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Marine solids/$NaNO_3$: As Natural and Efficient Catalysts for Aldol condensation

Research Article

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Abstract

A new and efficient method have been developed for the synthesis of α,β-unsaturated carbonyl compounds from various aldehydes and ketones, using marine calcinated coral/$NaNO_3$ and cuttlebone/$NaNO_3$, as natural and efficient catalysts for cross aldol condensation. The aim of present study was to study the marine solids/$NaNO_3$: as natural and efficient catalyst for Aldol condensation. The materials were purchased from Merck and Aldrich Companies. The IR spectra were recorded on a Perkin-Elmer RXI infrared spectrometer. H NMR spectra were recorded on a 400 MHz Brucker FT-NMR spectrometer. The SEM image was recorded on 1455 VP LEO-Germany. TLC accomplished the purity of substrates and reactions monitored on silica gel (Merck, Germany) Polygram SIGL/UV254 plates. The melting points are uncorrected. Results showed that, the marine solid are efficient catalysts for aldol condensation, but cuttlebone/$NaNO_3$ catalyze this reaction in shorter time (1 hr) than calcinated coral/$NaNO_3$ (6 hr). However, these marine solids have several advantages such as small amount of the catalyst, good absorbent natural solid, easy to handle, and products in good-to-high yields. In conclusion we found marine catalysts, Calcinated Cuttlebone/$NaNO_3$ or Coral/$NaNO_3$ to be an effective catalyst for aldol condensation from ketones having α-hydrogens and aldehydes in 50 % ethanol at reflux conditions. The α,β-unsaturated carbonyl products were obtained in good to high yields. This method offered marked improvement compared to previously reported ones.

Keywords: Aldol condensation, calcinated, marine coral, cuttlebone, α,β-unsaturated carbonyl.

Introduction

Reactions involving C–C bond formation are of utmost importance for obtaining many fine chemicals of commercial interest. The base-catalyzed aldol condensation, which belongs to this type of reaction is indeed very useful for the preparation of α,β-unsaturated carbonyl compounds from corresponding aldehydes and/or ketones (1). As base catalysts NaOH (2), hydrotalcites (1) and calcined $NaNO_3$/natural phosphates (3) have been used in aldol reaction.

Heterogeneous catalysts for the synthesis of fine chemicals have attracted considerable attention from both environmental and economical points of view, because they offer several advantages in organic synthesis, e.g. simplification of reaction procedures, easy separation of products, repeated use, and so on (4). Solid-base catalysts, which can be synthesized by functionalization of various solid-state materials, constitute a class of heterogeneous catalysts that are capable of catalyzing various C–C bond forming reactions such as the Henry, Knoevenagel, and aldol reactions (5, 6, 7).

Recently PEG/$AlCl_3$ has been reported as efficient catalyst for aldol condensation of cycloketones and aldehydes at room temperature (8). More recently animal bone meal (ABM) (9) and gelatin protein as natural catalysts (10) have been used for cross aldol condensation.

Marine natural solids are known as a prolific source of biologically active and structurally unique metabolites (11,12). As we described the catalytic, chirality and absorbent abilities of marine sponge powder of Iranian coast of Persian Gulf in organic reaction such as sulfonamides synthesis (13), and researches of its application in organic reactions such as various oxidation, and reduction reactions (14); therefore we decided to study marine coral and cuttlefish bone (*Sepia Pharaonis* sp.) of Bushehr Islands in offshore zone as an efficient natural solid catalysts. $CaCO_3$ is the main composition of coral framework. Cuttlebone, as another natural solid, is the hard tissue in cuttlefish with high porosity, which functions as a rigid buoyant tank in the animal; the framework of cuttlebone is an inorganic–organic composite composed of aragonite, protein and β-chitin. To date, the investigations aiming at cuttlebone are focused on bio-mimetic mineralization, immobilization of enzyme and elimination of heavy metal ions (15, 16, 17). More recently CDOM (cuttlebone-derived organic matrix) has

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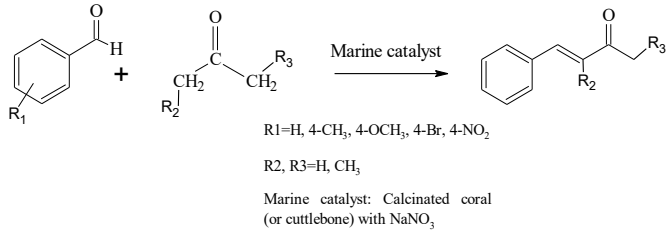
been used as scaffold and reducer for the formation of AgNPs; the resulting AgNPs–CDOM composite can be utilized to catalyze the reduction of 4-nitrophenol (18).

