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New Protocol for the Synthesis of 2-Alkanoyl- and 2-Aryloyl-5,5-dimethylcyclohexane-1,3-diones by the Reaction of Dimedone with Various Aldehydes and Cyanogen Bromide in the Presence of Triethylamine

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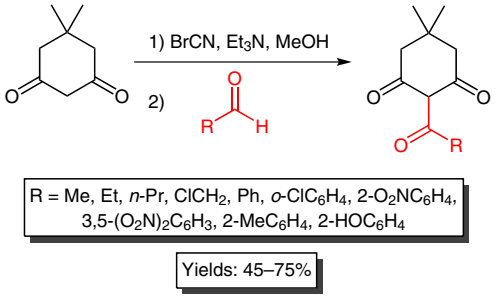

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Abstract A new route for the synthesis of 2-alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones as cyclic β-triketones is described. This synthesis was conducted by the reaction of dimedone with cyanogen bromide and triethylamine to form first the intermediate salt, followed by the addition of various aliphatic and aromatic aldehydes. The structures of the products were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopic techniques. A reaction mechanism is proposed.

Key words 2-alkanoyl(aryloyl)dimedone, dimedone, cyanogen bromide, aldehyde, cyclic β-triketone, acylation

Among β-triketones, α-acyl-β-diketones are represented by the 2-acylcyclohexane-1,3-diones and 1,3,5-triones derivatives. These types of compounds are an important group of natural products.[1,2]

2-Aryloylcyclohexane-1,3-dione compounds and their derivatives have a wide variety of important biological effects including fungicidal, insecticidal, and insect behavior controlling activities,[3–8] and are an important component in herbicidal compounds.[9–11] For instance, the benzoyl moiety substituted at the 2-position with groups such as halo or alkyl, at the 4-position with an alkylsulfonyl group, and at the 3-position with an acyclic or cyclic derivatized amino group were prepared and found to be useful in the control of a variety of broad leaf and grassy weeds. These compounds can be applied either pre-emergently or post-emergently and can be used to control undesirable vegetation in corn, rice, and wheat.[12] The inhibitory effect of some β-triketones such as 2-benzoyl-5,5-dimethylcyclohexane-1,3-dione (compound **3e** in this work) has been reported by Tarun et al.[13]

Cyclic β-triketones represent useful building blocks for the synthesis of various heterocyclic compounds due to their high degree of functionalization and their high reactivity. Heterocycles from the reaction of 2-acylcyclohexane-1,3-diones with malononitrile are reviewed elsewhere.[14] The reaction of 2-formyl- and 2-acetyldimedone with hydroxylamine, proceeding through nucleophilic attack at the exocyclic carbonyl for the formation of an acyloxime intermediate has been used for the synthesis of isoxazoles.[15–17] 2-Acetyldimedone, condensing with 2 equivalents of hydroxylamine, gives rise to oxime isoxazole.[15,16] For example, 2-formylcyclohexane-1,3-diones have been reported through heterocyclic synthesis.[18]

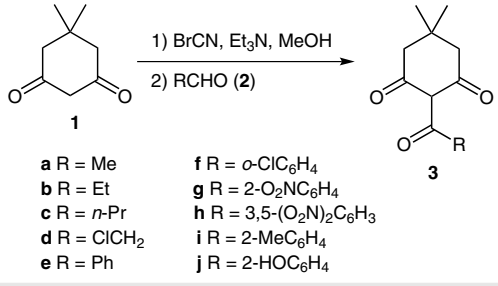
Some β-triketones such as 3,6-β-dihydroxy-2-(13-phenyltridecanoyl)-2-cyclohexen-1-one has been obtained from the natural source of *Virola oleifera*,[19] and the natural products 2-oleoylcyclohexane-1,3-dione and 4-hydroxy-2-oleoylcyclohexane-1,3-dione have been extracted from the larval mandibular glands of *Anagasta kuehniella*.[20] Many kinds of β-triketones have been synthesized in the laboratory through different strategies including 1,3-dipolar cycloaddition of nitrile oxide to cyclohexenone, followed by the hydrogenation and aqueous hydrolysis, which afforded 2-acylcyclohexane-1,3-diones,[21] and from acid anhydrides (succinic and glutaric anhydrides) and isopropenyl acetate.[22] The chemistry of 2-acylcycloalkane-1,3-diones was reviewed by Rubinov et al.[23]

