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F. Jiménez-Cruz [a], L. A. Maldonado [a], R. Cetina [a] & H. Ríos-Olivares [a]

[a] Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior. Ciudad Universitaria, Coyoacán, 04510 México, D.F, MEXICO

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SYNTHESIS OF 1-ARYL-1,3-DIKETONES CONTAINING THE DIMETHYL MALONATE MOIETY. §

F. Jiménez-Cruz,* L. A. Maldonado, R. Cetina and H. Ríos-Olivares

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior.
Ciudad Universitaria, Coyoacán, 04510 México, D.F, MEXICO.

Abstract: The synthesis of new 1,3-diketones malonates **3 a-j** were prepared in good yield from 1,5-diketones **2 a-j** by employing the 1,5 → 1,3 diketone rearrangement.

1,3-Diketones are compounds of great interest in organic synthesis.[1] They have been used in the preparation of heterocycles and metals complexes.[2] They are interesting physicochemical models, the tautomeric equilibrium was studied in detail,[3] reaction with alkylendiamines gives tautomeric β-diketone diimines,[4] and metal chelates have been prepared with these Schiff's bases.[5] The widespread methods for the synthesis of 1,3-diketones are based on Claisen condensations

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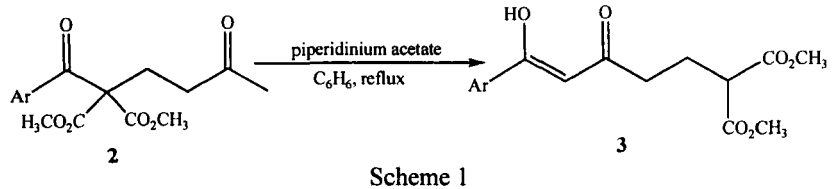
* To whom correspondence should be addressed. E-mail: fjimenez@servidor.unam.mx

between an ester and ketone enolates,[6a] Stork enamine acylation,[6b] Vilsmeier acylation of ketals,[6c] or rearrangement of epoxy ketones with Pd (0) catalyst.[6d]

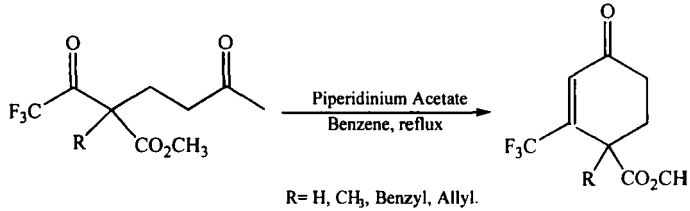
We have previously reported a simple rearrangement of the 1,5-diketones **2** into the strongly enolic 1,3-diketone malonates **3** with piperidinium acetate[7] (Scheme 1).



2 **3**

Scheme 1

It should be noticed that these conditions are well known for the cyclization of 1,4- or 1,5-diketones to enones by consecutive aldol and dehydration reactions.[8] For instance, 1-CF_3-1,5-diketones related to **2** (with only one CO_2CH_3 in the molecule) give 3-CF_3-cyclohexenones in good yield[9] (Scheme 2). However, with substrates such as **2** this was not the case, 1,3-diketones **3** were obtained instead.[7]

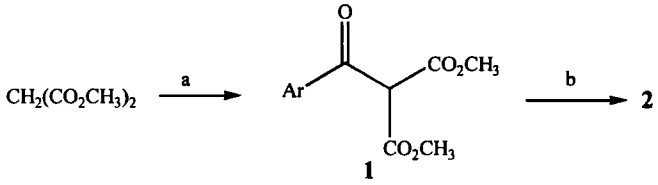


R= H, CH_3, Benzyl, Allyl.

Scheme 2

In this communication we report the preparation of new 1,5-diketones **2 a-j** and the corresponding 1,3-diketones **3 a-j**. The starting materials, compounds **1**, were obtained by C-aroylation of the sodium dimethyl malonate anion with the corresponding aroyl chlorides in THF at room temperature. Further base catalyzed Michael addition of acylmalonates **1** to methylvinyl ketone (MVK) led to the 1,5-

diketones **2**. Triton B was a convenient base catalyst for this reaction with the exception of **2 j** which gave a better yield with Et_3N (Scheme 3).