However, few attentions have been paid concerning the application of cuttlebone and coral composites, which will lead to a new class of natural solid base, especially in the presence of $NaNO_3$ in organic reactions. Calcinated cuttlebone/$NaNO_3$ and coral/$NaNO_3$ composites were applied to catalyze aldol condensation reaction of aldehydes and ketones for preparing of corresponding α,β-unsaturated carbonyl compounds in good to high yields, as shown in scheme 1. The advantages of these natural solids are that they can act as basic absorbent to activate substrates for nucleophilic reaction, and can be removed easily from the products.



Scheme 1. Aldol condensation in the presence of Marine base

Materials and Methods

Reagents and Materials

All starting materials were purchased from Merck and Aldrich Companies. The IR spectra were recorded on a Perkin-Elmer RXI infrared spectrometer. H NMR spectra were recorded on a 400 MHz Brucker FT-NMR spectrometer. The SEM image was recorded on 1455 VP LEO-Germany. TLC accomplished the purity of substrates and reactions monitored on silica gel (Merck, Germany) Polygram SIGL/UV254 plates. The melting points are uncorrected.

Preparation of coral and cuttlebone powders

In this study marine coral and cuttlebone (*Sepia Pharaonis* sp.*)* collected from Bushehr coasts, Iran (North coast of Persian Gulf), in September 2012 and were washed several times using methanol-ethylacetate and then deionized water to remove some organic compounds, extraneous and salts. Then, they were dried in an oven at 80 °C for 48 h. The dried marine solids were ground to give fine powders. Identification of marine organisms was carried out kindly by Khoramshahr marine science and Technology University. The pictures of marine coral and cuttlebone were shown in figure 1.

Figure 1. (a) Marine coral -left image;

Figure 1. (b) cuttlebone-right image.

Preparation of calcinated coral and cuttlebone

Coral or cuttlebone is put in an oven at 800 ºC for 2 hours. Then it is washed several times with water and then it is dried in an oven at 80 ºC for 24 hours. In the next step it is washed with water and then calcinated at 400 º C for 4 hours. The pH of these solids was determined as 8-9.

Preparation of calcinated coral (or cuttlebone)/ $NaNO_3$

Calcinated coral (or cuttlebone) and sodium Nitrate (1:1) were well stirred in sufficient water for about 5 hours. Then the mixture was heated until its water evaporated and then it was calcinated in an oven at 800 ºC for 2 hours. The pH of these compounds was determined as 10-11.

General procedure

The reaction was carried out by mixing aldehyde (150 mmol), ketone (50 mmol), 0.1 g of calcinated coral (or cuttlebone)/$NaNO_3$, 5 ml water-ethanol (1:1) as a solvent and the mixture was stirred at reflux condition for the appropriate time reported in Table 2. The progress of reaction was monitored by TLC. After completion of the reaction, the products were extracted with $CHCl_3$, and washed with $NaHCO_3$ %5 and water. Then the solution was dried over anhydrous $CaCl_2$ and filtered. The solvent evaporated under reduced pressure, and the crude products were afforded in good to high yields.

Results and Discussion

Characterization of products

Selected spectral data for the products in Tables 2 and 3 are given:

4-phenyl-3-buten-2-one (Table 2-entry 1): IR(cm $^{-1}$, KBr): 3026 (CH Ar), 1648 (C=O), 1625, 1589 (C=C), 762, 635 (aromatic), ^{1}HNMR (400 MHz, $CDCl_3$, TMS, δ ppm): 7.55(2H, m, CH Ar), 7.4 (3H, m, CH Ar), 7.42 (1H, d, =CH), 6.75 (1H, d, =CH), 2.39 (3H, s, CH_3).

