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Synthesis of substituted and unsubstituted 5-(1,3-diaryl-1-oxopropyl)pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-triones

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Reactions of 1,3-diaryl-2-propene-1-ones **2a-i** give the corresponding 5-(1,3-diaryl-1-oxopropyl)pyrimidine-(1*H*,3*H*,5*H*)-2,4,6-triones **3a-i** with barbituric acid **1** under refluxing condition without using any catalyst.

Keywords: Diarylpyrimidinetriones, diarylpropeneones, barbituric acid

IPC: Int.Cl.[8] C07D

A number of barbituric acid derivatives- 5-(1,3-diaryl-1-oxopropyl)pyrimidine(1*H*,3*H*,5*H*)-2,4,6-triones **3a-i** were synthesized and characterized. These compounds seem to be new in literature.

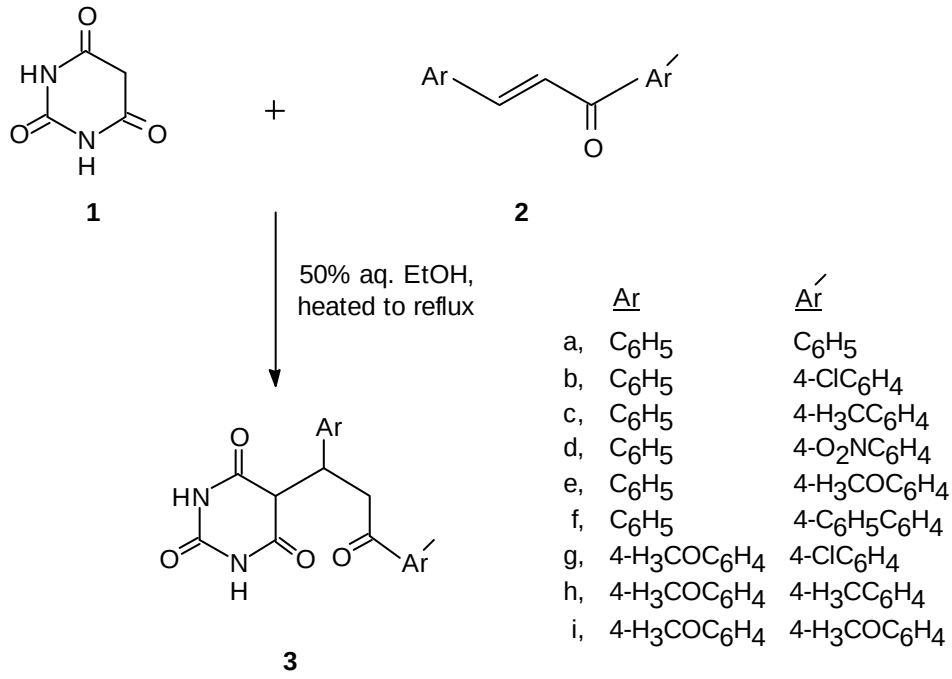
The formation of compounds **3a-i** may be explained by applying a general addition reaction of Michael type (**Scheme I**). These were formed during the synthesis of 1:2 adducts (2 being arylidene-acetophenone) which may undergo subsequent intramolecular Aldol condensation leading to the formation of spiro structures[5]. In continuation of the work[5-7] on barbituric acid derivatives, herein is reported the synthesis of compounds **3a-i** in the present paper.

Compound **1** reacted with 1,3-diphenyl-2-propene-1-one **2a** to give a yellowish crystalline solid at refluxing temperature in 50% aqueous ethanol. Its mass spectrum gave a peak at m/z 336 (M^+). The ^{1}H NMR spectrum of compound **3a** showed besides other usual signals, two singlets at δ 11.08 (NH, 1H, H-1) and 11.03 (NH, 1H, H-3), one multiplet at δ 4.17 (1H, H-7), one doublet at δ 3.81 (J=4.0 Hz, 1H, H-5), two doublet of doublet at δ 4.04 (J_1=8.5 Hz, J_2=18.0 Hz, 1H, H-8) and δ 3.62 (J_1=6.5 Hz, J_2=18.5 Hz, 1H, H-8) and ^{13}C NMR showed signals at δ 197.0 (C-9), 169.94 (C-4), 169.57 (C-6), 150.23 (C-2), 51.65 (C-5), 41.54 (C-7), 40.62 (C-8), on the basis of which it was assigned the structure 5-(1,3-diphenyl-1-oxopropyl)-pyrimidine(1*H*,3*H*,5*H*)-2,4,6-triones **3a**. Similarly **1** on condensation with other arylideneacetophenones **2b-i** afforded the adducts **3b-i** (**Scheme I**). The structures of all these compounds were assigned on the basis of their spectral data and elemental analysis.

