

The Persian Gulf Calcined Coral, *Acropora* Species: An Efficient Catalyst for Aldol Condensation

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Abstract

Background: Coral, a marine organism, is known for its unique solid, natural, and efficient catalyst in organic reactions. Calcium carbonate (CaCO₃), the main component of marine coral, is an efficient, basic, and natural solid for catalytic aldol condensation reaction of aldehydes and ketones having α -hydrogens to produce β -hydroxy carbonyl compounds with good yields at room temperature.

Objectives: The purpose of this research was to study using calcined coral as an efficient catalyst for aldol reaction at room temperature.

Materials and Methods: Marine coral (*Acropora* sp.) was washed several times using methanol-ethyl acetate and deionized water and then dried in an oven at 80°C for 48 hours. The dried coral was ground to get fine powder. For preparation of calcined coral, its powder was put in an oven at 800°C for 2 hours. Calcined coral and sodium nitrate (1:1) were well stirred in sufficient water for about 5 hours. Then, the mixture was calcined in an oven at 800°C for 2 hours. In general experiment, the reaction was carried out by mixing aldehyde (150 mmol), ketone (50 mmol), 0.1 g of calcined coral/sodium nitrate, 5 mL water-ethanol (1:1) as a solvent. Finally, the mixture was stirred at room temperature for the appropriate time.

Results: The best conditions for condensation reaction are using the calcined coral/sodium nitrate, as a catalyst in the presence of ethanol/water at room temperature. Aldol condensation reaction of nitro-substituted benzaldehydes with ketones has greater yields than benzaldehydes. Electron-withdrawing groups such as NO₂ on benzaldehyde ring activate aldol condensation reaction. In comparison, 4-methoxybenzaldehyde reacts more slowly with ketones and decreases the yield of products.

Conclusions: Calcined coral/sodium nitrate as a new, efficient, and natural heterogeneous catalyst used in aldol condensation reaction of ketones and aldehydes led to β -hydroxyketones in good to high yields in appropriate condition.

Keywords: Marine Coral, The Persian Gulf, Natural Solid, Calcinated, Aldol Condensation, *Acropora* species

1. Background

Marine organisms such as corals and sponges besides helping to have a healthy environment can be used as natural solid in chemical reactions such as oxidation, pharmaceutical and biological compounds production. In order to reduce chemical pollution, preparation of natural compounds such as alkali catalysts have been considered for any chemical reactions. Given its importance as a C-C bond-forming reaction, the aldol condensation has been a common target for catalyst design. This reaction is catalyzed by alkali and acid compounds such as potassium hydroxide (1), hydrotalcites (2) and natural phosphates/KF (3). So depending on the molar ratio of substrates, temperature, catalyst and reaction condition, β -hydroxyketones or α , β -unsaturated carbonyl compounds are formed as major product (1, 4, 5). Recently, using natural substrates derived from animal sources such as bone powder and other marine resources (6) have been reported. Our group has recently developed the preparation and use of marine organisms such as sponge

and coral for catalytic chemical reactions. This new natural heterogeneous method produces β -hydroxyketones in good to high yields in appropriate conditions (7).

2. Objectives

In continuation of our research program concerning the development of marine natural catalyst, we report calcined coral/sodium nitrate as an efficient natural catalyst for aldol condensation reaction of ketones and aldehydes in water-ethanol (1:1) as a solvent for 5 - 10 hours, to produce β -hydroxy carbonyl compounds (Figure 1) in good to high yields.

3. Materials and Methods

All materials were purchased from Merck and Aldrich companies. The IR spectra were recorded on a PerkinElmer RXI infrared spectrometer. ¹H NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer.

The X-ray diffraction was recorded on ID 3003 SIEFRET model. The purity of substrates was accomplished by thin layer chromatography (TLC) and reactions were monitored on silica gel (Merck, Germany) Polygram SIGL/UV254 plates. The melting points are uncorrected.