Due to the importance of α-acyl-β-diketones (as cyclic β-triketones), we have now synthesized 2-alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones **3** by the reaction of dimedone (**1**) with cyanogen bromide (BrCN) in the pres-

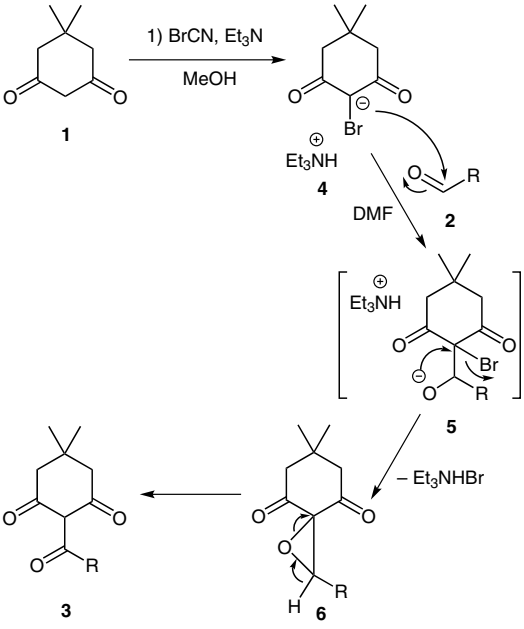
ence of triethylamine followed by the reaction with aliphatic and aromatic aldehydes as a new synthetic route. There was no report of this synthetic reaction route in the literature.

Thus, this paper describes a new synthetic route for 2-alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones **3**. The reaction of dimedone (**1**) with BrCN in the presence of triethylamine and subsequently with various aldehydes **2** afforded **3** in two steps (Scheme 1). The reaction mechanism for the synthesis of **3** is shown in Scheme 2. First, the reaction of dimedone (**1**) with BrCN and triethylamine gives the salt of triethylammonium 1-bromo-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**4**).[24] The reaction mechanism and structural elucidation of **4** is already described by our research group.[24] The nucleophilic attack of **4** to the carbonyl group in **2** produces the intermediate **5**, then intramolecular nucleophilic attack of oxygen anion to carbon atom containing bromine atom (pushing the bromide ion out) gives 2,6,6-trimethyl-1-oxaspiro[2.5]octane-4,8-dione **6**. The intramolecular rearrangement in **6** affords **3**. The results of these reactions are summarized in Table 1.

Representatively, the ^{1}H NMR spectrum of **3a** showed a singlet at δ = 1.07 (a shoulder on the right side of the peak) for geminal methyl protons, a singlet at δ = 2.17 (for the methyl protons of acetyl), and two singlets at δ = 2.23 and 2.37 (the latter had a shoulder on the left side of the peak) for two methylene protons of dimedone ring moiety. Apparently a singlet at δ = 5.87 corresponded to a CH proton. Essentially this peak was not a singlet and showed three singlets at δ = 5.861, 5.865, and 5.869. The expanded peak of CH is shown in Figure 1. ^{13}C NMR spectrum of this compound showed three peaks for carbonyl groups at δ = 199.4, 168.0, and 167.4 and surprisingly, five distinct peaks for CH carbon atom at δ = 117.9, 117.0, 116.4, 115.9, and 115.0. It seems that two methyl groups have non-equivalent chemical shifts on dimedone ring moiety and this was also true for the two methylene groups. The comparison of the ^{1}H and ^{13}C NMR peaks of CH in **3a** and **3e** is shown in Figure 1.