Ar= 4-X-C_6H_4, X: **a** = H, **b** = F, **c** = Cl, **d** = Br, **e** = OCH_3

f = CH_3, **g** = $C(CH_3)_3$, **h** = CF_3, **i** = C_6H_5, **j** = NO_2

a.ArCOCl, NaH, THF, N_2 b. MVK, Triton B, THF, N_2

Scheme 3

After the chromatography purification of 1,5-diketones **2**, these were refluxed with piperidinium acetate in benzene to afford the corresponding 1,3-diketones **3** (Scheme 1). Reaction times (monitored by TLC) and yields for these transformations are outlined in Table 1.

^{1}H- and ^{13}C-NMR spectra for **2 a-j** and **3 a-j** confirmed the proposed structures (See experimental part). The ^{1}H-NMR spectra of diketones **3** exhibited singlets at δ 6.1-6.2 ppm and 15.7-16.1 ppm (broad) for the vinylic proton and the

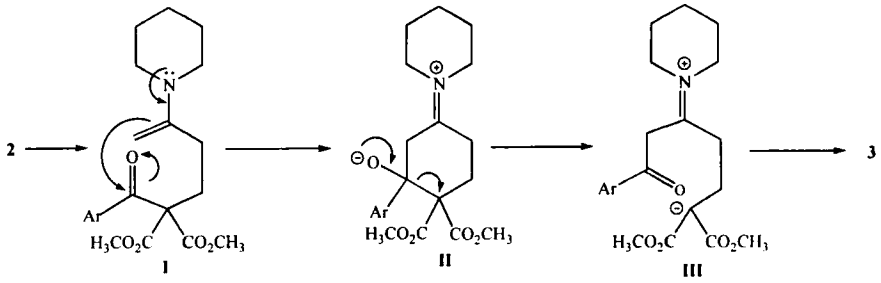
Table 1. Yields and reaction times for the synthesis of compounds **1**, **2** and **3**.

Entry	time (h)	Yield (%)	2	Time (h)	Yield (%)	3	time (h)	Yield (%)
1-a	3.0	87	**2-a**	48	80	**3-a**	24	60
1-b	2.5	85	**2-b**	24	81	**3-b**	18	60
1-c	2.5	88	**2-c**	24	78	**3-c**	24	62
1-d	3.0	61	**2-d**	24	66	**3-d**	48	57
1-e	3.0	72	**2-e**	48	67	**3-e**	48	55
1-f	3.0	90	**2-f**	48	88	**3-f**	48	51
1-g	3.0	92	**2-g**	48	89	**3-g**	48	56
1-h	2.5	89	**2-h**	24	85	**3-h**	24	47
1-i	3.0	92	**2-i**	24	88	**3-i**	24	51
1-j	2.5	87	**2-j**	72	64	**3-j**	24	41

OH proton of the tautomeric enol, respectively. In addition, a singlet at δ 3.7-3.8 ppm for the methyl esters and a triplet at δ 3.5-3.6 ppm for the CH proton of the malonate moiety are observed. The triplet at 2.5-2.6 ppm and the quartet at δ 2.2-2.3 ppm were attributed to the methylenes linked to the **CO** and malonate groups, respectively. The aryl group was confirmed for each particular substituent. The ^{13}C-NMR signals were assigned with the aid of DEPT experiments. Due to the unsymmetrical characteristics of 1,3-diketones **3**, two keto-enol tautomerisms are conceivable, and in fact the ^{13}C-NMR spectra of these compounds showed two ketone carbonyl signals at δ 180-195 ppm. However, only one signal at approximately δ 96 ppm is observed for the vinyl proton of the enolic forms.

In striking contrast to compounds **3**, the electron impact mass spectra (EIMS) of 1,5-diketones **2** failed to show the corresponding molecular ion peaks. Apparently, the strong ionization conditions under electronic impact allowed the easy rupture of the weak carbonyl-malonate moiety bond. Anyway, they were observed if spectra were recorded under chemical ionization techniques.

The reaction mechanism for this interesting rearrangement has not been elucidated, but one can reasonably assume (Scheme 4) that after enamine **I** formation and intramolecular aldol type cyclization, the intermediate iminium alkoxide **II** suffers a retroaldol, malonate-assisted cleavage to give intermediate **III**. Protonation and hydrolysis of the iminium ion completes the sequence of events to **3**. We are currently studying this reaction mechanism by experimental and theoretical methods.