3.1. Preparation of Marine Coral Powder

In this study, marine corals were collected from Bushahr province coast, Iran (North coast of the Persian Gulf), in September 2012 and then washed several times using methanol-ethyl acetate and next with deionized water to remove organic compounds, extraneous, and salts. Afterwards, they were dried in an oven at 80°C for 48 hours. The dried coral was ground to get fine powder. Identification of coral, *Acropora* sp. was carried out kindly by Khoramshahr Marine Science and Technology University. Figure 2 shows the pictures of the Persian Gulf coral.

3.2. Preparation of Calcined Coral

Coral powder was put in an oven at 800°C for 2 hours. Then it was washed several times with water and dried again in an oven at 80°C for 24 hours. In the next step, it was washed with water and then calcined at 400°C for 4 hours. The pH of calcined coral was determined as 8 - 9.

3.3. Preparation of Calcined Coral/Sodium Nitrate

Calcined coral 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 was calcined in an oven at 800°C for 2 hours. The pH of calcined coral was determined as 10 - 11.

3.4. General Procedure

The reaction was carried out by mixing aldehyde (150 mmol), ketone (50 mmol), of calcined coral/sodium nitrate (0.1 g), and water-ethanol (1:1) (5 mL) as a solvent.

Then, the mixture was stirred at room temperature for the appropriate time reported in Table 1. The progress of reaction was monitored by TLC. After completion of the reaction, the products were extracted with CHCl₃, and washed with distilled water. Then the solution was dried over anhydrous CaCl₂ and filtered. The solvent was evaporated under reduced pressure, and the crude products were afforded in good to high yields.

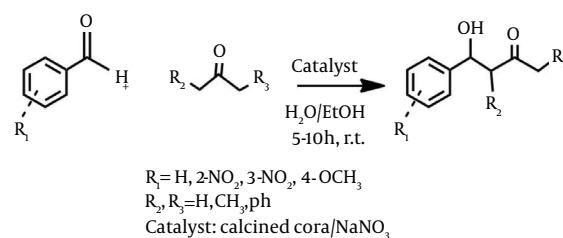


Figure 1. Aldol Condensation in the Presence of Calcined Coral/ NaNO_3 as a Basic Natural Catalyst



Figure 2. The Persian Gulf Coral, *Acropora* sp.

Table 1. Preparation of β -Hydroxy Ketones Using Aldol Reaction of Benzaldehyde and Acetone at Room Temperature in the Presence of Different Solvents and Catalysts

Entry	Catalyst, g	Solvent	Time, h	Yield, %
1	0.1 coral	Solvent free	24	–
2	0.5 coral	Solvent free	24	–
3	0.5 coral + 0.5 sodium nitrate	Solvent free	24	–
4	0.5 calcined + 0.5 sodium nitrate	Solvent free	24	–
5	0.5 calcined + 0.5 sodium nitrate	Ethanol	24	37
6	0.5 coral + 0.5 calcium carbonate	Water/Ethanol	24	85

4. Results

β -Hydroxy ketones can be synthesized via aldol condensation of the corresponding aldehydes, and ketones that involve α -hydrogen atom as starting materials. Different solids such as potassium carbonate, zeolite, and so on can be catalyzed this reaction in various solvents. Among solid catalysts, marine natural composite such as coral is mainly formed from CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$.

The raw materials, i.e. marine corals were collected from

Bushehr province coast and then washed, dried, powdered and finally calcined in an oven at 800°C for 2 hours to remove organic materials. The obtained catalysts were characterized by X-ray diffraction and compared with similar spectrum (8) as indicated in Figure 3. Calcined coral as natural basic material was used in the aldol reaction of aldehyde and ketone with ratio 2:1, in water-ethanol solvent; but the yields of the reaction was not favored.