Scheme 1



Scheme 2

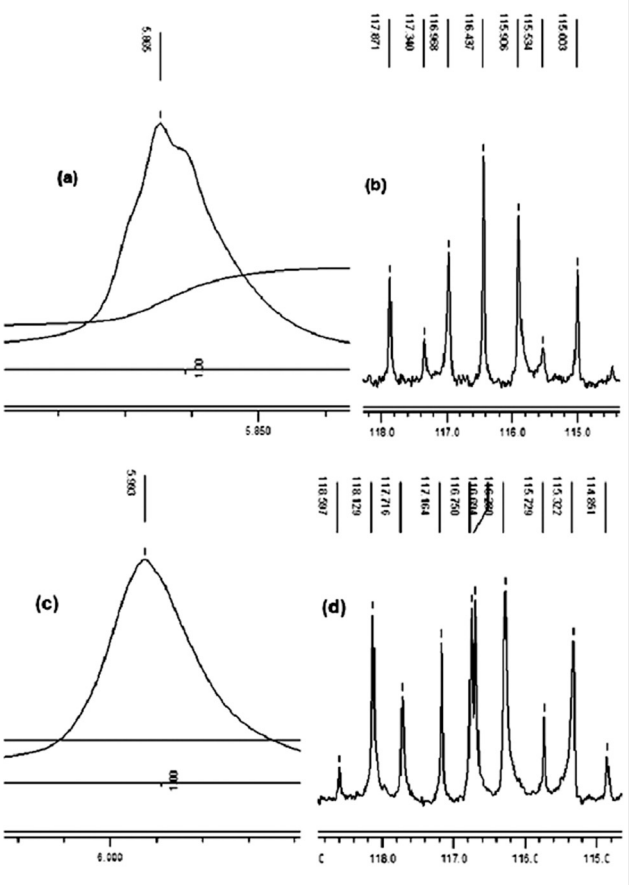
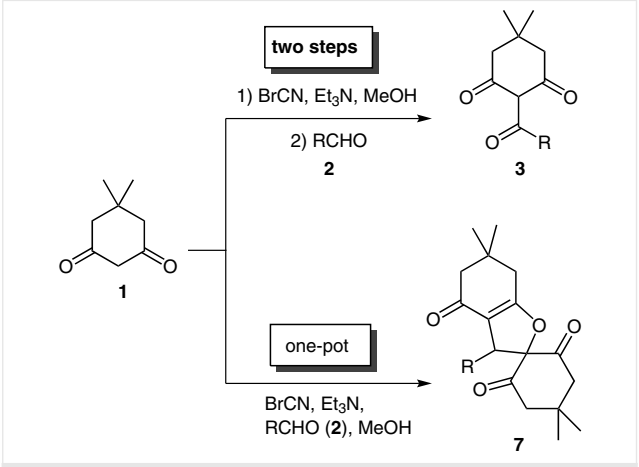


Figure 1 The expanded peaks of CH proton in ^{1}H NMR (a) and CH carbon atom in ^{13}C NMR spectrum (b) in **3a**, and ^{1}H NMR (c) and ^{13}C NMR spectrum (d) of **3e**



Scheme 3

Interestingly, when this reaction was carried out as a one-pot reaction, 4′,4′,6,6-tetramethyl-3-(alkyl and/or aryl)-3,5,6,7-tetrahydrospiro[benzofuran-2(4*H*),1′-cyclohexane]-2′,4,6′-trione **7** was obtained as the sole product.[24] In contrast, when we prepared and separated the salt **4** (see Scheme 2) its reaction with aldehydes **2** gave 2-alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones **3** in good yields (Scheme 3).

Aldehydes consisting of strong electron-donor substituents did not give the cyclic β-triketones **3** under the same conditions. Strong electron-donor substituents inactivate the aldehyde carbonyl group by resonance effect[25] (Table 1, entries 11–14). We examined the reaction of acetone as a ketone with the salt **4** under the same conditions and observed that no reaction occurred probably due to the hindrance effect of ketone compared to aldehyde (entry 15).

Table 1 Reaction of Dimedone (**1**) with Various Aldehydes **2** Producing Cyclic β-Triketones **3** via the Salt **4**