Scheme 4

The presence of the 1,3 diketone and malonate functionalities in compounds **3** suggests a plethora of potentially useful transformations on these substrates (e.g. alkylation and Michael addition reactions; heterocycle and enaminone formation) and we are working in these possibilities.

In summary, we report an easy synthesis of several 1,5-(**2**) and 1,3-diketones **3** in good yields from accessible reagents.

EXPERIMENTAL

NMR spectra were recorded on Varian Gemini 200 or Varian VXR 300 spectrometers with TMS as internal standard in $CDCl_3$. IR spectra were carried out on a FT-Nicolet SX. Low and high resolution mass spectra were obtained on a JEOL JMS-AX 505 mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc. All reagents were purchased from Aldrich Inc. Melting points were obtained in a Fisher-Johns apparatus and are uncorrected. All reactions were run under an inert atmosphere of nitrogen. Tetrahydrofuran and benzene were distilled from sodium-benzophenone ketyl. The reactions were monitored by TLC using silica gel plates with 254 nm fluorescent indicator from Merck and visualized by ultraviolet light and iodine vapors. The Still procedure[10]

for flash chromatography was followed using Aldrich Silica Gel 200-400 mesh as stationary phase.

General Procedure for the acylation of dimethyl malonate: To a cold (ice bath) suspension of sodium hydride (0.276 mol) in dry THF (90 mL) was added dropwise a solution of dimethyl malonate (0.230 mol) in 90 ml of THF with magnetic stirring. Evolution of H_2 was observed and it was necessary a purge valve outlet. To the resulting white suspension is slowly added a solution of aroyl chloride (0.230 mol) in 90 mL of dry THF. Then the mixture was stirred for 3 h, poured into dilute HCl (200 mL) and extracted with dichloromethane (3 x 200 mL). The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated under reduced pressure and the residue used without purification in the next reaction.

Dimethyl 2-benzoyl malonate 1-a: IR (KBr) ν (cm^{-1}): 2850 (w), 1739 (s), 1689 (s), ^{1}H NMR δ (ppm): 7.62-7.37 (m, 5H) H in Ph, 5.35 (s, 1H, C***H***), 3.79 (s, 6H, C***H***$_3$OCO).

Dimethyl 2-(4-fluorobenzoyl) malonate 1-b: IR (KBr) ν (cm^{-1}): 2963 (w), 1740 (s), 1692 (s), ^{1}H NMR δ (ppm): 7.95 (dd, J= 5, 9 Hz, 2H), 7.17 (dd, J=9, 9 Hz, 2H), 5.29 (s, 1H) C***H***, 3.81 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-(4-chlorobenzoyl) malonate 1-c: IR (KBr) ν (cm^{-1}): 2955 (w), 1738 (s), 1693 (s), ^{1}H NMR δ (ppm): 7.85 (d, J= 8 Hz, 2H), 7.47 (d, J=8 Hz, 2H), 5.27 (s, 1H) C***H***, 3.81 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-(4-bromobenzoyl) malonate 1-d: IR (KBr) ν (cm^{-1}): 2956 (w), 1738 (s), 1687 (s), ^{1}H NMR δ (ppm): 7.80 (d, J= 8.62 Hz, 2H), 7.47 (d, J=8.62 Hz, 2H), 5.31 (s, 1H) C***H***, 3.81 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-(4-methoxybenzoyl) malonate 1-e: IR (KBr) ν (cm^{-1}): 2958 (w), 1728 (s), 1678 (s); ^{1}H NMR δ (ppm): 7.89 (d, J= 9.12 Hz, 2H), 6.95 (d, J= 9.12 Hz, 2H), 5.29 (s, 1H) C***H***, 3.87 (s, 3H) C***H***$_3$OAr, 3.79 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-p-toluoyl malonate 1-f: IR (KBr) ν (cm^{-1}): 2958 (w), 1739 (s), 1688 (s), ^{1}H NMR δ (ppm): 7.80 (d, J= 8 Hz, 2H), 7.28 (d, J=8 Hz, 2H), 5.32 (s, 1H) C***H***, 3.80 (s, 6H) C***H***$_3$OCO, 2.42 (s, 3H) C***H***$_3$Ar

Dimethyl 2-(4-terbutylbenzoyl) malonate 1-g: IR (KBr) ν (cm^{-1}): 2956 (w), 1741 (s), 1690 (s), ^{1}H NMR δ (ppm): 7.85 (d, J= 8 Hz, 2H), 7.50 (d, J=8 Hz, 2H), 5.33 (s, 1H) C***H***, 3.81 (s, 6H) C***H***$_3$OCO, 1.34 (s, 9H) (C***H***$_3$)$_3$Ar.