4-(4-bromophenyl)-3-buten-2-one (Table 2-entry 2): IR(cm^{-1}, KBr): 3026 (CH Ar), 1648 (C=O), 1625, 1589 (C=C), 824 (aromatic), ^{1}HNMR (400 MHz, $CDCl_3$, TMS, δ ppm): 7.65(1H, d, =CH), 7.60 (2H, d, CH Ar), 7.50 (2H, d, CH Ar), 7.07 (1H, d, =CH), 2.42 (3H, s, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$, TMS, δ ppm): 188 (C=O), 142, 133, 132, 129, 124, 125 (142-125 Ar), 78 (2C=C), 29 (CH_3).

4-(p-tolyl)-3-buten-2-one (Table 2-entry 3): IR (cm^{-1}, KBr): 3024 (CH Ar), 2914 (CH Alkyl), 1644 (C=O), 1621, 1589 (C=C), 826 (aromatic), ^{1}HNMR

(400 MHz, $CDCl_3$, TMS, δ ppm): 7.75 (1H, d, =CH), 7.55 (2H, d, CH Ar), 7.25 (2H, d, CH Ar), 7.08 (1H, d, =CH), 2.6 (3H, s, CH_3), 2.42 (3H, s, CH_3).

*4-(4-*methoxyphenyl*)-1-penten-3-one (Table 3-entry 4):* IR(cm^{-1}, KBr): 3026 (CH Ar), 2977 (CH Alkyl), 1683 (C=O), 1655, 1599 (C=C), 824 (aromatic), ^{1}HNMR (400 MHz, $CDCl_3$, TMS, δ ppm): 7.55 (1H, d, =CH), 7.53 (2H, d, CH Ar), 6.93 (2H, d, CH Ar), 6.66 (1H, d, =CH), 3.8 (3H, s, OCH_3), 2.65 (2H, q, CH_2), 1.15 (3H, t, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$, TMS, δ ppm): 201 (C=O), 161, 142, 130, 128, 124, 117 (161-117 Ar), 78 (2C=C), 55.9 (OCH_3), 33 (CH_2), 7.9 (CH_3).

The α,β-Unsaturated carbonyl compounds can be synthesized via the cross aldol condensation of corresponding aldehydes, and ketones that involve α-hydrogen atom as starting materials. Different solids such as basic alumina, zeolite and so on can be catalyzed this reaction in various solvents. Among solid catalysts, marine natural composites such as coral, cuttlebone which are mainly formed from $CaCO_3$ and $Ca_3(PO_4)_2$.

The raw materials, marine coral and cuttlebone, were collected from Bushehr coasts and then washed, dried, powdered and finally calcinated in an oven at 800 ºC for 2 hours to remove organic materials. The catalysts obtained were characterized by X-ray diffraction and compared with similar spectrum which calcinated at 350 °C (19) as indicated in Figures 2 and 3. Calcinated coral and cuttlebone as natural basic materials were used in the aldol reaction of aldehyde and ketone with ratio 2:1, in water-ethanol solvent; but the yields of the reaction did not favored.

In order to active these marine catalysts, the modified calcinated coral and cuttlebones were prepared by impregnating the marine solids with aqueous solution of sodium nitrate. The weight ratio used for marine solid and $NaNO_3$, was 1:1. The mixture was stirred vigorously at room temperature, evaporated to dryness, dried, and calcinated at 800 °C for 2 h. This marine catalysts obtained were characterized by X-ray diffraction, as indicated in Figure 4 and then were used for desired aldol reactions, as shown in Table 1.

