

Preparation of Various Derivatives of Dibenzalpropanone by using Lithium Hydroxide as Green Approach

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ABSTRACT

The α,β -unsaturated ketones known as benzalacetones are an interesting class of compounds frequently used as key intermediates in organic synthesis. Due to their conjugated system, benzalacetone and derivatives have been described as radical scavengers with potential antioxidant properties. We report here a simple and direct method to prepare functionalized α,β -unsaturated ketones via a microwaves activated Aldol Condensation reaction. The experimental protocol developed selectively produces benzalacetones of self-condensation product in very short reaction times and good yields.

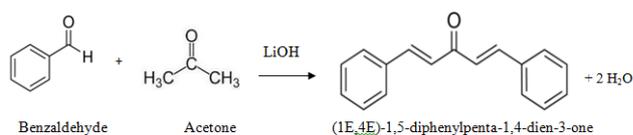
Keywords: Benzalacetones, microwave, Aryl Aldehyde.

I. INTRODUCTION

The synthesis of α,β -unsaturated ketones known as benzalacetones, which possess interesting properties for organic synthesis. Due to their conjugated system, benzalacetone and derivatives have been described as radical scavengers with potential antioxidant properties. Various methods of synthesis for this type of compounds have been described in the literature. The Aldol condensation reaction is one of the simplest condensation methods. This reaction is typically catalyzed by acids ($AlCl_3$ or HCl) and more often by bases with or without solvent at room temperature or under conventional heating. In order to increase the yield and to avoid the formation of by-products, several protocols relative to aldol condensation reaction have also been reported using different catalysts, sonochemical activation or microwaves irradiation. However, in all these conditions, side reactions start decreasing the yield of the desired product and entail further purification steps. Consequently, we were particularly interested in developing an efficient preparation of benzalacetones from acetone and aromatic substituted aldehydes in basic conditions under microwave-activation.

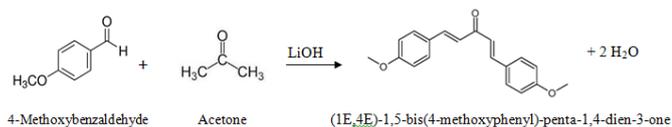
1) Preparation of (1E,4E)-1,5-diphenylpenta-1,4-dien-3-one:

Place 0.9ml benzaldehyde in to conical flask containing acetone 0.3ml add 95% ethanol. Over a period of 15 min. Slowly added 2ml 40% LiOH solution to the mixture at room temp. For 10 min, pour the reaction mix. into the ice & stir until the precipitation occurs. The progress of the reaction was monitored by TLC. The separated solid was filtered & recrystallized from ethanol. Their physical constant. data give in table.



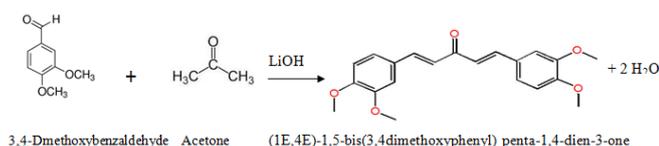
2) Preparation of (1E,4E)-1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one:

Place 0.9ml 4-Methoxybenzaldehyde in to conical flask containing acetone 0.3ml add 95% ethanol. Over a period of 15 min. Slowly added 2ml 40% LiOH solution to the mixture at room temp. For 10 min, pour the reaction mix. into the ice & stir until the precipitation occurs. The progress of the reaction was monitored by TLC. The separated solid was filtered & recrystallized from ethanol. Their physical constant. data give in table.



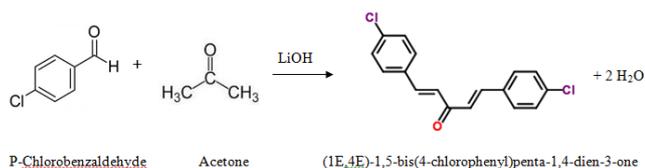
3) Preparation of (1E,4E)-1,5-bis(3,4-dimethoxyphenyl)penta-1,4-dien-3-one

Place 0.9ml 3,4-Dimethoxybenzaldehyde in to conical flask containing acetone 0.3ml add 95% ethanol. Over a period of 15 min. Slowly added 2ml 40% LiOH solution to the mixture at room temp. For 10 min, pour the reaction mix. into the ice & stir until the precipitation occurs. The progress of the reaction was monitored by TLC. The separated solid was filtered & recrystallized from ethanol. Their physical constant. data give in table.



