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Microwave Assisted, Silica Gel Mediated, Solvent Free, Michael-Addition of Aryl Methyl Ketones with Chalcones for the Synthesis of 1,3,5-triarylpentane-1,5-diones

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Rengasamy Chithiravel[1*], Kandasamy Rajaguru[2], Shanmugam Muthusubramanian[2]

[1]Department of Chemistry, Rajah Serfoji Government College, Thanjavur - 613006, India.
[2]Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai - 625 021, India.

***Corresponding author:** Rengasamy Chithiravel, email: vel14raj@gmail.com

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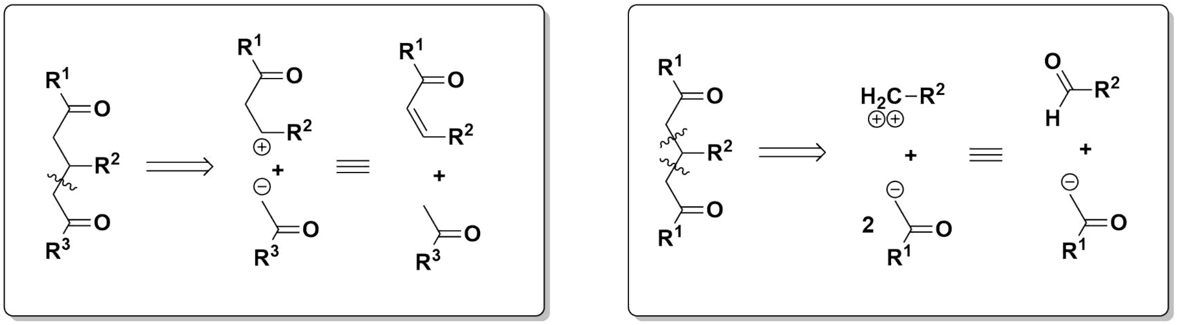
Abstract. A series of symmetrical/unsymmetrical 1,3,5-Triarylpentane-1,5-diketone derivatives have been prudently synthesized via direct Michael addition of Chalocones with Aryl Methyl Ketones using microwave irradiation using Silica gel without any solvents. This method affords several advantages such as operational simplicity, short reaction time and easy work up by recrystallization and excellent yields.
Keywords: 1,5-diketone; silica gel; microwave; Michael addition; 1,5-dicarbonyl compounds.

Resumen. Se prepararó una serie de derivados simétricos y asimétricos de 1,3,5-triaril-1,5-pentanodiona, a través de la adición de Michael entre arilmetilcetonas y chalconas empelando microondas y gel de sílice con y sin disolvente. El método ofrece ventajas como simplicidad operativa, reducción de los tiempos de reacción y fácil procesamiento por recristaización, así como excelentes rendimientos.
Palabras clave: Síntesis de 1,5-dionas, adición de Michael, síntesis asistida por microondas, química verde, metil cetonas, chlaconas.

Introduction

Enormous significance has been taken in solvent-free synthesis in order to develop conventional methods from the economic and environmentally benign perspective since the method does not employ harmful solvents [1-2]. Michael additions are the effective tool for the generation of new C-C bonds especially, applied for the synthesis of pharmacologically significant β-substituted carbonyl compounds [3-5]. Diketones are the promising precursor for the synthesis of various many heterocyclic and polyfunctional compounds, complex organic molecules and some diverse materials such as OLEDs, DNA binding ligands [3-8]. Several synthetic methods has been explored using a variety of toxic and expensive metal catalysts both acidic and basic such as lanthanides, $Bi(NO_3)_3$, $Bi(OTf)_3$, $Cu(BF_4)_2$ and others [9-14]. The conjugate addition of aryl ketones to acetohydrazone of aromatic aldehyde with catalyst of 1,2-di-enamine is also an efficient approach [15] to develop the novel organic synthesis by eco-friendly technique accelerate organic synthesis [16-19]. Traditional approaches for the synthesize of 1,5-dicarbonyl compounds typically appeal the use of enolates with aryl/alkyl vinyl ketones through 1,4-addition [20-21]. In many cases, the synthesis of this desired 1,5-dicarbonyl systems can be promoted or catalyzed under strongly basic, Brønsted acid or Lewis acid catalysis conditions [22-26]. The general methods used for the synthesis of 1,3,5-triaryl-1,5-pentanedione in the presence of volatile organic solvents afford only moderate to low yields [27]. However, the use of toxic and expensive catalysts is not economically viable and limits their use in large scale production and also conflicts with aspects of green chemistry. Adsorbent mediated syntheses in solvent-free conditions have fascinated much interest owing to mild conditions, high selectivity and remarkable acceleration [28-29].

It has been planned to synthesize several heterocyclic compounds from simple starting materials during this investigation. α,ω-Diketones are excellent precursors to prepare heterocyclic compounds as they can be reacted with several nucleophiles such as nitrogen, oxygen, sulfur nucleophiles [30-35]. Out of this different α,ω-diketones, the 1,5-diketones are excellent building blocks towards this protocol, as they would lead to stable six membered rings [36-39]. Considering the structural feature of 1,3,5-triarylpentane-1,5-diones, a simple retrosynthetic approach can suggest that a Michael type addition of an acetophenone over a chalcone may lead to the target product. However, a symmetrical 1,3,5-triarylpentane-1,5-diones can be synthesized by a pseudo multicomponent approach involving two molecules of acetophenone and one molecule of arylaldehyde.



