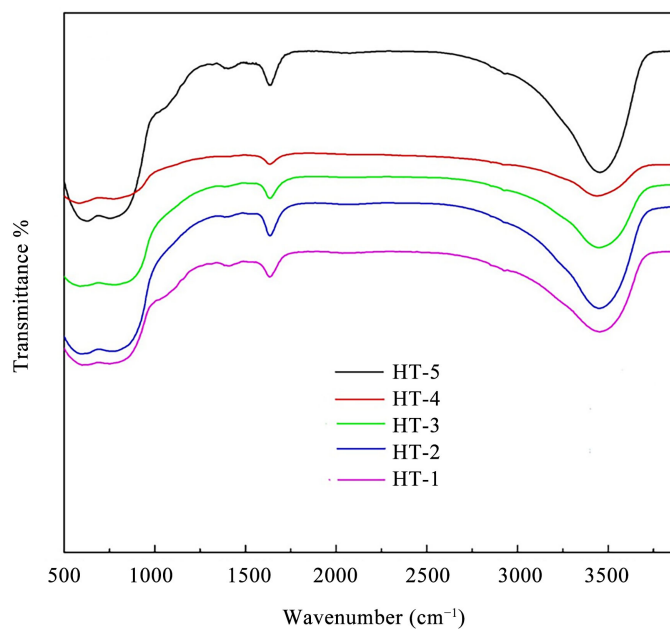


Figure 7. FTIR of HT-catalyst series.

3. Methodology

All chemicals used were purchased from Sigma Alderich, analytical trade. ¹H-NMR spectra, ¹³C-NMR spectra were recorded on Bruker AM250 NMR spectrometer using CDCl₃ as solvent for the samples. Mass spectra were recorded on Shimadzu LCMS-QP 800 LC-MS, IR for the synthesised compounds

were recorded in potassium bromide discs on Shimadzu FT IR 8101 PC infrared spectrophotometer. Elemental analysis was obtained using PerkinElmer 2400 II series CHN Analyser. Thin-layer chromatography (TLC) was carried out on pre-coated Merck silica gel F254 plates to 80°. Melting points of the prepared compounds were measured on a Gallenkamp melting point apparatus.

1) Catalysts

a) Synthesis

Catalysts were prepared by co-precipitation methods as literature [29] [30], LDHs have the structures $[M_{1-x}^{2+}, M_x^{3+}(\text{OH})_2]^{x+} [A_{x/y}]^{y-} \cdot m\text{H}_2\text{O}$, where the divalent may be (Mg^{2+} , Cu^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , or Zn^{2+}), and the trivalent are metal cation (e.g., Al^{3+} , Cr^{3+} , Ga^{3+} , Ln^{3+} , Mn^{3+} or Fe^{3+}) which forms the positively charged layers, where A^{y-} are called inorganic or organic anions (e.g., CO_3^{2-} , Cl^- , SO_4^{2-} , RCO_2^-).

i- HT-1 (LDH-As)

Mixing of magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 0.2213 mol, and aluminium nitrate $\text{Al}(\text{NO}_3)_3$ 0.0885 mol, in a 0.2213 L of dist. H_2O , mix (A). Mixing of 0.7162 mol of NaOH , and 0.2084 mol of Na_2CO_3 , in a 0.221 L, mix (B). Drop using a burette drops from Mix (A) and Mix (B) to a Round bottom flask 1 L containing 0.5 L distilled water under vigorous stirring and heating at 60°C and measure pH during precipitation to be 10-11. Keep the temperature at 60°C overnight (16 h) in water bath. Filter using (Whatmann 1 filter paper) and washing the cake by hot distilled water till pH = 7. Dry the filtrate at 80°C in an oven for 16 h.

ii- Cu:Mg:Al (1:2:1) HT-2, Clacined Cu:Mg:Al (1:2:1) HT-3, and Clacined Cu:Mg:Al (2:1:1) HT-4

Cu metal modified HT Mg:Al was prepared by memory effect [30], where typically, 1.0 g the as-prepared HT-As was treated with an aqueous Cu^{2+} nitrate or sulfate solution (0.1 mol/L, 100 mL) with stirring at room temperature for 48 h to reconstruct into the layered hydrotalcite structure. The resulting products were filtered, washed several times with distilled water and dried at 100°C for 12 h, while the HT-Cu catalyst was obtained.