Dimethyl 2-(4-trifluoromethyl benzoyl) malonate 1-h: IR (KBr) ν (cm^{-1}): 2958 (w), 1740 (s), 1702 (s), ^{1}H NMR δ (ppm): 8.01 (d, J= 8 Hz, 2H), 7.76 (d, J=8 Hz, 2H), 5.31 (s, 1H) C***H***, 3.82 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-(4-phenyl benzoyl) malonate 1-i: IR (KBr) ν (cm^{-1}): 2956 (w), 1739 (s), 1688 (s), ^{1}H NMR δ (ppm): 7.98 (d, J= 8 Hz, 2H), 7.71 (d, J=8 Hz, 2H), 7.65-7.41 (m., 5H), 5.37 (s, 1H) C***H***, 3.83 (s, 6H) C***H***$_3$OCO.

Dimethyl 2-(4-nitrobenzoyl) malonate 1-j: IR (KBr) ν (cm^{-1}): 2958 (w), 1759 (s), 1693 (s), 1539 (s), 1350 (s). ^{1}H NMR δ (ppm): 8.04 (d, J= 10 Hz, 2H), 7.72 (d, J=10 Hz, 2H), 5.28 (s, 1H) C***H***, 3.74 (s, 6H) C***H***$_3$OCO.

General procedure for the preparation of 2 a-j: A solution of **1** (0.2 mol) in 200mL of dry tetrahydrofurane was treated with a solution of Triton B in MeOH (40 % wt) (0.1 eq). After 5 min., freshly distilled MVK (0.219 mol) was added to the resulting yellow solution, and stirring was continued for 24 h. The reaction mixture was poured into dilute HCl (pH=2) and extracted with dichlorometane (3 x 200 mL), the combined extracts were washed with water (3 x 200 mL), brine (200 mL) and dried over anhydrous sodium sulfate. After removal the solvent under vacuum, the crude residues was crystallized from ethyl acetate-hexanes to afford compounds **2**. In the case of **2-j** the same procedure was followed out but with triethylamine (0.4 eq) as base and the mixture was stirred for 48 h.

Dimethyl 2-benzoyl-2-(3-oxobutyl) malonate 2-a: m.p.70-72 °C, IR (KBr) ν (cm^{-1}): 2957 (w), 1766 (s), 1723 (s), 1688 (s); ^{1}H NMR δ (ppm) : 7.81 (dd, 2H, J= 8.5, 1.5 Hz), 7.6-7.4 (m, 3H) m- and p- H, 3.74 (s, 6H) C***H***$_3$OCO, 2.71-2.53 (m, 4H) C***H***$_2$C***H***$_2$, 2.13 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.8, 191.9, 168.3, 135.3, 133.2, 128.7, 128.5, 67.7, 53.0, 39.0, 29.9, 27.7; MS (CI$^+$) m/z: M$^+$+1 307, 105

(100%), 237, 205, 145. Anal. Calcd. for $C_{16}H_{18}O_6$: C 62.74, H 5.92. Found C 62.66, H 5.94.

Dimethyl 2-(4-fluorobenzoyl)-2-(3-oxobutyl) malonate 2-b: m.p.60-62 °C, IR (KBr) ν (cm^{-1}): 2959 (w), 1767 (s), 1722 (s), 1690 (s); ^{1}H NMR δ (ppm): 7.86 (dd, 2H, J= 9.0 Hz, J_{HF}= 5.2 Hz), 7.10 (dd, 2H, J= 9.0 Hz, J_{HF}= 9.0 Hz), 3.74 (s, 6H) C***H***$_3$OCO, 2.67-2.52 (m, 4H) C***H***$_2$C***H***$_2$, 2.13 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.6, 190.2, 168.2, 165.5, 132.3, 131.5, 115.7 (J_{CF} in Hz: 3.37, 8.7, 21.8, 254.4) 67.7, 53.1, 38.9, 29.8, 27.7; MS (CI^+) m/z: M^++1 325, 123 (100 %), 255, 223, 145. Anal. Calcd. for $C_{16}H_{17}FO_6$: C 59.26, H 5.28, F 5.86. Found C 59.37, H 5.36, F 5.46.