Unsymmetrical 1,3,5-Diketones

Symmetrical 1,3,5-Diketones

Fig. 1. Retrosynthetic approach for 1,3,5-Diketones.

Though there are several methods available to get an unsymmetrical 1,3,5-triarylpentane-1,5-diones by the above strategy involving chalcone and aryl methyl ketone, protocols via greener conditions may be more attractive. In last three decades Microwave irradiation has extensively been believed as a clean and useful method for the initiation and acceleration of progressions in organic synthesis and has been consistently used in enormous number of organic syntheses to result higher yield in shorter reaction time under milder conditions [40-41]. In this paper, we desire to report that solvent-free Michael addition for the synthesis of 1,3,5-triarylpentane-1,5-dione derivatives from chalcones and aryl methyl ketones in the presence of silica gel.

Experimental

A CEM Discover microwave synthesizer (Model No: 908010) operating at 180/264 V and 50/60 Hz with microwave power maximum level of 300 W and microwave frequency of 2455 MHz was employed for the microwave-assisted experiments. Nuclear Magnetic Resonance (^{1}H, ^{13}C - NMR) spectra were recorded on 300 MHz spectrometer (Bruker) in $CDCl_3$ using TMS as an internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (*J* values) are reported in Hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), p (pentet), m (multiplet). ^{13}C NMR spectra were routinely run with broadband decoupling. Pre coated silica gel on aluminium plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60 – 80 °C) and ethyl acetate as the eluent. Electrospray ionization (ESI) mass

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spectra were obtained on an LCQ Fleet mass spectrometer, Thermo Fisher Instruments Limited, US and an Agilent mass spectrometer. HRMS was recorded on Brucker-Daltonics, Micro-TOF-Q II mass spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyser.

General procedure for the synthesis of 1,3,5-triarylpentan-1,5-diones (3)

A mixture of chalcone **1** (1.0 equiv), aryl methyl ketone **2** (1.0 equiv.) and Silica gel 60 (spherical, 63-200 µm) (3 g) was taken in a 10 mL quartz vial and placed in the microwave oven. The vial was sealed with a pressure cap and subjected to microwave irradiation. The irradiation was programmed between 100 – 120 °C, 120 W, 5 bar, for 10 min. The reaction was monitored by TLC using petroleum ether/ethyl acetate mixture (7:3) as the eluent. After the reaction mixture was cooled to room temperature, ethanol was added, and reaction mixture was separated from the silica gel. The obtained crude was filtered, dried in vacuum, and recrystallized from ethanol to afford **3**. Then, the silica gel was carefully washed well with methanol: dichloromethane (1:1) and dried in hot air oven at 130 °C under reduced pressure for 1 h. The recovered silica gel could be recycled.

Characterization of compounds 3

3-(4-Methylphenyl)-1,5-diphenyl-1,5-pentanedione (3a) [42]: Isolated as colorless solid; mp: 120 – 121 ºC; IR (KBr): 3069, 3037, 2898, 1678 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94 (dt, *J* = 3.5, 1.5 Hz, 3H), 7.53 (dd, *J* = 10.4, 4.2 Hz, 2H), 7.42 (dd, *J* = 11.5, 4.3 Hz, 3H), 7.28 – 7.20 (m, 3H), 7.12 (dd, *J* = 27.9, 8.1 Hz, 3H), 4.03 (p, *J* = 6.8 Hz, 1H), 3.48 (dd, *J* = 16.5, 6.9 Hz, 2H), 3.33 (dd, *J* = 16.6, 6.2 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.6, 140.7, 136.9, 136.1, 132.9, 129.3, 128.5, 128.1, 127.2, 44.9, 36.8, 20.9. ESI-MS *m/z* calcd for $C_{24}H_{22}O_2$: 342.43 [M]$^+$; Found: 343.59 [M+H]$^+$. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48 %. Found: C, 84.14; H, 6.52 %.

1,5-Bis(4-methylphenyl)-3-phenyl-1,5-pentanedione (3b) [42]: Isolated as colorless solid; mp: 108 – 110 ºC; IR (KBr): 3059, 3028, 2891, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.1 Hz, 4H), 7.45 – 7.39 (m,6H), 4.00 (p, *J* = 6.8 Hz, 1H), 3.45 (dd, *J* = 16.9, 6.8 Hz, 2H), 3.27 (dd, *J* = 16.8, 7.2 Hz, 2H), 2.41 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 198.0, 144.0, 142.4, 134.3, 132.2, 129.3, 128.9, 128.7, 128.2, 44.6, 36.6, 21.6. ESI-MS *m/z* calcd for $C_{25}H_{24}O_2$: 356.46 [M]$^+$; Found: 357.21 [M+H]$^+$. Anal. Calcd for: C, 84.24; H, 6.79 %. Found: C, 84.27; H, 6.75 %.