Then Cu-modified Mg-Al catalysts were prepared in oven at 500°C for 7 h under a flowing stream of pure N_2 .

iii- Clacined Cu:Al (3:1) HT-5

It was prepared also by coprecipitation methods as mentioned in literature, where mixing of magnesium nitrate $\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$ 0.028 mol, and aluminium nitrate $\text{Al}(\text{NO}_3)_3$ 0.01 mol, in a dist. H_2O , mix (C), mixing of 0.7162 mol of NaOH , and 0.2084 mol of Na_2CO_3 , in a dist. H_2O , mix (D). Drop using a burette drops from Mix (C) and Mix (D) to a round bottle flask 1L containing 0.5 L distilled water under vigorous stirring and heating at 60°C and measure pH during precipitation to be 10-11. Keep the temperature at 60°C overnight (16 h) in water bath. Filter using (Whatmann 1 filter paper) and washing the cake by hot distilled water till pH = 7 gives (HT-5). Dry the filtrate at 80°C in an oven for 16 h. Heat 2 g of the above paste product in oven at 450°C for 6 h in N_2 atmosphere,

then dissolve in adequate amount of NaOH (0.1 M) to form a paste. Dry the Paste at 80°C in an oven for 16 h gives HT-5.

2) Synthesis of β -Nitroalcohol, via Henry Reaction

a) Microwave Irradiation Method

i- Without Catalyst

A mixture of an aldehyde series (10 mmol) and nitroalkane series (10 mmol) were added to a vesicle, and the mixture was mixed strongly with a glass-rod at room temperature. The mixture was added in a Teflon vial and irradiated under 350 W microwave till the reaction temperature raised to 120°C with fixed microwave pressure. The vial was exposed to microwaves for a required time to complete the reaction. Check the reaction and monitor it using TLC using (eluent; Diethyl ether: chloroform) every 1 min. until the reaction reached the end. Then the product mixture was cooled and extracted using ethanol analytical grade. The process were repeated using different aldehyde and different to form compounds from a - o.

The product compounds were purified by crystallization using EtOH/DMF solvent mixture to afford the pure crude β -nitroalcohols a - o in an excellent yield.

ii- Using catalyst

Catalysts 0.5 g from HT-1 up to HT-5 were used and added by repeated adequate sequence to a reaction mixture as mentioned above for the series a - o till the reaction completed as before.

Each time and each run the catalysts were removed by filtration and washing by hot ethanol after that the excess solvent was removed by vaporization to get the final solid product. The product compounds were purified by crystallization using EtOH/DMF solvent mixture to afford the pure crude β -nitroalcohols a - o in an excellent yield.

b) Conventional Method

The reaction were carried on electrical heating hotplate with stirrer and the methods as mentioned above in microwave irradiated were applied without catalyst at 90°C and with the catalysts series at 60°C for the series of catalysts and series of the aldehydes and nitro alkanes. The reactants aldehydes, nitroalkanes and catalyst were added together in a round flask bottle, closed with rubber septum connected to a condenser, after the completion of the reaction, the mixture cooled room air temperature then separated and purified as above mentioned and also the catalyst was treated as the above method.

i- *p*-2-Nitroethenylchlorobenzene ($C_8H_6ClNO_2$)

mp. 262°C, IR (KBr) ν max/cm⁻¹: 1515 - 1560 (NO₂), ¹H NMR (DMSO): δ 5.1 (d, 1H, -C=C), 5.6 (d, 1H, -C=C) δ 7.27 - 7.4 (dd, 4H, Ar), ¹³C NMR (CDCl₃): δ 77.8, 111.22, 127.4, 128.2, 131.8, 134.3, 134.7, MS (m/z): 183.01 (M⁺), Anal. Calcd for $C_8H_6ClNO_2$ (183.6), C-52.61; Cl-19.31; H-3.3; N-7.65% Found: C-52.66; Cl-19.3; H-3.3; N-7.63; %.