Dimethyl 2-(4-chlorobenzoyl)-2-(3-oxobutyl) malonate 2-c: m.p. 167-170 °C, IR (KBr) ν (cm^{-1}): 2953 (w), 1770 (s), 1722 (s), 1691 (s); ^{1}H NMR δ (ppm): 7.76 (d, 2H, J= 9.00 Hz), 7.42 (d, 2H, J= 9.00 Hz), 3.74 (s, 6H) C***H***$_3$OCO, 2.66-2.51 (m, 4H) C***H***$_2$C***H***$_2$, 2.13 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.6, 190.5, 168.1, 139.7, 133.7, 130.1, 128.8, 67.6, 53.0, 38.8, 29.8, 27.6; MS (CI^+) m/z: M^++1 341, 139 (100 %), 271, 239, 145.

Dimethyl 2-(4-bromobenzoyl)-2-(3-oxobutyl) malonate 2-d: m.p.68-70 °C, IR (KBr) ν (cm^{-1}): 2955 (w), 1776 (s), 1714 (s), 1691 (s); ^{1}H NMR δ (ppm): 7.69 (d, 2H, J= 9.00 Hz), 7.57 (d, 2H, J= 9.00 Hz), 3.74 (s, 6H) C***H***$_3$OCO, 2.67-2.53 (m, 4H) C***H***$_2$C***H***$_2$, 2.12 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.6, 190.8, 168.1, 134.1, 131.9, 130.2, 128.5, 67.6, 53.2, 38.9, 29.9, 27.6; MS (CI^+) m/z: M^++1 385-387, 183-185 (100 %), 315-317, 283-285, 145. Anal. Calcd. for $C_{16}H_{17}BrO_6$: C 49.89, H 4.45, Br 20.74. Found C 50.70, H 4.71, Br 20.34.

Dimethyl 2-(4-methoxybenzoyl)-2-(3-oxobutyl) malonate 2-e: m.p.60-62 °C, IR (KBr) ν (cm^{-1}): 2956 (w), 1774 (s), 1716 (s), 1690 (s); ^{1}H NMR δ (ppm): 7.81 (d, 2H, J= 9.00 Hz), 6.90 (d, 2H, J= 9.00 Hz), 3.87 (s, 3H) C***H***$_3$O, 3.74 (s, 6H) C***H***$_3$OCO, 2.67-2.52 (m, 4H) C***H***$_2$C***H***$_2$, 2.12 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.9, 190.0, 168.5, 131.2, 127.9, 116.9, 113.8, 67.6, 55.5, 53.0, 39.0, 29.9, 27.8; MS (CI^+) m/z: M^++1 337, 135 (100 %), 267, 235, 145. Anal. Calcd. for $C_{17}H_{20}O_7$: C 60.71, H 5.99. Found C 60.74, H 6.10.

Dimethyl 2-(4-methylbenzoyl)-2-(3-oxobutyl) malonate 2-f: m.p.40-42 °C, IR (KBr) ν (cm^{-1}): 2955 (w), 1770 (s), 1719 (s), 1686 (s); ^{1}H NMR δ (ppm): 7.71 (d, J= 9.00 Hz), 7.22 (d, J= 9.00 Hz), 3.73 (s, 6H) C***H***$_3$OCO, 2.67-2.54 (m, 4H) C***H***$_2$C***H***$_2$, 2.39 (s, 3H) C***H***$_3$Ph, 2.11 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.7, 191.4, 168.4, 144.2, 132.7, 129.2, 128.9, 67.7, 53.0, 39.0, 29.9, 27.8, 21.6; MS (CI^+) m/z: M^++1 321, 119 (100 %), 251, 219, 145. Anal. Calcd. for $C_{17}H_{20}O_6$: C 63.74, H 6.29. Found C 63.94, H 6.37.

Dimethyl 2-(4-tertbutylbenzoyl)-2-(3-oxobutyl) malonate 2-g: IR (KBr) ν (cm^{-1}): 2958 (w), 1733 (s), 1720 (s), 1687 (s); ^{1}H NMR δ (ppm): 7.75 (d, 2H, J= 9.00 Hz), 7.44 (d, 2H, J= 9.00 Hz), 3.75 (s, 6H) C***H***$_3$OCO, 2.69-2.52 (m, 4H) C***H***$_2$C***H***$_2$,

2.12 (s, 3H) C***H***$_3$CO, 1.33 (s, 9H) (C***H***$_3$)$_3$C; ^{13}C NMR δ (ppm): 206.9, 191.4, 168.5, 148.5, 132.5, 128.8, 125.5, 67.8, 53.0, 39.1, 35.1, 31.1, 29.9, 27.7; MS (CI$^+$) m/z: M$^+$+1 363, 161 (100 %), 293, 261, 145.