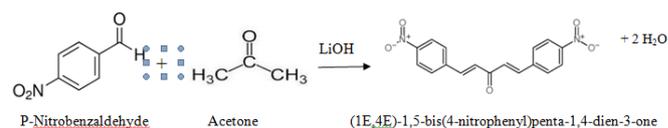
4) Preparation of (1E,4E)-1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one :-

Place 0.9ml P-Chlorobenzaldehyde in to conical flask containing acetone 0.3ml add 95% ethanol. Over a period of 15 min. Slowly added 2ml 40% LiOH solution to the mixture at room temp. For 10 min, pour the reaction mix. into the ice & stir until the precipitation occurs. The progress of the reaction was monitored by TLC. The separated solid was filtered & recrystallized from ethanol. Their physical constant. data give in table.



5) Preparation of (1E,4E)-1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one:-

Place 0.9ml P-Nitrobenzaldehyde in to conical flask containing acetone 0.3ml add 95% ethanol. Over a period of 15 min. Slowly added 2ml 40% LiOH solution to the mixture at room temp. For 10 min, pour the reaction mix. into the ice & stir until the precipitation occurs. The progress of the reaction was monitored by TLC. The separated solid was filtered & recrystallized from ethanol. Their physical constant. data give in table.



II. RESULT AND DISCUSSION

- ✓ Microwave activation for the synthesis of benzalacetones has not been widely described in the literature. Kappe *et al* reported the aldol condensation of *p*-methoxybenzaldehyde with acetone using microwave activation.
- ✓ As a wide variety of aryl aldehydes is commercially available, microwave activation would provide a higher degree of flexibility with respects to functional groups which may be introduced in the benzalacetone skeleton. The details of the synthesis were previously described by our group.
- ✓ Following our interest in establishing an efficient, rapid and selective access to benzalacetones and considering our results previously obtained under conventional heating.

Sr. No.	Compound Name	Molecular formula	Molecular Weight	M.P. °C	Yield %
01	(1E,4E)-1,5-diphenylpenta-1,4-dien-3-one	C ₁₇ H ₁₄ O	234.298	130°C	85
02	(1E,4E)-1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one	C ₁₉ H ₁₈ O ₃	294.35	175°C	65
03	(1E,4E)-1,5-bis(3,4-dimethoxyphenyl)penta-1,4-dien-3-one	C ₂₁ H ₂₂ O ₅	354.396	142°C	40
04	(1E,4E)-1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one	C ₁₇ H ₁₂ Cl ₂ O	303.182	172°C	70
05	(1E,4E)-1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one	C ₁₇ H ₁₂ NO ₂ O ₅	324.292	220°C	72

All the compound synthesized were adequately characterized by their spectral IR, ¹H-NMR & Mass Spectra.

***Spectral Study of (1E,4E)-1,5-diphenylpenta-1,4-dien-3-one :-**

IR(KBr cm⁻¹):1725cm⁻¹(C=O),1570cm⁻¹(C=C), ¹H NMR (ppm) (CDCl₃):7.60(dt, 1.5Hz & 8 Hz, 2H); 7.40(dt 1.5 & 8Hz, 2H); 7.33(dt, 1.5 & 8Hz, 1H); 7.82(d,18Hz, 1H); 7.03(d,18Hz, 1H).

***Spectral Study of (1E,4E)-1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one**

IR(KBr cm⁻¹):1725cm⁻¹(C=O),1570cm⁻¹(C=C);¹HNMR(ppm) (CDCl₃):7.62(td, 0.5 & 8 Hz, 2H); 6.94(td, 0.5 & 8Hz, 2H); 3.83(s, 3H); 7.82(d, 18Hz,1H); 7.03(d, 8Hz, 1H)

***Spectral Study of (1E,4E)-1,5-bis(3,4-dimethoxyphenyl)penta-1,4-dien-3-one**

IR(KBr cm⁻¹):1725cm⁻¹(C=O),1570cm⁻¹(C=C);¹HNMR(ppm) (CDCl₃): 7.18(dd, 1.5 & 8Hz, 1H); 6.94(dd, 0.5 & 8Hz, 1H); 7.22(dd, 1.5&0.5Hz, 1H); 3.83(s, 6H); 7.82(d, 18Hz, 1H); 7.03(d, 18Hz, 1H)

***Spectral Study of (1E,4E)-1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one**

IR(KBr cm⁻¹):1725cm⁻¹(C=O),1570cm⁻¹(C=C);¹HNMR(ppm) (CDCl₃):7.44(td, 1.5 & 8Hz, 2H); 7.68(td, 1.5 & 8 Hz, 2H); 7.82(d, 18Hz, 1H); 7.03(d, 18Hz, 1H).

***Spectral Study of (1E,4E)-1,5-bis(4-nitrophenyl)penta-1,4-dien-3-one**

IR(KBr cm⁻¹):1725cm⁻¹(C=O),1570cm⁻¹(C=C);¹HNMR(ppm) (CDCl₃):8.03(td, 0.5 & 8Hz, 2H); 8.21(td, 0.5 & 8Hz, 2H); 7.96(d, 18Hz, 1H); 7.32(d, 18Hz, 1H).

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