1,3,5-Tri(4-methylphenyl)-1,5-pentanedione (3c) [6]: Isolated as colorless crystal; mp: 87 – 89 ºC; IR (KBr): 3058, 3027, 2891, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.86 (d, *J* = 8.1 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.05 (p, *J* = 6.9 Hz, 1H), 3.45 (dd, *J* = 16.5, 6.9 Hz, 2H), 3.32 (dd, *J* = 16.5, 6.9 Hz, 2H), 2.39 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 198.3, 143.8, 140.9, 136.1, 134.4, 129.3, 129.2, 128.3, 127.3, 45.0, 36.9, 21.6, 21.0. ESI-MS *m/z* calcd for $C_{26}H_{26}O_2$: 370.49 [M]$^+$; Found: 371.77 [M+H]$^+$. Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07%. Found: C, 84.32; H, 7.11 %.

3-(4-Chlorophenyl)-1,5-di(4-methylphenyl)-1,5-pentanedione (3d) [42]: Isolated as colorless solid; mp: 113 – 114 ºC; IR (KBr): 3065, 3031, 2888, 1677 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.70 (d, *J* = 8.6 Hz, 4H), 7.23 (d, *J* = 8.6 Hz, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.80 (p, *J* = 6.9 Hz, 1H), 3.27 (dd, *J* = 16.6, 7.0 Hz, 2H), 3.10 (dd, *J* = 16.6, 7.0 Hz, 2H), 2.41 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.8, 143.9, 141.9, 136.1, 132.7, 129.6, 128.9, 128.7, 128.2, 44.5, 39.0, 21.1. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}ClO_2$: 390.9019 [M]$^+$; Found: 390.9021 [M]$^+$. Anal. Calcd for $C_{25}H_{23}ClO_2$: C, 76.81; H, 5.93 %. Found: C, 76.85; H, 5.99 %.

1,5-Bis(4-chlorophenyl)-3-(4-methylphenyl)-1,5-pentanedione (3e) [6]: Isolated as colorless crystal; mp: 72 – 73 ºC; IR (KBr): 3077, 3037, 2886, 1679 cm^{-1}; ^{1}H NMR (300 MHZ, CDCl$_3$) δ_H: 7.88 (d, *J* = 8.6 Hz, 4H), 7.40 (d, *J* = 8.6 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.97 (p, *J* = 6.9 Hz, 1H), 3.44 (dd, *J* = 16.6, 7.0 Hz, 2H), 3.27 (dd, *J* = 16.6, 7.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 197.4, 140.3, 139.5, 136.4, 135.3, 129.5, 129.3, 128.9, 127.2, 44.9, 36.9, 20.9. HRMS (ESI) *m/z* calcd for $C_{24}H_{20}Cl_2O_2$: 411.3204 [M]$^+$; Found: 411.3207 [M]$^+$. Anal. Calcd for $C_{24}H_{20}Cl_2O_2$: C, 70.08; H, 4.90 %. Found: C, 70.12; H, 4.92 %.

J. Mex. Chem. Soc. **2022**, *66*(3)
Regular Issue

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3-(4-Bromophenyl)-1,5-bis(4-chlorophenyl)-1,5-pentanedione (3f) [6]: Isolated as colorless solid; mp: 95 – 96 ºC; IR (KBr): 3060, 3027, 2894, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.30 (dd, *J* = 14.7, 8.6 Hz, 4H), 4.08 (p, *J* = 7.2 Hz 1H), 3.52 (dd, *J* = 16.9, 6.8 Hz, 2H), 3.34 (dd, *J* = 17.4, 7.7 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 197.0, 141.9, 139.8, 135.4, 131.9, 129.6, 129.5, 129.0, 128.7, 44.7, 36.5. HRMS (ESI) *m/z* calcd for: 476.1899 [M]$^+$; Found: 476.1895 [M]$^+$. Anal. Calcd. for $C_{23}H_{17}BrCl_2O_2$; C, 58.01; H, 3.60 %. Found: C, 58. 03; H, 3.58 %.

3-(3-Bromophenyl)-1,5-bis(4-chlorophenyl)-1,5-pentanedione (3g) [6]: Isolated as colorless solid; mp: 92 – 93 ºC; IR (KBr): 3052, 3031, 2882, 1675 cm^{-1}; ^{1}HNMR (300 MHz, CDCl$_3$) δ_H: 7.88 (d, *J* = 8.4 Hz, 4H), 7.42 – 7.12 (m, 8H), 4.06 (p, *J* = 6.9 Hz, 1H), 3.45 (dd, *J* = 17.0, 6.8 Hz, 2H), 3.28 (dd, *J* = 16.9, 6.9 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 196.8, 145.9, 139.6, 134.9, 130.4, 130.2, 129.9, 129.5, 128.9, 126.3, 122.7, 44.4, 36.6. HRMS (ESI) *m/z* calcd for: 476.1899 [M]$^+$; Found: 477.1894 [M]$^+$. Anal. Calcd. for $C_{23}H_{17}BrCl_2O_2$: C, 58.01; H, 3.60%. Found: C, 58.04; H, 3.64 %.