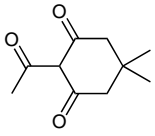
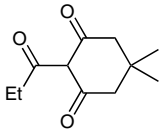
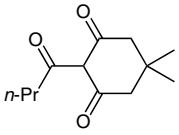
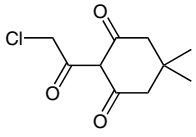
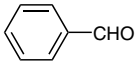
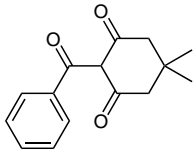
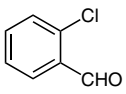
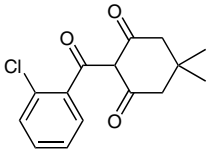
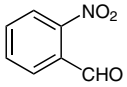
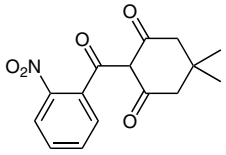
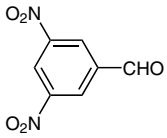
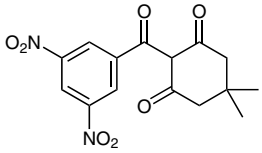
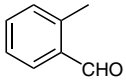
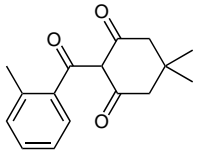
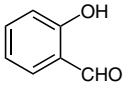
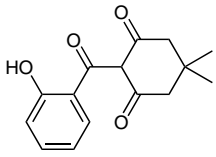
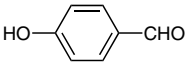
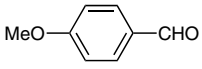
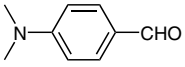
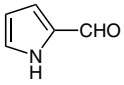
Entry	Aldehyde **2**		Cyclic β-triketone **3**		Mp (°C)	Yield (%)
1	**2a**	MeCHO	**3a**		36[22,26]	50
2	**2b**	EtCHO	**3b**		48[26]	50
3	**2c**	*n*-PrCHO	**3c**		69[26]	40
4	**2d**	$ClCH_2CHO$	**3d**		–[a26]	15
5	**2e**		**3e**		–[a26]	75
6	**2f**		**3f**		–[a26]	75

Table 1 (continued)

Entry	Aldehyde **2**	Cyclic β-triketone **3**	Mp (°C)	Yield (%)
7	**2g** 	**3g** 	118[26]	45
8	**2h** 	**3h** 	130[26]	50
9	**2i** 	**3i** 	120[26]	75
10	**2j** 	**3j** 	–[a26]	45
11	**2k** 	NR[b]	–	–
12	**2l** 	NR	–	–
13	**2m** 	NR	–	–
14	**2n** 	NR	–	–
15	**2o** 	NR	–	–

[a] A viscous solid was obtained. Many of these compounds are commercially available.
[b] NR: No reaction.

In summary, a new route has been introduced for the synthesis of 2-alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones **3** as cyclic β-triketones. This is conducted by the reaction of dimedone (**1**) with cyanogen bromide and triethylamine to form the salt **4**, followed by the addition of various aliphatic and aromatic aldehydes **2**. Aliphatic and aromatic aldehydes including electron-withdrawing substituents formed cyclic β-triketones. Aromatic aldehydes including strong electron-donor substituents did not form cyclic β-triketones.

The drawing and nomenclature of the compounds were done by ChemDraw Ultra version 8.0. Melting points were measured with a digital melting point apparatus (Electrothermal) and are uncorrected. IR spectra were recorded in the region 4000–400 cm^{-1} on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on Bruker 300 FT-NMR at 300 and 75 MHz, respectively (Urmia University, Urmia, Iran). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as internal standard. Standard abbreviations were used to denote the signal multiplicities. Coupling constants are in hertz. All reactions were monitored by TLC with silica gel-coated plates. BrCN was synthesized based on the literature report.[27] Compounds **1**, **2**, Et_3N, and solvents were purchased from Merck and Aldrich and used without further purification.

Triethylammonium 2-Bromo-5,5-dimethylcyclohexane-1,3-dione-2-ide (4)[24]

In a 25 mL round bottom flask equipped with a magnetic stirrer was placed BrCN (106 mg, 1.0 mmol) in MeOH (5 mL) and the flask was immersed in an ice-bath. In a separate vessel, dimedone (**1**; 140 mg, 1.0 mmol) and Et_3N (101 mg, 1.0 mmol) were dissolved in MeOH (5 mL). Then, the latter solution was added dropwise to the solution of BrCN at 0 °C. The salt **4** formed was collected by suction filtration; yield: 223 mg (70%); colorless crystalline solid; mp 75–76 °C.

FT-IR (KBr): 3417, 2958, 2870, 2678, 2495, 1644, 1610, 1509, 472 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 6 H, $C(CH_3)_2$], 1.17 [t, *J* = 7.5 Hz, $(CH_3CH_2)_3NH^+$, 9 H], 2.18 (s, 4 H, 2 × CH_2CO), 3.02 [q, *J* = 7.5 Hz, $(CH_3CH_2)_3NH^+$, 6 H], 7.27 (br s, 1 H, $(CH_3CH_2)_3NH^+$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.0 (C=O), 96.7 (CBr), 50.2 [$(CH_3CH_2)_3NH^+$], 46.2 (CH_2CO), 31.7 [$C(CH_3)_2$], 28.3 [$C(CH_3)_2$], 8.7 ($CH_3CH_2)_3NH^+$).

