

**Zn-H₂O Promoted homo coupling reactions of α,β -Unsaturated ketones**

**Barun K. Mehta,¹ Guttikonda Raja,² D. Rambabu,³ ASG. Prasad,³ and
Mandava V. Basaveswara Rao,^{4*}**

1. Department of Chemistry, National Defence Academy, Khadakwasla, Pune-411023, **INDIA**

2. Department of Chemistry, Acharya Nagarjuna University, Guntur-522510, A.P, **INDIA**

3. Department of Chemistry, K L University, Vaddeswaram, Guntur-522 502, A.P, **INDIA**

4. Department of Chemistry, Krishna University, Machilipatnam-521001, A.P, **INDIA**

Email: professormandava@gmail.com

Received on 21st May and finalized on 23rd May 2013

ABSTRACT

Zn-H₂O Promoted homo coupling reactions of α, β -Unsaturated Ketones under hydrothermal conditions. The products obtained in good yields.

Keywords: α, β -unsaturated ketones, Zinc, Water, Hydrothermal condition.

INTRODUCTION

Aldol homo coupling reactions are important synthetic reactions and generally these reactions are performed in the presence of strong acids and bases[1]. In order to perform these reactions under neutral conditions, metal ions are used as catalyst or reagent[2-6]. Growing importance of these structural units is due to the fact that they are useful in the synthesis of naturally occurring compounds and antibiotics[7]. Thrust in the development of green process reactions that avoid the use of potential harmful organic solvents[8] is increasing. Hence, over the past decade, considerable effort has been directed towards developing a method for replacing medium of organic solvents used in the synthetic reactions to an aqueous environment. Water has a specific characteristic properties among various solvents. The hydrothermal solution at high temperature show unique properties as a function of the temperature during the course of reactions. In general, water leads to hydrolysis function for the reactants during the reaction and however results are often unusual and unique due to the unusual behavior of water at high temperature. In recent aspects of organic synthesis, the matter of primary interest is to accelerate the reaction rates as well as to improve selectivity via more green or environmentally friendly chemical process. The use of zinc metal for synthetic purposes is attractive because this element is readily available, cheap, and more environmentally and the process is benign in comparison with some other metals commonly used in synthesis. In order to establish approaches towards the development of environmentally friendly synthetic methodologies, we have exploited the use of aqueous reaction media under hydrothermal conditions[9-11]. We are reporting Zn-H₂O Promoted homo coupling reactions of α, β -unsaturated ketones under hydrothermal conditions.

MATERIALS AND METHODS

General methods: Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution by using 400 and 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0.00$) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as bs (broad). Coupling constants (J) are given in hertz. MS spectra were obtained on a mass spectrometer.

General procedure for the preparation of compound 2: A mixture of ketone (2 mmol), Zinc (1 mmol), and Water (5 ml) was placed in a reaction vessel and reacted at 100°C for 12 h. After quenching with water, the mixture was extracted with ethyl acetate. The crude product was purified by silica gel column chromatography to afford **2**.

RESULTS AND DISCUSSION

To establish the optimum conditions, we first examined the reaction of cyclohexanone (**1a**) with zinc in aqueous medium at 100°C . The best results were obtained in the presence of 1 mmol zinc. Having established the optimum reaction conditions for the preparation of **2a** we then used this methodology for the preparation of our other target compounds related to **2a**. Thus, a variety of ketones (**1**) were employed under the reaction conditions and the results are summarized in Table 1. As evident from Table 1 that the reaction proceeded well with other ketones (Table 1). The hydrothermal reaction is undoubtedly quite effective as new tool for promoting the desired products **2a-h**.

Bi(cyclohexane)-3,3'-dione (2a): ^1H NMR (400 MHz, CDCl_3): δ 2.46-2.04 (m, 8H), 1.79-1.56 (m, 2H), 1.46-1.33 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ 213.13, 44.94, 43.58, 42.37, 28.13, 25.07; EI-MS: m/z 194.0 (M+H) $^+$.

1,1'-dimethylbi(cyclohexane)-3,3'-dione (2b): ^1H NMR (400 MHz, CDCl_3): δ 2.44-2.04 (m, 8H), 1.82-1.61 (m, 8H), 1.18 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.9, 54.5, 44.1, 37.3, 36.6, 20.6, 19.8; EI-MS: m/z 223.1 (M+H) $^+$.