Dimethyl 2-(3-oxobutyl)-2-(4-trifluoromethylbenzoyl)- malonate 2-h: m.p.78-80 °C, IR (KBr) ν (cm^{-1}): 2945 (w), 1777 (s), 1716 (s), 1698 (s); ^{1}H NMR δ (ppm): 7.70 (d, 2H, J= 9.00 Hz), 7.92 (d, 2H, J= 9.00 Hz), 3.74 (s, 6H) C***H***$_3$OCO, 2.69-2.55 (m, 4H) C***H***$_2$C***H***$_2$, 2.14 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.5, 191.0, 168.0, 138.4, 134.0, 129.0, 125.5, 125.9 (J_{CF}= 273 Hz) 67.7, 53.2, 38.9, 29.9, 27.6; MS (CI$^+$) m/z: M$^+$+1 375 (100 %), 305, 273, 173, 145. Anal. Calcd. for $C_{17}H_{17}F_3O_6$: C 54.55, H 4.58. Found C 54.64, H 4.57.

Dimethyl 2-(4-phenylbenzoyl)-2-(3-oxobutyl) malonate 2-i: m.p.89-91 °C, IR (KBr) ν (cm^{-1}): 2955 (w), 1771 (s), 1717 (s), 1688 (s); ^{1}H NMR δ (ppm): 7.89 (d, 2H, J= 9.00 Hz), 7.65 (d, 2H, J= 9.00 Hz), 7.62 (dd, 2H,J=1.5, 9.0 Hz), 7.49-7.40 (m, 3H), 3.76 (s, 6H) C***H***$_3$OCO, 2.71-2.58 (m, 4H) C***H***$_2$C***H***$_2$, 2.14 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.8, 191.3, 168.4, 145.9, 139.5, 133.9, 130.7, 129.3, 129.0, 127.2, 127.1, 67.8, 53.1, 39.0, 29.9, 27.8; MS (CI$^+$) m/z: M$^+$+1 383, 181 (100 %), 313, 281, 145. Anal. Calcd. for $C_{22}H_{22}O_6$: C 69.10, H 5.80. Found C 69.44, H 5.79.

Dimethyl 2-(4-nitrobenzoyl)-2-(3-oxobutyl) malonate 2-j: m.p.176-179 °C, IR (KBr) ν (cm^{-1}): 2957 (w), 1748 (s), 1726 (s), 1708 (s), 1523 (s), 1351 (s); ^{1}H NMR δ (ppm): 8.28 (d, 2H, J= 9.00 Hz), 7.98 (d, 2H, J= 9.00 Hz), 3.75 (s, 6H) C***H***$_3$OCO, 2.69-2.52 (m, 4H) C***H***$_2$C***H***$_2$, 2.15 (s, 3H) C***H***$_3$CO; ^{13}C NMR δ (ppm): 206.4, 190.8, 167.8, 150.0, 140.5, 129.8, 123.6, 67.8, 53.4, 38.8, 29.9, 27.5; MS (CI$^+$) m/z: M$^+$+1 352 (100 %), 150, 282, 250, 145. Anal. Calcd. for $C_{16}H_{17}NO_6$: C 54.70, H 4.88. Found C 54.40, H 3.94.

General procedure for the 1,5 → 1,3 diketone rearrangement: To a solution of **2** (0.065 mol) in benzene (160 mL) was added piperidine (0.016 mol) and glacial acetic acid (0.016 mol), and the mixture was refluxed for 24 h. The solvent was removed at reduced pressure and the residue was purified by flash chromatography eluting with hexanes/ethyl acetate 60:40 to give compounds **3**[11].

Dimethyl 2-(3,5-dioxo-5-phenylpentyl) malonate 3-a: see reference 7. Anal. Calcd. for $C_{16}H_{18}O_6$: C 62.74, H 5.92. Found C 62.87, H 6.00.