1,5-Bis(4-chlorophenyl)-3-[4-(dimethylamino)phenyl]-1,5-pentanedione (3h) [6]: Isolated as pale yellow solid; mp: 82 – 84 ºC; IR (KBr): 3061, 3029, 2894, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.89 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 3.91 (p, *J* = 7.0 Hz, 1H), 3.42 (dd, *J* = 16.4, 7.1 Hz, 2H), 3.25 (dd, *J* = 16.4, 6.9 Hz, 2H), 2.90 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 197.9, 149.6, 139.5, 135.4, 131.1, 129.7, 129.0, 128.1, 112.9, 45.4, 40.7, 36.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{23}Cl_2NO_2$: 440.3616 [M]$^+$; Found: 440.3617 [M]$^+$. Anal. Calcd for $C_{25}H_{23}Cl_2NO_2$: C, 68.19; H, 5.26; N, 3.18 %. Found: C, 68.14; H, 5.30; N, 3.22 %.

3-(2,3-Dichlorophenyl)-1,5-bis(4-fluorophenyl)-1,5-pentanedione (3i): Isolated as colorless solid; mp: 70 – 72 ºC; IR (KBr): 3063, 3031, 2896, 1677 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 – 7.97 (m, 4H), 7.31 (d, *J* = 7.8, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.16 – 7.09 (m, 5H), 4.56 (p, *J* = 6.9 Hz, 1H), 3.55 – 3.35 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 196.5, 167.6, 164.2, 147.0, 143.1, 133.1, 130.9, 130.7, 128.8, 127.3, 115.9, 115.6, 42.7, 34.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{16}Cl_2F_2O_2$: 433.2747 [M]$^+$; Found: 433.2749 [M]$^+$. Anal. Calcd. for $C_{23}H_{16}Cl_2F_2O_2$: C, 63.76; H, 3.72 %. Found: C, 63.81; H, 3.75 %.

3-(4-Chlorophenyl)-1,5-bis(2-naphthyl)-1,5-pentanedione (3j) [6]: Isolated as colorless solid; mp: 120 – 122 ºC; IR (KBr): 3057, 3028, 2889, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 8.50 (s, 2H), 8.01 - 7.83 (m, 8H), 7.63 - 7.51 (m, 4H), 7.30 – 7.23 (m, 4H), 4.19 (p, *J* = 6.9 Hz, 1H), 3.67 (dd, *J* = 16.7, 6.7 Hz, 2H), 3.47 (dd, *J* = 16.7, 7.2 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.2, 142.3, 135.6, 134.0, 132.5, 132.3, 129.9, 129.6, 128.9, 128.8, 128.5, 128.4, 127.7, 126.8, 123.8, 44.8, 36.8. HRMS (ESI) *m/z* calcd for: 462.9661 [M]$^+$; Found: 462.9665 [M]$^+$. Found: %. Anal. Calcd. for $C_{31}H_{23}ClO_2$: C, 80.42; H, 5.01 %. Found: C, 80.38; H, 5.06 %.

3-(4-Chlorophenyl)-1,5-bis(thiophene-2-yl)-1,5-pentanedione (3k) [6]: Isolated as colorless crystal; mp: 110 – 111 ºC; IR (KBR) 3298, 3172, 2931, 2852, 1701 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.76 (dd, *J* = 3.8, 1.1 Hz, 2H), 7.64 (dd, *J* = 5.0, 1.1 Hz, 2H), 7.25-7.23 (m, 4H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 2H), 4.09 (p, *J* = 6.0 Hz, 1H), 3.43 (dd, *J* = 16.2, 6.8 Hz, 2H), 3.26 (dd, *J* = 16.2, 7.4 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 190.9, 143.9, 141.6, 133.8, 132.3, 132.1, 128.8, 128.6, 128.1, 45.0, 37.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}ClO_2S_2$: 374.9042 [M]$^+$; Found: 374.9047 [M]$^+$. Anal. Calcd for $C_{19}H_{15}ClO_2S_2$: C, 60.87; H, 4.03; S, 17.10 %. Found: C, 60.89; H, 4.07; S, 17.12 %.

1,3,5-Tris(thiophen-2-yl)-1,5-pentanedione (3l): Isolated as colorless crystal; mp: 103 – 105 ºC; IR (KBR) 3297, 3168, 2934, 2859, 1695 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.76 (d, *J* = 3.8 Hz, 2H), 7.62 (d, *J* = 4.9 Hz, 2H), 7.16 - 7.07 (m, 3H), 6.92 - 6.82 (m, 2H), 4.39 (p, *J* = 6.9 Hz, 1H), 3.47 (dd, *J* = 16.3, 6.8 Hz, 2H), 3.34 (dd, *J* = 16.2, 7.0 Hz, 2H).^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 190.6, 143.8, 133.6, 132.0, 127.9, 126.5, 124.2, 123.2, 121.9, 45.7, 32.7. ESI-MS *m/z* calcd for $C_{17}H_{14}O_2S_3$: 346.47 [M]$^+$; Found: 347.22 [M+H]$^+$. Anal. Calcd. for $C_{17}H_{14}O_2S_3$; C, 58.93; H, 4.07; S, 27.76 %. Found: C, 58.90; H, 4.12; S, 27.72 %.