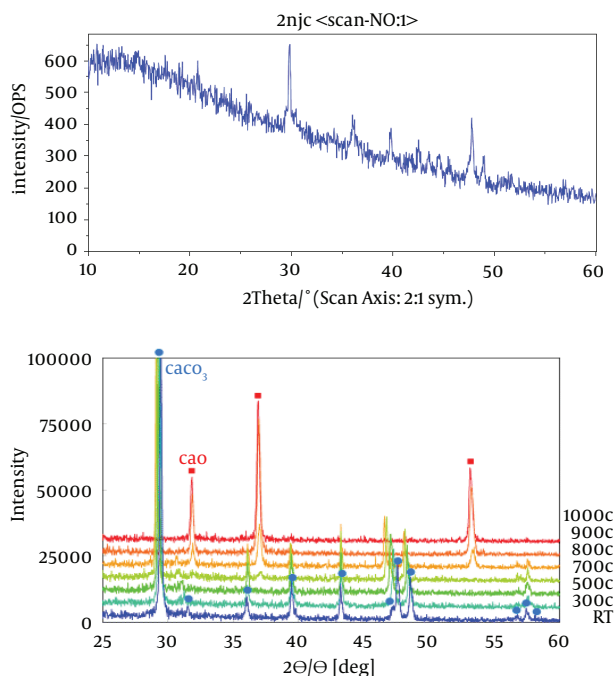


Figure 3. X-ray Diffraction Spectrum of CaO-Ref (at the Right) and Calcined Coral/Sodium nitrate (at the Left).

In order to active the marine catalyst, the modified calcined coral was prepared by impregnating the marine solid with aqueous solution of sodium nitrate, as shown in Table 1. The weight ratio used for marine solid and sodium nitrate was 1:1. The mixture was stirred vigorously at room temperature, evaporated, dried, and calcined at 800°C for 2 hours. The obtained catalyst was characterized by comparison of reported X-ray diffraction spectrum, as indicated in Figure 3.

4.1. Characterization of Products

Selected spectral data for the products in Table 2 are given (1, 6, 9, 10):

4-hydroxy-4-phenyl-2-butanone (Table 2, entry 1): IR (cm^{-1} , KBr): 3450 (OH), 3026 (CH Ar), 1648 (C=O), 1625, 1589 (C=C), 824 (aromatic), ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 7.65 (1H, day, =CH), 7.60 (2H, day, CH Ar), 7.50 (2H, day, CH Ar), 7.07 (1H, day, =CH), 2.42 (3H, second, CH_3); ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 188 (C=O), 142, 133, 132, 129, 124, 125 (125-142 Ar), 78 (2C=C), 29 (CH_3).

1-hydroxy-2-methyl-1-phenylpentan-3-one (Table 2, entry

2): IR (cm^{-1} , KBr): 3550 (OH) 3360 (CH Ar), 1662 (C=O), 1619 (C=C), 850 (aromatic), ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 1.06 (3H, T, CH_3); 1.1 (3H, day, CH_3); 2.5 (2H, q, CH_2); 3 (1H, qu, CH); 3.6 (1H, second, OH); 4.7 (1H, day, CH); 7.4 (2H, day, CH, Ar); 7.4 (3H, T, CH, Ar). ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 180 (C=O), 145, 129, 128, 128, 128, 126 (126-145 Ar), 73 (2C=C), 27, 52 (CH_3).

4-hydroxy-4-(2-nitrophenyl)-butan-2-one (Table 2, entry 6): IR (cm^{-1} , KBr): 3524 - 3600 (OH), 3350 (CH Ar), 1709 (C=O), 1600 (C=C), 800 (aromatic), 1515 - 1350 (NO_2). ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 7.5 - 7.9 (4H, M, CH, Ar); 5.50 (1H, M, CH); 3.91 (1H, br second, OH); 2.86 (1H, day, CH); 2.65 (1H, day, CH); 2.1 (3H, second, CH_3). ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 200 (C=O), 138, 129, 128, 128, 128 (128-129 Ar), 63 (2C=C), 30, 48 (CH_3).