1,1',5,5',5'-hexamethylbi(cyclohexane)-3,3'-dione (2c): ^1H NMR (400 MHz, CDCl_3): δ 2.30-2.02 (m, 8H), 1.80-1.55 (m, 4H), 1.16 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.6, 62.2, 55.4, 44.6, 32.8, 30.1, 27.6, 20.4; EI-MS: m/z 279.2 (M+H) $^+$.

1,1'-(bi(cyclohexane)-2,2'-diyl)diethanone (2d): ^1H NMR (400 MHz, CDCl_3): δ 2.22-2.30 (m, 2H), 2.10 (s, 6H), 1.81-1.25 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3): δ 209.8, 052.85, 39.6, 29.3, 28.9, 26.3, 25.8, 25.2; EI-MS: m/z 251.1 (M+H) $^+$.

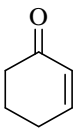
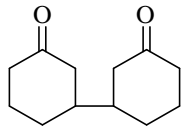
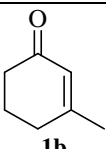
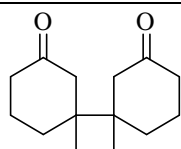
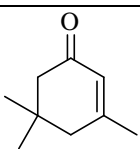
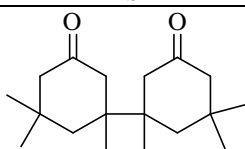
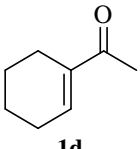
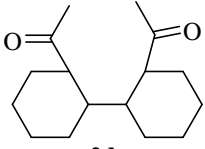
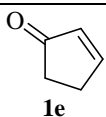
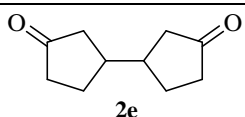
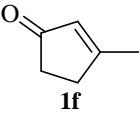
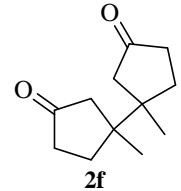
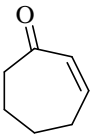
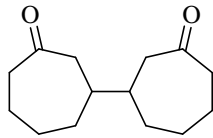
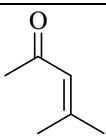
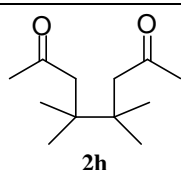
Bi(cyclopentane)-3,3'-dione (2e): ^1H NMR (400 MHz, CDCl_3): δ 2.26-2.04 (m, 10H), 1.96-1.88 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 218.0, 46.5, 46.1, 40.8, 26.1; EI-MS: m/z 167.1 (M+H) $^+$.

1,1'-dimethylbi(cyclopentane)-3,3'-dione (2f): ^1H NMR (400 MHz, CDCl_3): δ 2.29-2.01 (m, 8H), 1.91-1.86 (m, 4H), 1.16 (d, $J = 5.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 218.5, 50.5, 47.6, 38.2, 23.8, 13.1; EI-MS: m/z 195.1 (M+H) $^+$.

Bi(cycloheptane)-3,3'-dione (2g): ^1H NMR (400 MHz, CDCl_3): δ 2.58-2.41 (m, 8H), 1.71-1.56 (m, 6H), 1.39-1.17 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ 212.1, 48.5, 44.8, 36.1, 30.6, 29.8, 24.4; EI-MS: m/z 223.1 (M+H) $^+$.

4,4,5,5-tetramethyloctane-2,7-dione (2h): ^1H NMR (400 MHz, CDCl_3): δ 2.41 (s, 4H), 2.11 (s, 6H), 1.16 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 208.1, 51.4, 36.8, 31.7, 22.1; EI-MS: m/z 198.1 ($\text{M}+\text{H}$) $^+$.

Table 1. Zn-H₂O Promoted homo coupling reactions of α, β -Unsaturated Ketones ^a

S.No	Ketone	product	Yield ^b
1	 1a	 2a	85
2	 1b	 2b	75
3	 1c	 2c	80
4	 1d	 2d	70
5	 1e	 2e	85
6	 1f	 2f	75
7	 1g	 2g	70
8	 1h	 2h	70

a..Ketone (2 mmol), Zinc (1 mmol), Water (5 ml), 100 °C for 12 h. b. Isolated Yield

CONCLUSIONS

In conclusion, the present work describes Zn-H₂O Promoted homo coupling reactions of α,β -Unsaturated Ketones under hydrothermal conditions.

ACKNOWLEDGEMENTS

M. V. Basaveswara Rao, thank University Grants Commission, New Delhi for the financial assistance under Major Research Project.

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