Dimethyl 2-[5-(4-fluorophenyl)-3,5-dioxopentyl] malonate 3-b: oil, IR (KBr) ν (cm^{-1}): 3400 (w), 2958 (m), 1752 (s), 1734 (s), 1602 (s); ^{1}H NMR δ (ppm): 15.99 (broad s, 1H) O***H*** enol, 7.89 (dd, 2H, 5.4, 9.0 Hz), 7.13 (dd, 2H, 9.0, 9.0 Hz), 6.11

(s, 1H) C*H*=COH, 3.76 (s, 6H) C*H*$_3$OCO, 3.51 (t, 1H, J =7.2 Hz) C*H* $(COOCH_3)_2$, 2.53 (t, 2H, J=7.5 Hz) COC*H*$_2$, 2.29 (q, 2H, J=7.5 Hz) $COCH_2CH_2$; ^{13}C NMR δ (ppm): 194.6, 182.2, 169.4, 165.4 (J_{CF}=252 Hz), 130.9 (J_{CF}=3.0 Hz), 129.4 (J_{CF}=10 Hz), 115.8 (J_{CF}=22 Hz), 95.9, 50.6, 52.7, 36.2, 24.4; MS (EI) m/z : M^+ 324, 306, 165, 123 (100 %). HRMS calcd. for $C_{16}H_{17}FO_6$ 324.1008. Found 324.1009.

Dimethyl 2-[5-(4-chlorophenyl)-3,5-dioxopentyl] malonate 3-c: m.p.53-55 °C, IR (KBr) ν (cm^{-1}): 3400 (w), 2955 (m), 1752 (s), 1735 (s), 1597 (s); ^{1}H NMR δ (ppm): 15.91 (broad s, 1H) O*H* enol, 7.81 (d, 2H, 9.0 Hz), 7.43 (d, 2H, 9.0 Hz), 6.13 (s, 1H) C*H*=COH, 3.76 (s, 6H) C*H*$_3$OCO, 3.50 (t, 1H, J =7.2 Hz) C*H* $(COOCH_3)_2$, 2.54 (t, 2H, J=7.5 Hz) COC*H*$_2$, 2.29 (q, 2H, J=7.5 Hz) $COCH_2CH_2$; ^{13}C NMR δ (ppm): 195.5, 181.4, 169.4, 138.6, 133.0, 128.3, 128.9, 96.2, 50.6, 52.6, 36.4, 24.2; MS (EI) m/e : M^+ 340, 322, 181, 209, 139 (100 %). Anal. Calcd. for $C_{16}H_{17}ClO_6$: C 56.40, H 5.03. Found C 56.43, H 4.98.

Dimethyl 2-[5-(4-bromophenyl)-3,5-dioxopentyl] malonate 3-d: reference 7. Anal. Calcd. for $C_{16}H_{17}BrO_6$: C 49.89, H 4.45, Br 20.74. Found C 50.06, H 4.53, Br 20.44.

Dimethyl 2-[5-(4-methoxyphenyl)-3,5-dioxopentyl] malonate 3-e: reference 7. Anal. Calcd. for $C_{17}H_{20}O_7$: C 60.71, H 5.99. Found C 60.70, H 5.90.

Dimethyl 2-[5-p-toluoyl-3,5-dioxopentyl] malonate 3-f: m.p.36-38 °C, IR (KBr) ν (cm^{-1}): 3400 (w), 2955 (m), 1750 (s), 1735 (s), 1605 (s); ^{1}H NMR δ (ppm): 16.05 (broad s, 1H) O*H* enol, 7.78 (d, 2H, 9.0 Hz), 7.25 (d, 2H, 9.0 Hz), 6.14 (s, 1H) C*H*=COH, 3.76 (s, 6H) C*H*$_3$OCO, 3.51 (t, 1H, J =7.2 Hz) C*H* $(COOCH_3)_2$, 2.52 (t, 2H, J=7.5 Hz) COC*H*$_2$, 2.41 (s, 3H) C*H*$_3$Ph, 2.29 (q, 2H, J=7.5 Hz) $COCH_2CH_2$; ^{13}C NMR δ (ppm): 194.7, 183.1, 169.41, 143.1, 131.9, 127.0, 129.3, 95.8, 50.6, 52.6, 36.3, 24.4, 21.6; MS (EI) m/e: M^+ 320, 302, 189, 161, 119 (100 %). Anal. Calcd. for $C_{17}H_{20}O_6$: C 63.74, H 6.29. Found C 63.80, H 6.27.