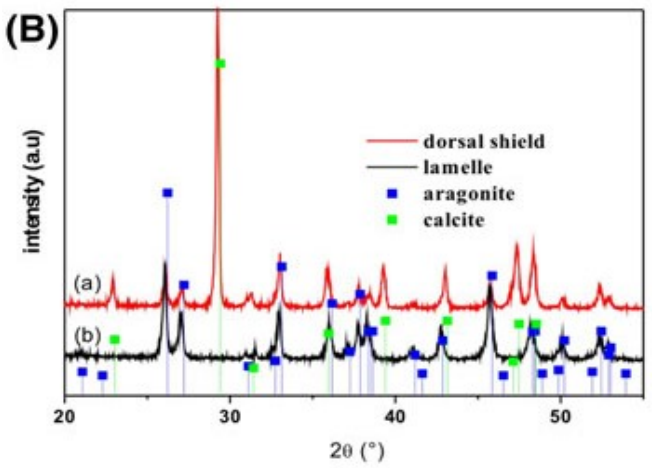


Figure 2- XRD of calcinated cuttlebone at 350 °C [31]

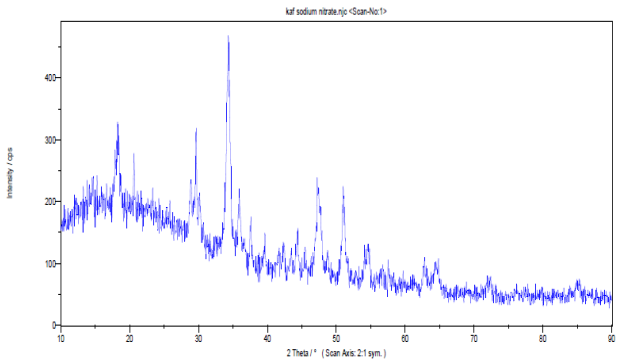


Figure 3- XRD of calcinated cuttlebone with Sodium Nitrate

Table 1. Aldol condensation of acetone and benzaldehyde (1:3) in the presence of different catalysts (0.1 g) in ethanol (50%) at reflux condition.

Catalysts	Time (hr)	Yield (%)
Calcinated coral	24	52
Calcinated cuttlebone	24	61
$NaNO_3$	12	--
Calcinated coral/$NaNO_3$	6	88
Calcinated cuttlebone/$NaNO_3$	1	80

As the results indicated in Table 1, these marine solid are efficient catalysts for aldol condensation, but cuttlebone/$NaNO_3$ catalyze this reaction in shorter time (1 hr) than calcinated coral/ $NaNO_3$ (6 hr). However, these marine solids have several advantages such as small amount of the catalyst, good absorbent natural solid, easy to handle, and products in good-to-high yields. Structures of α,β-unsaturated carbonyl compounds as products were characterized by their spectral (H NMR and IR) data (7,8).

In order to explain the reproducibility of catalysts, cuttlebone/$NaNO_3$ was used 3 times repetition in aldol condensation reaction, the yield of products and performance of catalyst did not have any change, as shown in Table 2.

Table 2. Aldol condensation of acetone and benzaldehyde (1:3) in the presence of 3 times repetition of marine catalysts (0.1 g) in ethanol (50%) at reflux condition.

Catalysts in 3 times repetition	Time (hr)	Yield (%)
Run 1	1	80
Run 2	1	80
Run 3	1	78

Ketone such as acetone or 2-butanone was reacted with various aldehydes in the presence marine catalyst as a natural base in aldol reaction at reflux condition. As shown in Tables 3, time and the yields of products are more suitable other than desired products in Table 4.

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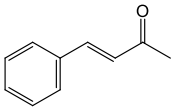
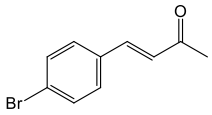
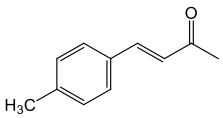
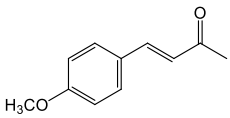
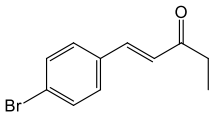
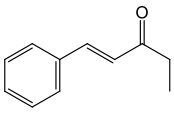
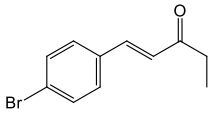
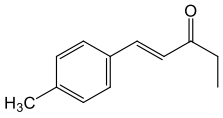
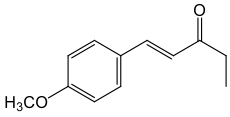
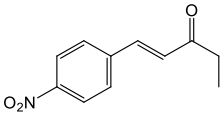
Table 3. Aldol condensation reaction of acetone with aldehydes (1:3) in the presence of calcinated cuttlebone/ Sodium Nitrate