ii- 1-(*p*-Chlorophenyl)-2-nitro-1-propene ($C_9H_8ClNO_2$)

mp. 386°C, IR (KBr) ν max/cm⁻¹: 1525 - 1570 (NO₂), ¹H NMR (DMSO): δ 1.7 (d, 3H, CH₃), δ 4.9 (q, 1H, -C=CH), δ 7.2 - 7.45 (dd, 4H, Ar), ¹³C NMR (CDCl₃): δ 25.5, 39.5, 77.82, 81.1, 126.66, 130.8, 134.5, MS (m/z): 230.01 (M⁺), Anal. Calcd for C₁₀H₁₂ClNO₃ (229), C-52.30; Cl-15.44; H-5.27; N-6.10% Found: C-52.2; Cl-15.44; H-4.01; N-6.8; %.

iii- 1-(4-chlorophenyl)-2-methyl-2-nitropropan-1-ol (C₁₀H₁₂ClNO₃)

mp. 465°C, IR (KBr) ν max/cm⁻¹: 1530 (NO₂), ¹H NMR (DMSO): δ 1.1 (s, 3H, CH₃), δ 5.1 (s, H, CH), δ 7.27 - 7.4 (dd, 4H, ArH's), ¹³C NMR (CDCl₃): δ 25.5, 39.5, 77.82, 81.1, 126.66, 130.8, 134.5, MS (m/z): 230.01 (M⁺), Anal. Calcd for C₁₀H₁₂ClNO₃ (229), C-52.30; Cl-15.44; H-5.27; N-6.10% Found: C-52.2; Cl-15.44; H-4.01; N-6.8; %.

iv- 2-Nitroethenyl-3,5-dibromobenzene C₈H₅Br₂NO₂

mp. 491°C, IR (KBr) ν max/cm⁻¹: 1480 (NO₂), 670 (C-Br), ¹H NMR (DMSO): δ 5.2 (d, 1H, -C=CH), 6.2 (d, 1H, -C=CH), 7.7 - 7.9 (m, 3H, ArH's), ¹³C NMR (CDCl₃): δ 77.8, 112.33, 123, 128, 131.1, 135.4, 139.5, MS (m/z): 306.5 (M⁺), Anal. Calcd for C₈H₅Br₂NO₂ (307), Br-52; C-31.5; H-1.7; N-4.58% Found: Br-51.7; C-30.57; H-1.6; N-4.46%.

v- 1-(3,5-Dibromophenyl)-2-nitro-1-propene (C₉H₇Br₂NO₂)

mp. 538°C, IR (KBr) ν max/cm⁻¹: 1545 (NO₂), 672 (C-Br), ¹H NMR (DMSO): δ 1.1 (d, 3H, CH₃), δ 3.45 (m, 2H, CH₂), δ 5.15 (d, 1H, -CH), δ 7.27 - 7.8 (m, 3H, ArH's), ¹³C NMR (CDCl₃): δ 18.9, 44.5, 77.8, 84.75, 126.66, 129.8, 131.77, 134.7, MS (m/z): 338.9 (M⁺), Anal. Calcd for C₉H₇Br₂NO₂ (339), Br-47.2; C-31.85; H-2.65; N-6.85% Found: Br-47.14; C-31.89; H-2.68; N-4.13; %.

vi- 1-(3,5-dibromophenyl)-2-methyl-2-nitropropan-1-ol C₁₀H₁₁Br₂NO₃

mp. 440.3°C, IR (KBr) ν max/cm⁻¹: 3550 (OH), 1523-1550 (NO₂), 670 (C-Br), ¹H NMR (DMSO): δ 3.15 (d, 2H, CH₂), δ 7.27 - 7.4 (dd, 4H, ArH's), δ 5.2 (t, 1H, -CH), ¹³C NMR (CDCl₃): δ 25.5, 39.8, 77.8, 88.7, 124.4, 129.8, 131.1, 135.1, MS (m/z): 353.3 (M⁺), Anal. Calcd for C₁₀H₁₁Br₂NO₃ (353), Br-45.27; C-34.02; H-3.14; N-3.97% Found: Br-45.3, C-34.01; H-3.15; N-3.95; %.