Experimental Section

Melting points are uncorrected. IR spectra were recorded as KBr pellets using Shimadzu IR-470 infrared spectrometer in the range of 4000-400 cm^{-1}. ^{1}H NMR spectra were recorded in DMSO-d_6 on a JEOL 500 MHz NMR spectrometer using TMS as internal standard (chemical shifts in δ, ppm). ^{13}C NMR spectra were recorded in DMSO-d_6 at 125 MHz and MS on a JEOL JMS-HX 110A spectrometer. All the compounds gave satisfactory C, H and N analyses.

1,3-Diphenyl-2-propen-1-one[1] **2a**, 1-(4-chlorophenyl)-3-phenyl-2-propen-1-one[2] **2b**, 1-(4-methylphenyl)-3-phenyl-2-propen-1-one[2] **2c**, 1-(4-nitrophenyl)-3-phenyl-2-propen-1-one[3] **2d**, 1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one[3] **2e**, 1-(4-phenylphenyl)-3-phenyl-2-propen-1-one **2f**, 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-2-propen-1-one[4] **2g**, 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-1-one[2] **2h** and



Scheme I

1,3-(4-dimethoxyphenyl)-2-propene-1-one[2] **2i** were prepared by following primarily literature methods[1] and by changing the reaction conditions whenever necessary. The reactions described in the present paper were carried out following a general procedure.

General Procedure. A mixture of barbituric acid (0.005 mole) and arylideneacetophenone (0.005 mole) was dissolved in 50% aqueous ethanol in a round bottomed flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was refluxed for 18-20 h and was cooled and filtered. A solid mass obtained was purified by recrystallisation from rectified spirit. The progress of reaction and the formation of the products were monitored by TLC (eluting solvents, ethyl acetate: methanol, 10:1).

5-(1,3-Diphenyl-1-oxopropyl)pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3a: Yellowish white solid. Yield 39%; m.p. 185–87°C; R_f 0.18; UV-Vis: 272 ($\pi\rightarrow\pi^*$ of C=O), 242, 209 ($\pi\rightarrow\pi^*$ of C=C); IR (KBr): 3220, 3100 (OH, NH), 1760, 1700, 1680 (C=O), 1590, 1575, 1530 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.08 (s, 1H, NH, H-1)$^{\tau}$, 11.03 (s, 1H, NH, H-3)$^{\tau}$, 7.98-7.16 (m, 10H, aromatic), 4.17 (m, 1H, H-7), 4.04 (dd, J_{vic}=8.5, J_{gem}=18.0, 1H, H-8), 3.81 (d, J=4.0, 1H, H-5), 3.62 (dd, J_{vic}=6.5, J_{gem}=18.5, 1H, H-8); ^{13}C NMR (DMSO-d_6): δ 197.0 (C-9), 169.94 (C-4)‡, 169.59 (C-6)‡, 150.23 (C-2), [139.38, 136.46, 133.10, 128.56, 128.20, 127.67, 127.12 (aromatic)], 51.65 (C-5), 41.54 (C-7), 40.62 (C-8); MS: m/z 336 (M^+), 231, 216, 208, 132, 128, 120, 105 (100%), 103, 102. Anal. Found: C, 67.95; H, 4.79; N, 8.29. Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.88; H, 4.76; N, 8.32%.