2-Alkanoyl(aryloyl)-5,5-dimethylcyclohexane-1,3-diones 3; General Procedure

In a 25 mL round bottom flask equipped with a magnetic stirrer was placed the salt **4** (321 mg, 1.0 mmol) and dissolved immediately in DMF (5 mL). Aldehyde **2** (1.0 mmol) was then added and the reaction mixture was stirred for 24 h. The reaction progression was monitored by TLC [eluent: *n*-hexane–EtOAc (3:1, v/v)]. After completion of the reaction, H_2O was added, the mixture was extracted with EtOAc (3 × 2 mL), and the combined organic layers were washed with brine. The organic phase was dried with Na_2SO_4, filtered, and the solvent was evaporated. The solvent was removed under reduced pressure, the residue was washed with cold EtOH, and dried.

2-Acetyl-5,5-dimethylcyclohexane-1,3-dione (3a)

Yield: 0.091 g (50%); brown solid; mp 36 °C.

FT-IR (KBr): 2956, 2888, 1770, 1669, 1365, 1189, 1118 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.065, 1.060 [2 s, 6 H, $C(CH_3)_2$, overlapped], 2.17 (s, 3 H, $COCH_3$), 2.23 (s, 2 H, $COCH_2$), 2.37 (s, 2 H, $COCH_2$), 5.861, 5.865, 5.869 [3 s, 1 H, $CH(C=O)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4 (C=O), 168.0 (C=O), 167.4 (C=O), 117.6, 117.0, 116.4, 115.9, 115.0 [$CH(C=O)_3$], 50.7, 42.2 ($COCH_2$), 33.1 [$C(CH_3)_2$], 28.8, 27.4 [$C(CH_3)_2$].

5,5-Dimethyl-2-propionylcyclohexane-1,3-dione (3b)

Yield: 0.098 g (50%); brown solid; mp 48 °C.

FT-IR (KBr): 2958, 2889, 1768, 1671, 1358, 1121 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 [2 s, 6 H, $C(CH_3)_2$, overlapped], 1.14 (t, *J* = 7.5 Hz, CH_3CH_2, 3 H), 2.21 (s, 2 H, $COCH_2$), 2.36 (s, 2 H, $COCH_2$), 2.44 (q, *J* = 7.5 Hz, CH_3CH_2, 2 H), 5.84 [3 s, 1 H, $CH(C=O)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3 (C=O), 171.0 (C=O), 168.2 (C=O), 117.746, 116.889, 116.309, 115.733, 114.873 [$CH(C=O)_3$], 50.75, 42.15 ($COCH_2$), 33.05 ($COCH_2CH_3$), 28.77 [$C(CH_3)_2$], 27.76, 27.34 [$C(CH_3)_2$], 9.40, 7.94 ($COCH_2CH_3$).

5,5-Dimethyl-2-butanoylcyclohexane-1,3-dione (3c)

Yield: 0.084 g (40%); brown solid; mp 69 °C.

FT-IR (KBr): 2958, 2887, 1766, 1672, 1362, 1121 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.5 Hz, $CH_3CH_2CH_2$, 3 H), 0.99 [2 s, 6 H, $C(CH_3)_2$, overlapped], 1.59 (sext, *J* = 7.2 Hz, $CH_3CH_2CH_2$, 2 H), 2.14 (s, 2 H, $COCH_2$), 2.29 (s, 2 H, $COCH_2$), 2.33 (t, *J* = 7.2 Hz, $CH_3CH_2CH_2$, 3 H), 5.76 [3 s, 1 H, $CH(C=O)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1 (C=O), 170.1 (C=O), 168.1 (C=O), 117.65, 116.83, 116.30, 116.21, 115.68, 114.87 [$CH(C=O)_3$], 50.68, 42.09 ($COCH_2$), 36.09, 36.03 ($COCH_2CH_2CH_3$), 32.98 [$C(CH_3)_2$], 28.71, 27.29 [$C(CH_3)_2$], 17.98, 16.77 ($COCH_2CH_2CH_3$), 14.16 ($COCH_2CH_2CH_3$), 12.54 ($COCH_2CH_2CH_3$).