J. Mex. Chem. Soc. **2022**, *66*(3)
Regular Issue

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1-(4-Chlorophenyl)-3,5-diphenyl-1,5-pentanedione (3m) [6]: Isolated as colorless solid; mp: 97 – 99 ºC; IR (KBr): 3060, 3029, 2894, 1675, 1680 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.96 (d, *J* = 7.3 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.33 – 7.22 (m, 5H), 4.10 (p, J = 6.0 Hz, 1H), 3.50 (dd, *J* = 16.8, 7.2 Hz, 2H), 3.34 – 3.27 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 198.4, 197.4, 143.5, 139.4, 136.7, 135.1, 133.1, 129.5, 128.8, 128.6, 128.5, 128.0, 127.4, 126.7, 44.8, 44.7, 37.1. HRMS (ESI) *m/z* calcd for $C_{23}H_{19}ClO_2$: 362.8488 [M]$^+$; Found: 362.8490 [M]$^+$. Anal. Calcd for $C_{23}H_{19}ClO_2$: C, 76.13; H, 5.28 %. Found: C, 76.18; H, 5.25 %.

1-(4-Methylphenyl)-3,5-diphenyl-1,5-pentanedione (3n) [43]: Isolated as colorless solid; mp: 99 – 101 ºC; IR (KBr): 3058, 3027, 2890, 1677, 1679 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.01 (dt, *J* = 3.5, 1.5 Hz, 3H), 7.59 (dt, *J* = 10.4, 1.4 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.34 – 7.13 (m, 6H), 4.17 – 4.05 (m, 1H), 3.58 – 3.50 (m, 2H), 3.42 – 3.37 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.6, 198.5, 143.8, 140.7, 136.9, 136.1, 132.9, 129.3, 129.2, 128.5, 128.2, 128.1, 127.4, 127.2, 44.8, 37.2, 21.6. ESI-MS *m/z* calcd for $C_{24}H_{22}O_2$: 342.43 [M]$^+$; Found: 343.22 [M+H]$^+$. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48 %. Found: C, 84.22; H, 6.43 %.

1-(4-Chlorophenyl)-5-(4-methylphenyl)-3-phenyl-1,5-pentanedione (3o): Isolated as colorless solid; mp: 101 – 102 ºC; IR (KBr): 3052, 3031, 2890, 1676, 1681 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.23 – 7.15 (m, 3H), 3.63 (p, *J* = 6.8 Hz, 1H), 3.44 (dd, *J* = 12.4, 8.0 Hz, 1H), 3.37 (dd, *J* = 12.5, 3.3 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.51, 143.7, 143.6, 138.6, 135.8, 129.3, 128.9, 128.8, 128.2, 127.9, 127.5, 127.1, 44.2, 38.7, 20.8. HRMS (ESI) *m/z* calcd for: 376.8753 [M]$^+$; Found: 376.8756 [M]$^+$. Ana. Calcd. for $C_{24}H_{21}ClO_2$; C, 76.49; H, 5.62 %. Found: C, 76.54; H, 5.68 %.

1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-5-(4-methylphenyl)-1,5-pentanedione (3p): Isolated as colorless crystal; mp: 111 – 113 ºC; IR (KBr): 3066, 3029, 2898, 1678, 1681 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.89 (d, *J* = 6.7 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 6.7 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.02 – 3.91 (m, 1H), 3.75 (s, 3H), 3.43 (ddd, *J* = 16.6, 12.0, 6.8 Hz, 2H), 3.25 (ddd, *J* = 16.2, 14.0, 7.1 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.3, 197.6, 158.4, 143.9, 139.5, 135.7, 135.4, 134.6, 129.6, 129.3, 128.9, 128.4, 128.3, 114.1, 55.2, 45.1, 45.0, 36.6, 21.7. HRMS (ESI) *m/z* calcd for: 406.9013 [M]$^+$; Found: 406.9017 [M]$^+$. Anal. Calcd. for $C_{25}H_{23}ClO_3$; C, 73.79; H, 5.70 %. Found: C, 73.82; H, 5.68 %.