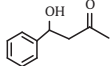
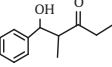
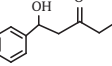
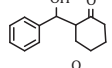
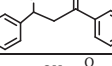
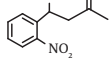
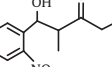
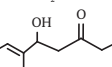
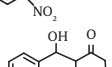
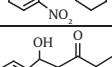
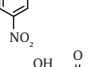
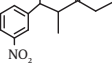
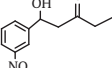
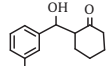
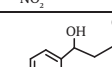
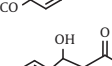
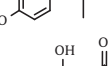
4-hydroxy-4-(3-nitrophenyl)-butan-2-one (Table 2, entry 10): IR (cm^{-1} , KBr): 3400 - 3500 (OH), 3300 (CH Ar), 1722 (C=O), 1584 - 1614 (C=C), 1515 - 1350 (NO_2), 810 (aromatic). ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 7.4 - 8.0 (4H, M, CH, Ar); 5.2 (1H, M, CH); 3.71 (1H, br second, OH); 2.8 (2H, m, CH_2); 2.1 (3H, second, CH_3). ^{13}C NMR (400 MHz, CDCl_3 , TMS,

δ ppm): 210 (C = O), 150, 140, 133, 133, 125, 124 (150 - 124 Ar), 68 (2C = C), 51, 30 (CH₃).

4-hydroxy-4-(4-methoxyphenyl)-butan-2-one (Table 2, entry 14): IR (cm⁻¹, KBr): 3410 - 3500 (OH), 2950 (CH Ar), 1700 (C = O), 1610 (C = C), 1250 (OCH₃), 800 (aromatic). ¹H

NMR (400 MHz, CDCl₃, TMS, δ ppm): 6.9 - 7.2 (4H, day, CH, Ar); 5.0 (1H, day, CH); 4.1 (1H, br second, OH); 3.8 (3H, second, CH₃); 2.8 (2H, m, CH₂), 2.2 (3H, second, CH₃). ¹³C NMR (400 MHz, CDCl₃, TMS, δ ppm): 207 (C = O), 160, 136, 127, 127, 114, 114 (114 - 136 Ar), 69 (2C = C), 55, 51, 30 (CH₃).

Table 2. Preparation of β -Hydroxy Ketones Using Calcined Coral/Sodium Nitrate in the Presence of Ethanol/Water at Room Temperature

Entry	Aldehyde, 1mmol	Ketone, 3mmol	Production	Time, h	Yield, %
1		Acetone		6	85
2		3 - pentanone		5	87
3	Benzaldehyde	2 - butanone		8	75
4		cyclohexanone		6	88
5		Acetophenone		7	70
6		Acetone		5	88
7	2 - nitro - benzaldehyde	3 - pentanone		5	92
8		2 - butanone		5	90
9		2 - butanone		5	92
10		Acetone		5	89
11	3 - nitro - benzaldehyde	3 - pentanone		5	90
12		2 - butanone		6	88
13		cyclohexanone		5	89
14		Acetone		10	68
15	4 - methoxy benzaldehyde	3 - pentanone		8	72
16		2 - butanone		8	68
17		Cyclohexanone		10	70

5. Discussion

To develop marine natural catalyst, calcined coral/sodium nitrate was used as an efficient natural base catalyst for aldol condensation reaction of ketones and aldehydes to afford β -hydroxy carbonyl compounds in good to high yields. The obtained catalyst was characterized by X-ray diffraction signals at θ 31° and 48° in comparison with reported CaO signals at θ 32° and 47°, as indicated in Figure 3. The CaCO_3 was transformed to CaO using calcination at 800°C, as shown in XRD spectrum. The observed XRD signal at $\theta = 31^\circ$ corresponds to the existence of CaO, as shown in the desired signal in references, but the signal for CaCO_3 is reported at $\theta = 29^\circ$ (11).