2-(2-Chloroacetyl)-5,5-dimethylcyclohexane-1,3-dione (3d)

Yield: 0.032 g (15%); brown viscous solid.

FT-IR (KBr): 2941, 1736, 1663, 1451, 1375, 1235, 1123, 744 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 [s, 6 H, $C(CH_3)_2$], 1.83 (m, 2 H, $CO-CH_2$), 2.24–2.46 (m, 4 H, $COCH_2$ and $COCH_2Cl$), 5.98 [s, 1 H, $CH(C=O)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2 (C=O), 177.2 (C=O), 116.4, 111.7 [$CH(C=O)_3$], 75.9, 62.2 ($COCH_2Cl$), 50.6 ($COCH_2$), 34.3 ($COCH_2$), 29.02 [$C(CH_3)_2$], 27.8, 27.5 [$C(CH_3)_2$].

2-Benzoyl-5,5-dimethylcyclohexane-1,3-dione (3e)

Yield: 0.183 g (75%); brown viscous solid.

FT-IR (KBr): 3068, 2956, 2886, 1742, 1668, 1365, 1250, 1120, 703 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.086, 1.080 [2 s, 6 H, $C(CH_3)_2$, overlapped], 2.25 (s, 2 H, $COCH_2$), 2.49 (s, 2 H, $COCH_2$), 5.99 [s, 1 H, $CH(C=O)_3$], 7.42 (t, *J* = 7.2 Hz, 2 H_{arom}), 7.57 (t, *J* = 7.2 Hz, 1 H_{arom}), 8.01 (d, *J* = 7.2 Hz, 2 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2 (C=O), 168.4 (C=O), 163.2 (C=O), 134.97, 133.20, 131.15, 131.08, 129.78, 129.70, 129.19, 129.11, 128.68, 128.60, 127.65, 127.58 (C_6H_5), 118.13, 117.72, 117.16, 116.75, 116.69, 116.28, 115.73, 115.32 [$CH(C=O)_3$], 50.8, 42.2 ($COCH_2$), 33.2 [$C(CH_3)_2$], 28.9, 27.4 [$C(CH_3)_2$].

2-(2-Chlorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (3f)

Yield: 0.209 g (75%); brown viscous solid.

FT-IR (KBr): 3073, 2956, 2886, 1750, 1668, 1441, 1365, 1276, 1236, 1119, 1024, 741 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.116, 1.132 (2 s, 6 H, $C(CH_3)_2$), 2.297 (s, 2 H, $COCH_2$), 2.532 (s, 2 H, $COCH_2$), 6.02 [s, 1 H, $CH(C=O)_3$], 7.31–7.36 (m, 1 H_{arom}), 7.46 (d, J = 3.9 Hz, 2 H_{arom}), 7.89 (d, J = 7.5 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2 (C=O), 168.1 (C=O), 161.9 (C=O), 134.86, 134.75, 134.50, 133.09, 133.06, 132.62, 132.58, 130.99, 130.94, 130.39, 130.34, 127.88, 125.85, 125.81 (CH_{arom} and C_{arom}), 118.31, 117.93, 117.32, 116.94, 116.88, 116.50, 115.51 [$CH(C=O)_3$], 50.9 ($COCH_2$), 42.1 ($COCH_2$), 33.2 [$C(CH_3)_2$], 28.9, 27.4 [$C(CH_3)_2$].

2-(2-Nitrobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (3g)

Yield: 0.130 g (45%); white solid; mp 118 °C.

FT-IR (KBr): 3086, 2956, 2880, 1757, 1672, 1536, 1358, 1247, 1116, 1046 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 [s, 6 H, $C(CH_3)_2$], 2.33 (s, 2 H, $CO-CH_2$), 2.58 (s, 2 H, $COCH_2$), 6.06 [s, 1 H, $CH(C=O)_3$], 7.73–7.80 (m, 3 H_{arom}), 8.04 (d, *J* = 7.2 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.13 (C=O), 167.76 (C=O), 162.23 (C=O), 147.00, 132.58, 132.35, 131.62, 131.27, 131.19, 129.14, 125.31, 123.29 (CH_{arom} and C_{arom}), 118.43, 118.09, 116.99, 116.66, 115.62 [$CH(C=O)_3$], 50.91 ($COCH_2$), 41.26 ($COCH_2$), 33.25 [$C(CH_3)_2$], 28.87, 27.43 [$C(CH_3)_2$].