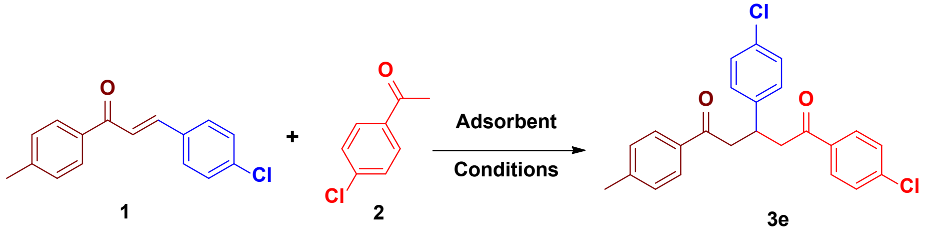
3-(4-Chlorophenyl)-1-(4-methylphenyl)-5-(2-naphthyl)-1,5-pentanedione (3q): Isolated as colorless solid; mp: 107 – 109 ºC; IR (KBr): 3061, 3031, 2882, 1679, 1683 cm^{-1}; IR (KBr) 3288, 3068, 2947, 2852, 1718, 1696, 1654, 1091, 702 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 8.48 (s, 1H), 7.97 (t, *J* = 8.2 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.64 – 7.51 (m, 3H), 7.25 (m, 5H), 4.16 (p, *J* = 6.9 Hz, 1H), 3.72 – 3.51 (m, 2H), 3.46 – 3.29 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 198.1, 197.8, 144.0, 142.4, 135.5, 134.2, 134.0, 132.4, 132.1, 129.8, 129.5, 129.3, 128.9, 128.7, 128.4, 128.4, 128.2, 127.7, 126.7, 123.7, 44.7, 44.6, 36.7, 21.6. HRMS (ESI) *m/z* calcd for: 426.9340 [M]$^+$; Found: 426.9343 [M]$^+$. Anal. Calcd. for $C_{28}H_{23}ClO_2$; C, 78.77; H, 5.43 %. Found: C, 78.01; H, 5.48 %.

1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-(thiophene-2-yl)-1,5-pentanedione (3r) [6]: Isolated as colorless crystal; mp: 90 – 91 ºC; IR (KBR) 3288, 3171, 2939, 2849, 1705, 1698 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H: 7.90 (d, *J* = 6.8 Hz, 2H), 7.76 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.18 – 7.08 (m, 5H), 4.04 (p, *J* = 6.0 Hz, 1H), 3.54 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.43 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.33-3.21 (m,2H) 2.30 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ_C: 197.7, 191.8, 144.6, 140.6, 139.8, 136.7, 135.5, 134.1, 132.5, 129.9, 129.7, 129.2, 128.5, 127.6, 46.0, 45.0, 37.5, 21.3. HRMS (ESI) *m/z* calcd for: 382.9031 [M]$^+$; Found: 382.9036 [M]$^+$. Anal. Calcd. for $C_{22}H_{19}ClO_2S$; C, 69.01; H, 5.00; S, 8.37 %. Found: C, 69.06; H, 5.04; S, 8.40 %.

Results and Discussion

First, to attain suitable reaction conditions for the synthesis of 1,3,5-triarylpentane-1,5-dione. We investigated Michael addition of aryl methyl ketones (**1**) with 1.0 equivalents of Chalcone **2** under Microwave conditions mediated by various adsorbents such as Activated alumina, Montmorillonite K10, Activated carbon. However, the reactions were not completed even for longer reaction time and also resulted in the lower yields of **3e** (12-48 %) simultaneously with the formation of complex mixture which attributed that this lower yield might be due to the more acidic nature of these adsorbents (Table 1. entries 1-4). The lower yield of **3e** by using activated carbon (12 %) indicating that activated carbon is much weaker acidic nature (able 1. entry 5). By employing silica gel (Silica gel 60, 63-200 µm) resulted the product **3e** in the reasonably excellent yield (95 %) (Table 1. entry 6). Even employing the same reaction condition with other silica gel gave nearly the same results (Table 1. entries 7 and 8). Even the same reaction condition applied with powdered silica gel too led to the as similar result (Table 1. entry 9). Michael addition mediated by sand resulted **3e** in the low yield (12 %) with the formation of a huge crude mess which indicating that sand cannot be able to adsorb a large amount of aryl methyl ketones (Table 1. entry 10).

Table1. Optimization of Michael addition mediated by some adsorbents[a].



Entry	Adsorbent	Conditions	Yield **3e** (%)[a]
1	Acidic Alumina[b]	Microwave, 120 ºC, 30 min	23
2	Acidic Alumina[b]	Microwave, 120 ºC, 60 min	32
3	Montmorillonite K10[c]	Microwave, 120 ºC, 60 min	27
4	H-Mordenite[d]	Microwave, 120 ºC, 60 min	48
5	Activated carbon[e]	Microwave, 120 ºC, 60 min	12
6	Silica gel[f]	Microwave, 120 ºC, 10 min	95
7	Silica gel[g]	Microwave, 120 ºC, 10 min	91
8	Silica gel[h]	Microwave, 120 ºC, 10 min	95
9	Silica gel[i]	Microwave, 120 ºC, 10 min	94
10	Sand[j]	Microwave, 120 ºC, 60 min	12

[a]Chalcone **1** (1.0 mmol), aryl methyl ketone **2** (2.0 mmol) and adsorbent (3 g). [b]Alumina (activated, acidic, 150 mesh) was used. [c]Montmorillonite K10 (surface area 220-270 m2/g) was used. [d]H-Mordenite (5-7 µm) was used was used. [e]Activated carbon (100 mesh) was used. [f]Silica gel 60 (spherical, 63-200 µm) was used. [g]Silica gel 60 (amorphous, 63-210 µm) was used. [h]Silica gel 60 (45-106 µm, spherical) was used. [i]Silica gel 60 (crushed, 63-200 µm,) was used. [j]Sand C (40-80 mesh) was used.