According to Table 1, the best conditions for condensation reaction comprised using calcined coral/sodium nitrate, as a catalyst in the presence of ethanol/water at

room temperature. Therefore, this method was used to prepare all derivatives and the results are given in Table 2. As shown in Table 2, the reaction of nitro-substituted benzaldehydes with ketones has greater yields than benzaldehydes. Electron-withdrawing groups such as NO_2 on benzaldehyde ring activate aldol condensation reaction. In comparison, 4-methoxybenzaldehyde reacts more slowly with ketones and decreases the yield of products.

The plausible mechanism of the reaction of benzaldehyde with acetone in the presence of calcined coral/sodium nitrate for the formation of 4-hydroxy-4-phenyl-2-butanone is shown in Figure 4. If the reaction condition, for example room temperature is changed to reflux, by dehydration of hydroxyl ketone, 4-phenyl-2-on-3-buten is formed.

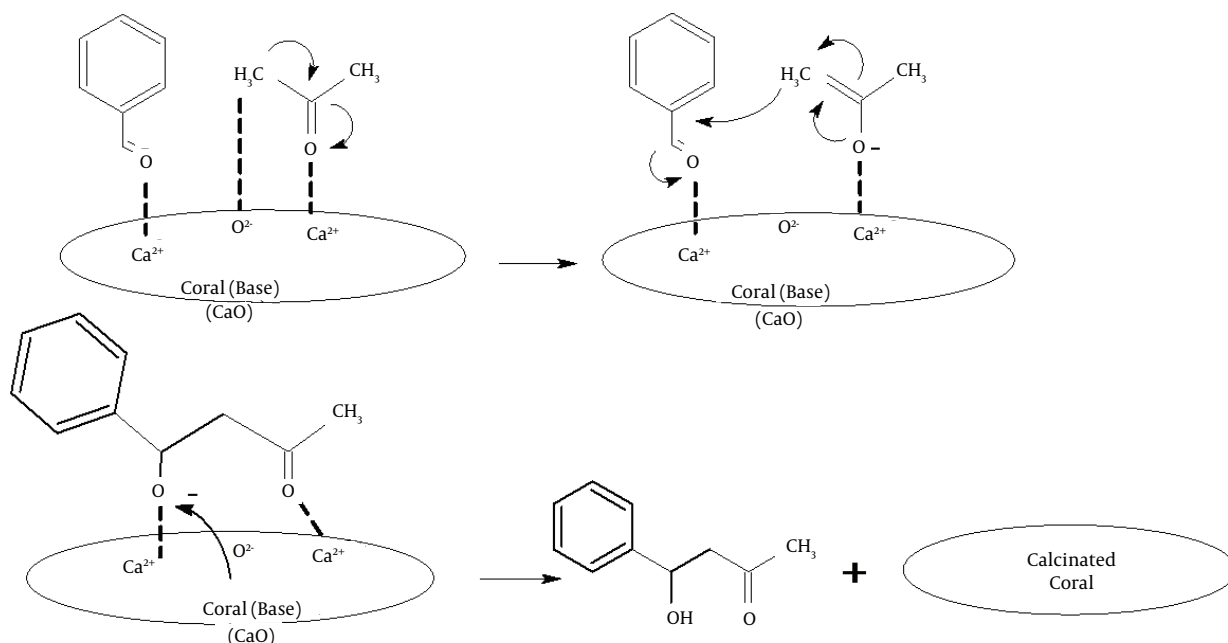


Figure 4. The Plausible Mechanism of Aldol Condensation in the Presence of Calcined Coral/ NaNO_3

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Footnotes

Authors' Contributions: Developing the original idea, design, and analyzing data: Mohammad Reza Bigdeli and Mohammad Reza Shushizadeh; performing the project:

Bahare Mohandespur; and writing the manuscript: Mohammad Reza Shushizadeh.

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