Dimethyl 2-[5-(4-terbutylphenyl)-3,5-dioxopentyl] malonate 3-g: oil, IR (KBr) ν (cm^{-1}): 3400 (w), 2959 (m), 1750 (s), 1736 (s), 1607 (s); ^{1}H NMR δ (ppm): 16.03 (broad s, 1H) O*H* enol, 7.80 (d, 2H, 9.0 Hz), 7.47 (d, 2H, 9.0 Hz), 6.14 (s, 1H) C*H*=COH, 3.76 (s, 6H) C*H*$_3$OCO, 3.51 (t, 1H, J =7.5 Hz) C*H* $(COOCH_3)_2$, 2.52 (t, 2H, J=7.5 Hz) COC*H*$_2$, 2.29 (q, 2H, J= 7.5 Hz) $COCH_2CH_2$, 1.34 (s, 9H) $(CH_3)_3C$; ^{13}C NMR δ (ppm): 194.9, 182.9, 169.4, 156.2, 131.8, 126.9, 125.6, 95.9, 50.6, 52.6, 36.5, 35.0, 31.1, 24.4; MS (EI) m/e: M^+ 362, 344, 231, 203, 161 (100 %). HRMS calcd. for $C_{20}H_{26}O_6$ 362.1729. Found 362.1741.

Dimethyl 2-[5-(4-trifluoromethylphenyl)-3,5-dioxopentyl] malonate 3-h: oil, IR (KBr) ν (cm^{-1}): 3455 (w), 2957 (m), 1750 (s), 1736 (s), 1607 (s); ^{1}H NMR δ (ppm): 15.79 (broad s, 1H) O*H* enol, 7.97 (d, 2H, 9.0 Hz), 7.71 (d, 2H, 9.0 Hz), 6.19 (s, 1H) C*H*=COH, 3.76 (s, 6H) C*H*$_3$OCO, 3.51 (t, 1H, J =7.2 Hz) C*H* $(COOCH_3)_2$, 2.58 (t, 2H, J=7.5 Hz) COC*H*$_2$, 2.30 (q, 2H, J=7.5 Hz) $COCH_2CH_2$;

^{13}C NMR δ (ppm): 197.0, 179.0, 169.3, 133.6, 137.8, 127.2, 125.6, 122.7 (***C***F_3, d, J_{CF}=271.5 Hz), 96.9, 50.5, 52.6, 36.8, 24.1; MS (EI) m/e: M^+ 374, 356, 243, 215, 173 (100 %). HRMS calcd. for $C_{17}H_{17}F_3O_6$ 374.0977. Found 374.0952.

Dimethyl 2-[5-(p-biphenyl)-3,5-dioxopentyl] malonate 3-i: m.p.78-80 °C, IR (KBr) ν (cm^{-1}): 3447 (w), 2960 (m), 1743 (s), 1735 (s), 1608 (s); ^{1}H NMR δ (ppm): 16.02 (broad s, 1H) O***H*** enol, 7.95 (d, 2H, 9.0 Hz), 7.68 (d, 2H, 9.0 Hz), 7.63 (dd, 2H, J=1.8, 8.5 Hz), 7.51-7.38 (m, 3H), 6.21 (s, 1H) C***H***=COH, 3.77 (s, 6H) C***H***$_3$OCO, 3.53 (t, 1H, J =7.5 Hz) C***H*** $(COOCH_3)_2$, 2.56 (t, 2H, J=7.5 Hz) COC***H***$_2$, 2.31 (q, 2H, J=7.5 Hz) $COCH_2C$***H***$_2$; ^{13}C NMR δ (ppm): 195.4, 182.2, 169.4, 145.2, 133.3, 128.9, 127.5, 139.9, 127.2, 128.1, 127.3, 96.2, 50.7, 52.6, 36.5, 24.4; MS (EI) m/e: M^+ 382, 364, 251, 223, 181 (100 %). Anal. Calcd. for $C_{22}H_{22}O_6$: C 69.10, H 5.80. Found C 68.94, H 5.79.

Dimethyl 2-[5-(4-nitrophenyl)-3,5-dioxopentyl] malonate 3-j: reference 7.

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11. In the case of **3-a** and **3-f**, the crude solid can be purified by re-crystallization from MeOH-H_2O instead of chromatography purification.

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