Utilizing these optimized conditions, we explore the scope of this strategy employing a library of 1,5-diketones with different aryl substituents at 1,3 and 5 positions. The aryl group bearing electron-releasing/electron-withdrawing groups in the aryl rings of either acetophenone or chalcone does not have any influence on the product yield. Thus, substituent scope of this reaction has been successfully established and their yields are listed in the Table 2.

J. Mex. Chem. Soc. **2022**, *66*(3)
Regular Issue

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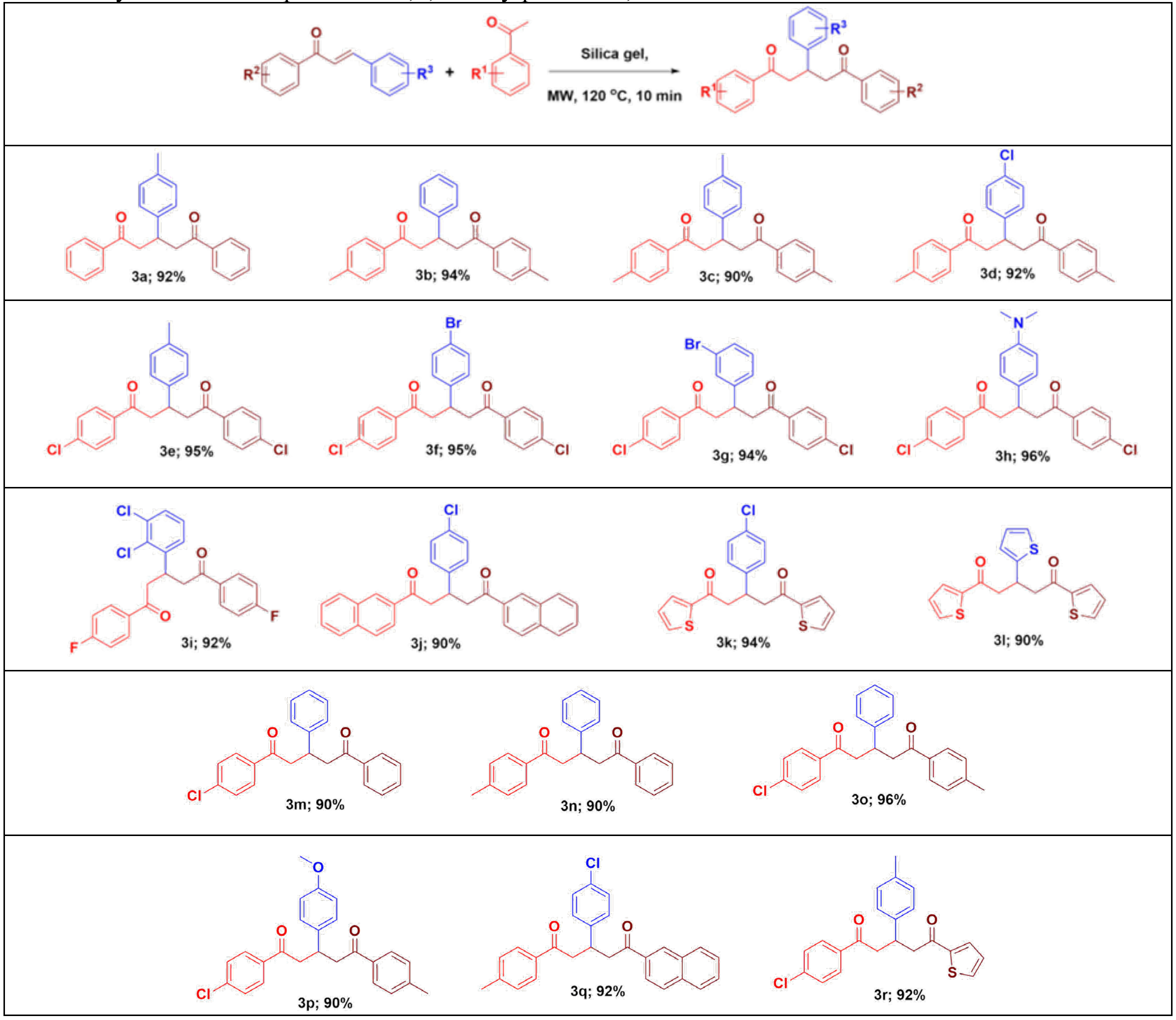
Table 2. Synthesis of compounds of 1,3,5-triarylpentane-1,5-diones **3**.



It is also to be noted that yields are excellent and the reaction mass does not require any column purification technique. Out of the twenty-two compounds synthesized, twelve of them are new and they have been fully characterized by spectral details (See Supporting information).