5-{1-(4-Chlorophenyl)-3-phenyl-1-oxopropyl}-pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3b: White solid. Yield 27%; m.p. 200-02°C; R_f 0.26; UV-Vis: 252 ($\pi\rightarrow\pi^*$ of C=O), 210 ($\pi\rightarrow\pi^*$ of C=C); IR (KBr): 3275, 3200 (OH, NH), 1730, 1690, 1670 (C=O), 1635, 1585, 1570, 1518 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.07 (s, 1H, NH, H-1)$^{\tau}$, 11.02 (s, 1H, NH, H-3)$^{\tau}$, 8.0 (d, J=9.0, 2H, H-2´´, 6´´), 7.59 (d, J=9.0, 2H, H-2´, 6´), 7.25 (m, 3H, H-3´, 4´, 5´), 7.16 (d, J=7.0, 2H, H-3´, 5´), 4.15 (m, 1H, H-7), 4.03 (dd, J_{vic}=8.5, J_{gem}=18.5, 1H, H-8), 3.80 (d, J=3.5, 1H, H-5), 3.60 (dd, J_{vic}=6.5, J_{gem}=18.5, 1H, H-8); ^{13}C NMR (DMSO-d_6): δ 197.50 (C-9), 169.89 (C-4)‡, 169.54 (C-6)‡, 150.21 (C-2), [139.26, 138.02, 135.10, 129.80, 129.55, 128.81, 127.65, 127.15 (aromatic)], 51.57 (C-5), 41.47 (C-7), 40.64 (C-8); MS: m/z 370 (M^+), 231, 216, 242, 166, 154, 139 (100%), 128, 111, 103, 102. Anal. Found: C, 61.33; H, 4.01; N, 7.44. Calcd. for $C_{19}H_{15}N_2O_4Cl$: C, 61.54; H, 4.07; N, 7.55%.

5-{1-(4-Methylphenyl)-3-phenyl-1-oxopropyl}-pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3c: White solid. Yield 10%; m.p. 180-82°C; R_f 0.45; UV-Vis:

$^{\tau}$ δ values for protons H-1 and H-3 are exchangeable
‡ δ values for carbons C-4 and C-6 are exchangeable

255 (π→π* of C=O), 225, 209 (π→π* of C=C); IR (KBr): 3400, 3200 (OH, NH), 1720, 1700, 1670 (C=O), 1520 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.07 (s, 1H, NH, H-1)$^{\tau}$, 11.02 (s, 1H, NH, H-3)$^{\tau}$, 7.90-7.02 (m, 9H, aromatic), 4.16 (m, 1H, H-7), 4.00 (dd, J_{vic}=8.42, J_{gem}=18.18, 1H, H-8), 3.80 (d, *J*=3.64, 1H, H-5), 3.58 (dd, J_{vic}=6.48, J_{gem}=18.16, 1H, H-8), 2.38 (s, 3H, Ar´-CH_3); ^{13}C NMR (DMSO-d_6): δ 197.75 (C-9), 170.16 (C-4)‡, 169.79 (C-6)‡, 150.42 (C-2), [143.64, 139.61, 134.12, 129.24, 127.25 (aromatic)], 51.72 (C-5), 41.61 (C-7), 40.45 (C-8), 21.10 (Ar´-CH_3); MS: m/z 350 (M^+), 231, 216, 222, 146, 134, 128, 119 (100%), 103, 102. Anal. Found: C, 68.34; H, 5.07; N, 7.83. Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 7.99%.

5-{1-(4-Nitrophenyl)-3-phenyl-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3d: White solid. Yield 38%; m.p. 210-12°C; R_f 0.45; UV-Vis: 303 (n→π* of C=O), 266 (π→π* of C=O), 206 (π→π* of C=C); IR (KBr): 3440, 3240 (OH, NH), 1755, 1740, 1705, 1680 (C=O), 1595, 1520 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.10 (s, 1H, NH, H-1)$^{\tau}$, 11.04 (s, 1H, NH, H-3)$^{\tau}$, 8.34 (d, *J*=8.5, 2H, H-2´´, 6´´), 8.21 (d, *J*=8.0, 2H, H-2´, 6´), 7.28 (t, 3H, H-3´´, 5´´), 7.23 (t, *J*=7.25, 2H, H- 4´´), 7.16 (d, *J*=8.5, 2H, H-3´, 5´), 4.17 (m, 1H, H-7), 4.12 (dd, J_{vic}=8.5, J_{gem}=18.5, 1H, H-8), 3.82 (d, *J*=2.5, 1H, H-5), 3.70 (dd, J_{vic}=5.25, J_{gem}=17.25, 1H, H-8); ^{13}C NMR (DMSO-d_6): δ 197.65 (C-9), 170.09 (C-4)‡, 169.77 (C-6)‡, 150.42 (C-2), [149.98, 141.17, 139.26, 129.32, 128.89, 128.40, 127.83, 127.38 (aromatic)], 51.50 (C-5), 41.38 (C-7), 40.0 (C-8); MS: m/z 381 (M^+), 363, 231, 216, 253, 177, 165, 150, 128, 122, 103 (100%), 102. Anal. Found: C, 59.77; H, 3.93; N, 11.02. Calcd. for $C_{19}H_{15}N_3O_6$: C, 59.84; H, 3.96; N, 11.01%.