vii- 1-(3,5-Dibromophenyl)-2-nitro-1-propene (C₉H₇Br₂NO₂)

mp. 362°C, IR (KBr) ν max/cm⁻¹: 3600 (OH), 1520 - 1580 (2NO₂), 675 (C-Br), ¹H NMR (DMSO): δ 1.75 (d, 3H, CH₃), 4.95 (m, H, C=CH), δ 7.7 - 7.9 (m, 3H, ArH's), ¹³C NMR (CDCl₃): δ 24.9, 77.8, 119.83, 123, 128, 130, 131.5, 139.5, MS (m/z): 320.91 (M⁺), Anal. Calcd for C₉H₇Br₂NO₂ (321), Br-50; C-33.5; H-2.30; N-4.4% Found: Br-49.79; C-33.68; H-2.20; N-4.36%.

viii- 4-bromo-2-(1-hydroxy-2-nitropropyl)-6-nitrophenol

mp. 609°C, IR (KBr) ν max/cm⁻¹: 3650 (OH), 1540 (2NO₂), 675 (C-Br), ¹H NMR (DMSO): δ 1.75 (d, 3H, CH₃), 4.95 (m, H, C=CH), δ 6.5 - 7.2 (dd, 2H, ArH's), ¹³C NMR (CDCl₃): δ 18.5, 44.37, 77.82, 84.1, 110.86, 112.4, 117.4, 118.3, 144.3, 146.27, MS (m/z): 319.5 (M⁺), Anal. Calcd for C₉H₇BrN₂O₆ (321), Br-24.89; C-33.67; H-2.83; N-8.72 Found: Br-24.89; C-33.8; H-2.87; N-8.6%.

ix- 4-bromo-2-(1-hydroxy-2-methyl-2-nitropropyl)-6-nitrophenol

mp. 765°C, IR (KBr) ν max/cm⁻¹: 3500 - 3700 (2OH), 1520 - 1580 (2NO₂), 690 (C-Br), ¹H NMR (DMSO): δ 1.09, (s, 3H, CH₃), δ 5.2 (s, 1H, -CH), δ 6.5 - 7.2 (m, 2H, ArH's), ¹³C NMR (CDCl₃): δ 25.1, 39.48, 88.7, 110.86, 112.36, 117.5, 118.3, 145.3, 147.9, MS (m/z): 334.9 (M⁺), Anal. Calcd for C₁₀H₁₁BrN₂O₆ (335), Br-23.84; C-35.9; H-3.3; N-8.4% Found: Br-23.84; C-35.75; H-3.35; N-8.36%.

x- 2-nitro-1-(2-nitrophenyl) ethanol

mp. 428.8°C, IR (KBr) ν max/cm⁻¹: 1510 - 1555 (2NO₂), ¹H NMR (DMSO): δ 3.15 (d, 2H, CH₂), δ 5.15 (t, 1H, -CH), δ 6.66 - 7.3 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 49.5, 77.8, 81.1, 112.87, 116.8, 126.66, 129.4, 150.97, MS (m/z): 212 (M⁺), Anal. Calcd for C₈H₈N₂O₅ (212), C-45.29; H-3.80; N-13.20% Found: C-45.29; H-3.80; N-13.20; %.

xi- 2-nitro-1-(2-nitrophenyl) propan-1-ol

mp. 552°C, IR (KBr) ν max/cm⁻¹: 1515 - 1560 (2NO₂), ¹H NMR (DMSO): δ 1.04, (d, 3H, CH₃), δ 3.45 (m, H, CH), δ 5.15 (d, H, CH), δ 6.7 - 7.3 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 18.1, 44.73, 77.8, 84.74, 112.87, 116.75, 129.3, 150.9, MS (m/z): 226 (M⁺), Anal. Calcd for C₉H₁₀N₂O₅ (226.2), C-47.79; H-4.46; N-12.39% Found: C-47.79; H-4.46; N-12.39%.