2-(3,5-Dinitrobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (3h)

Yield: 0.167 g (50%); white solid; mp 130 °C.

FT-IR (KBr): 3096), 2947, 2887, 1748, 1665, 1542, 1346, 1263, 1144, 725 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.20 [s, 6 H, $C(CH_3)_2$], 2.37 (s, 2 H, $COCH_2$), 2.60 (s, 2 H, $COCH_2$), 6.12 [s, 1 H, $CH(C=O)_3$], 9.21 (d, *J* = 1.8 Hz, 2 H_{arom}), 9.30 (dd, *J* = 2.1, 1.8 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.63 (C=O), 167.00 (C=O), 159.50 (C=O), 148.86, 132.42, 130.89, 129.91, 129.74, 128.76, 123.34, 123.20 (CH_{arom} and C_{arom}), 119.02, 118.71, 117.59, 116.47, 116.16 [*C*H(C=O)$_3$], 50.79 ($COCH_2$), 42.05 ($COCH_2$), 33.37 [*C*$(CH_3)_2$], 28.90, 27.46 [C(*C*$H_3)_2$].

2-(2-Methylbenzoyl)-5,5-dimethylcyclohexane-1,3-dione (3i)

Yield: 0.193 g (75%); brown solid; mp 120 °C.

FT-IR (KBr): 3065, 2958, 2888, 1742, 1670, 1460, 1369, 1234, 1119, 1023, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.08 [s, 6 H, $C(CH_3)_2$], 2.24 (s, 2 H, $COCH_2$), 2.48 (s, 2 H, $COCH_2$), 2.61 (s, 3 H, Ar*CH*$_3$), 5.97 [s, 1 H, $CH(C=O)_3$], 7.22 (m, 2 H_{arom}), 7.39 (s, *J* = 7.8 Hz, 1 H_{arom}), 7.93 (d, *J* = 7.8 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.06 (C=O), 168.47 (C=O), 163.56 (C=O), 141.52, 141.44, 134.32, 134.28, 134.23, 133.06, 132.21, 132.13, 131.04, 130.23, 130.15, 127.43, 127.03 (CH_{arom} and C_{arom}), 118.09, 117.64, 117.22, 116.77, 116.65, 116.20, 115.34 [*C*H(C=O)$_3$], 50.82 (CO*C*H_2), 42.26, 41.19 ($COCH_2$), 33.13 [*C*$(CH_3)_2$], 28.87, 27.39 [C(*C*$H_3)_2$], 21.92 (Ar*C*H_3).

2-(2-Hydroxybenzoyl)-5,5-dimethylcyclohexane-1,3-dione (3j)

Yield: 0.117 g (45%); brown viscous solid.

FT-IR (KBr): 3460, 3243, 3075, 2956, 2888, 1744, 1682, 1610, 1475, 1283, 1246, 1204, 1119, 1042, 751 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.91, 0.98 [2 s, 6 H, $C(CH_3)_2$, the peak at 0.98 ppm has a shoulder at the peak's left side), 2.18–2.33 (m, 4 H, 2 × $COCH_2$), 5.92 [s, 1 H, $CH(C=O)_3$], 6.98–8.24 (m, 4 H_{arom}), 10.29 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.35, 199.15 (C=O), 168.69, 168.02 (C=O), 162.51, 162.01, 161.11, 160.95 (C=O), 150.48 (ArC–OH), 137.46, 135.90, 135.39, 133.53, 131.59, 129.72, 129.62, 127.92, 127.34, 125.38, 123.16, 122.53, 122.32 (CH_{arom} and C_{arom}), 120.42, 118.62, 118.16, 117.30, 116.79, 116.17, 115.36 [*C*H(C=O)$_3$], 51.23 (CO*C*H_2), 41.94 ($COCH_2$), 33.01 [*C*$(CH_3)_2$], 28.66, 27.25 [C(*C*$H_3)_2$].

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561935. Spectroscopic data are supplied for compounds **3a**–**j**.

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