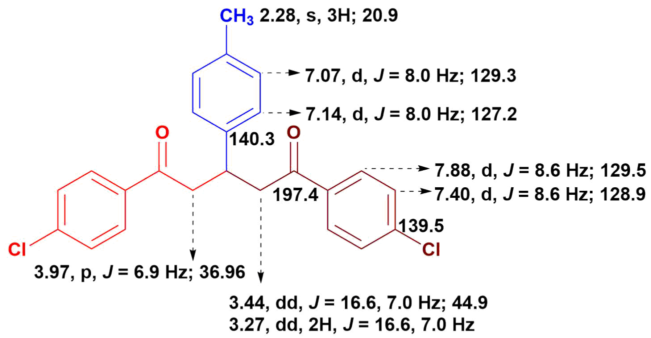
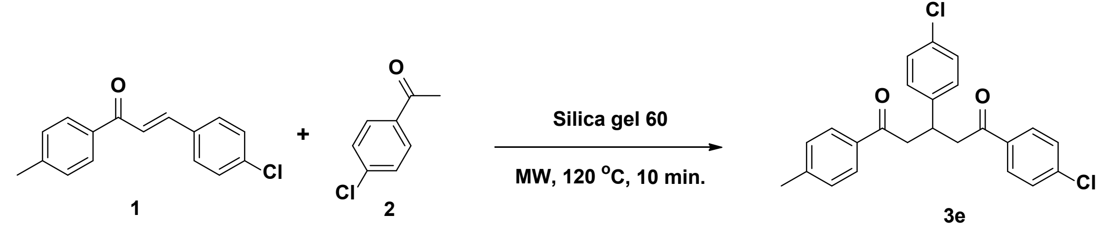


Fig. 2. NMR spectral features of **3e**.

Furthermore, the recycle experiments for the synthesis of **3e** were performed with recovered silica gel. The recovered silica gel was washed well with methanol: dichloromethane (1:1) and dried at 130 °C under reduced pressure for 1 h. Silica gel could be recycled five times without substantial decrease of the yields (Table 3).

Table 3. Recycle experiments for the silica gel mediated reaction.[a]

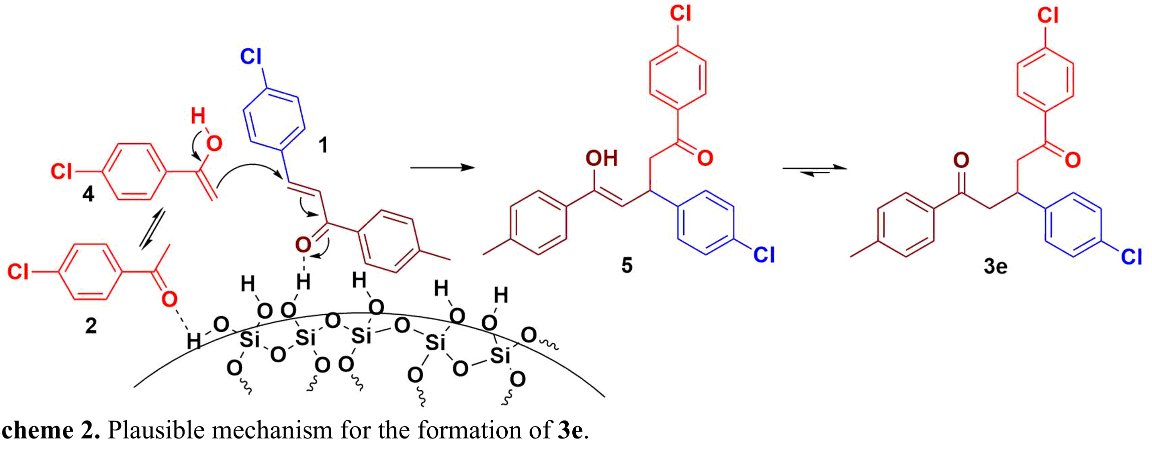


Number of times	1	2	3	4	5
Yields (10%)	95	95	94	93	93

[a]Chalcone **1** (1.0 mmol), aryl methyl ketone **2** (2.0 mmol) and Silica gel 60 (spherical, 63-200 µm, 3 g), Microwave, 120 °C, 10 min. [b] Isolated yields.

Mechanism

A plausible mechanism is shown in Scheme 2 for the formation of **3**. The keto form of the aryl methyl ketone **2** is in equilibrium with the enol form **4** which could be formed probably due to the shifting of equilibrium results the enol form **4** by coordination of the weakly acidic hydrogen to the oxygen in **2** from Silica gel. The enol for **4** would attack the Chalcone **1** which is a Michael acceptor to result **3** *via* the enol form **5**. In addition, enol **4** attacks the Chalcone **1** would be accelerated by the coordinating *via* hydrogen from the Silica gel to the oxygen atom of **1**. Accordingly, hydrogen bonding between hydroxy groups which is present on silica gel to substrates would participate in significant role in this particular Michael addition reaction.



Scheme 2. Plausible mechanism for the formation of **3e**.

Conclusion

In summary, the present work describes a series of symmetrical/unsymmetrical 1,3,5-Triarylpentane-1,5-diketone derivatives have been prudently synthesized from easily available starting materials such as aldehydes and acetophenones using silica gel as an adsorbent using microwave. The entire strategy is realized under mild reaction condition and easy work up by recrystallization with excellent yields. This ultrasonic strategy assures to generate synthetically useful 1,5-diketone precursors which could be utilized for the construction of various heterocyclic systems.

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J. Mex. Chem. Soc. **2022**, *66*(3)
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