xii- 2-methyl-2-nitro-1-(2-nitrophenyl)propan-1-ol

mp. 453.3°C, IR (KBr) ν max/cm⁻¹: 3650 (OH), 1520 - 1570 (2NO₂), ¹H NMR (DMSO): δ 1.04 (s, 3H, CH₃), δ 5.15 (s, H, CH), δ 6.7 - 7.2 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 25.12, 39.9, 77.82, 88.65, 112.86, 116.75, 129.36, 150.99, MS (m/z): 240.12 (M⁺), Anal. Calcd for C₁₀H₁₂N₂O₅ (240), C-50.00; H-5.04; N-11.66% Found: C- 49.90; H-5; N-11.66%.

xiii- 1-(4-methoxyphenyl)-2-nitroethanol

mp. 443.87°C, IR (KBr) ν max/cm⁻¹: 1545 (NO₂), 1150 (C-O), ¹H NMR (DMSO): δ 3.15 (s, H, CH₃), δ 5.2 (t, 1H, -CH), δ 6.57 - 7.2 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 49.5, 65.5, 77.8, 114.2, 120.86, 129.56, 159.96, MS (m/z): 197.2 (M⁺), Anal. Calcd for C₉H₁₁NO₄ (197), C-54.9; H-5.62; N-7.10% Found: C-54.8; H-5.66; N-7%.

xiv- 1-(4-methoxyphenyl)-2-nitropropan-1-ol

mp. 440°C, IR (KBr) ν max/cm⁻¹: 1565 (NO₂), 1210 (C-O), ¹H NMR (DMSO): δ 1.04(d, 3H, CH₃), δ 3.14 (s, 3H, CH₃), δ 3.5(m, 1H, -CH), δ 5.3 (d, H, CH), δ 7.27 - 7.4 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 18.02, 44.95, 65.01, 77.8, 84.7, 114.16, 120.86, 129.6, 159.99, MS (m/z): 211.2 (M⁺), Anal. Calcd for C₁₀H₁₃NO₃ (211), C-56.86; H-6.20; N-6.63% Found: C-56.86; H-6.20; N-6.63%.

xv- 1-(4-methoxyphenyl)-2-methyl-2-nitropropan-1-ol

mp. 468.8°C, IR (KBr) ν max/cm⁻¹: 3650 (OH), 1535 (NO₂), 1050 (C-O), ¹H NMR (DMSO), δ 1.04 (s, 3H, CH₃), δ 3.14 (s, 3H, CH₃), δ 5.2 (s, H, CH), δ 6.9 - 7.3 (m, 4H, ArH's), ¹³C NMR (CDCl₃): δ 18.02, 44.95, 65.01, 77.8, 84.7, 114.16, 120.86, 129.6, 159.99, MS (m/z): 225.3 (M⁺), Anal. Calcd for C₁₁H₁₅NO₃ (225), C-58.66; H-6.71; N-6.22% Found: C-58.66; H-6.71; N-6.22; %.

4. Conclusion

In brief, we reported Henry reaction between benzaldehyde and nitromethane

over solid base catalysts. Cu:Mg:Al-HT catalyst gave a precious advantage over all solid base catalysts under investigation especially calcied Cu:Al 3:1 (HT-5). Microwave irradiation technique introduced us high yields of β -alcohol derivatives using the prepared series of HT solid catalyst in very short time. Strong Basic characterization of catalyst was responsible for the power of catalytic activity. HT series kept their physical properties (texture and structure) even after many catalytic runs, which facilitated gaining of high yields beta nitro alcohols. These synthesized derivatives are of great importance in industry and medical uses.

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Conflict of Interest

The authors declare that, there is no conflict of interest.

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