Entry	Aldehyde	Product	Time (min.)	Yield (%)
1	C_6H_5CHO		60	80
2	4-Br-C_6H_4CHO		50	68
3	4-CH_3-C_6H_4CHO		90	70
4	4-CH_3O-C_6H_4CHO		120	75
5	4-NO_2-C_6H_4CHO		40	65

All products were confirmed by comparison with authentic samples (IR, 1HNMR and TLC).

Table 4. Aldol condensation reaction of 2-butanone with aldehydes (1:3) in the presence of calcinated cuttlebone/ Sodium Nitrate

Entry	Aldehyde	Product	Time (hr)	Yield (%)
1	C_6H_5CHO		8	70
2	4-Br-C_6H_4CHO		7	55
3	4-CH_3-C_6H_4CHO		11	60
4	4-CH_3O-C_6H_4CHO		12	68
5	4-NO_2-C_6H_4CHO		7	52

All products were confirmed by comparison with authentic samples (IR, 1HNMR and TLC).

In general, the basis of any base-catalyzed aldol condensation is the catalyst's ability to abstract the α-proton of ketone [20]. This depends on two factors: the basicity of the active site and the acidity of that proton. The reaction pathway for producing α,β-unsaturated carbonyl compounds from the aldol condensation of aldehydes with ketones, as shown in Figure 5, involves the initial abstraction of the α-proton from ketone, forming a carbanion that

consecutively attacks the carbonyl group of the contiguously adsorbed aldehyde molecule. Then a β-hydroxyl ketone intermediate is expected to form; however, this was never observed among the reaction products under the reaction conditions of this work. Therefore, this unstable intermediate is assumed to rapidly dehydrate, forming α,β-unsaturated carbonyl compounds and water.

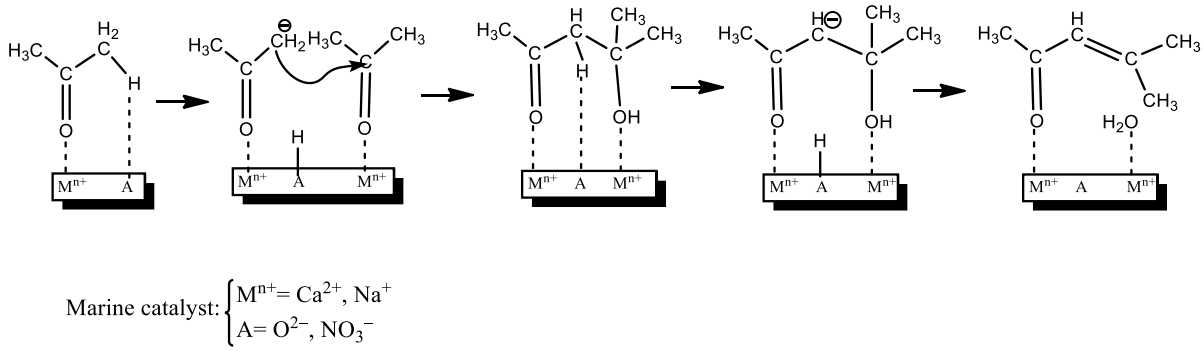


Figure 4-Reaction mechanism for α,β-unsaturated carbonyl compounds synthesis in the presence of marine catalyst

As shown in Figure 4, more hindered ethyl group than methyl, may be the effective parameter in reaction time and yields.

Conclusion

In conclusion we found marine catalysts, Calcinated Cuttlebone/$NaNO_3$ or Coral/$NaNO_3$ to be an effective catalyst for aldol condensation from ketones having α-hydrogens and aldehydes in 50 % ethanol at reflux conditions. The α,β-unsaturated carbonyl products were obtained in good to high yields. This method offered marked improvement compared to previously reported ones. Its advantages included good absorbent natural solid, operational simplicity, mild reaction condition and pure products.

Acknowledgments

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