5-{1-(4-Methoxyphenyl)-3-phenyl-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3e: White solid. Yield 71%; m.p. 130-32°C; R_f 0.19; UV-Vis: 268 (π→π* of C=O), 207 (π→π* of C=C); IR (KBr): 3440, 3200 (OH, NH), 1730, 1700, 1670 (C=O), 1595, 1570, 1502 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.49 (s, 1H, NH, H-1)$^{\tau}$, 11.45 (s, 1H, NH, H-3)$^{\tau}$, 8.38 (d, *J*=9.00, 2H, H-2´´, H-6´´), 7.68 (m, *J*=7.00, 3H, H-3´, H-4´, H-5´), 7.64 (d, *J*=7.00, 2H, H-2´ and H-6´), 7.57 (d, *J*=8.50, 2H, H-3´´, 5´´), 4.57 (m, 1H, H-7), 4.38 (dd, J_{vic}=8.5, J_{gem}=17.5, 1H, H-8), 4.21 (d, *J*=4.0, 1H, H-5), 3.95 (dd, J_{vic}=6.25, J_{gem}=18.25, 1H, H-8), 4.24 (s, 3H, Ar´-OCH_3); ^{13}C NMR (DMSO-d_6): δ 197.33 (C-9), 170.99 (C-4)‡, 170.59 (C-6)‡, 151.22 (C-2), [163.93, 140.41, 130.94, 130.31, 129.10, 128.56, 128.00, 114.63 (aromatic)], 52.49 (C-5), 42.47 (C-7), 40.87 (C-8), 56.25 (Ar´-OCH_3); MS: m/z 366 (M^+), 348, 231, 216, 238, 135 (100%), 150, 128, 107, 103, 102. Anal. Found: C, 64.99; H, 4.76; N, 7.87. Calcd. for $C_{20}H_{18}N_2O_5$: C, 65.56; H, 4.95; N, 7.64%.

5-{1-(4-Phenylphenyl)-3-phenyl-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3f: Light brownish solid. Yield 7%; m.p. 201-02°C; R_f 0.27; UV-Vis: 270 (π→π* of C=O), 207 (π→π* of C=C); IR (KBr): 3450, 3230 (OH, NH), 1740, 1710, 1670 (C=O), 1590, 1550 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.14 (s, 1H, NH, H-1)$^{\tau}$, 11.07 (s, 1H, NH, H-3)$^{\tau}$, 8.09-7.25 (m, 14H, aromatic), 4.36 (m, 1H, H-7), 4.16 (dd, J_{vic}=9.0, J_{gem}=18.5, 1H, H-8), 3.83 (d, *J*=3.5, 1H, H-5), 3.61 (dd, J_{vic}=5.5, J_{gem}=17.5, 1H, H-8); ^{13}C NMR (DMSO-d_6): δ 197.50 (C-9), 169.50 (C-4)‡, 169.37 (C-6)‡, 150.0 (C-2), [128.58, 128.23, 127.88, 127.65, 126.68 (aromatic)], 51.28 (C-5), 41.67 (C-7), 40.15 (C-8); MS: m/z 412 (M^+), 413 (100%), 414, 230, 216, 284, 208, 196, 181, 153, 128, 103, 102, 91, 77, 65, 43. Anal. Found: C, 72.55; H, 7.92; N, 6.65. Calcd. for $C_{25}H_{20}N_2O_4$: C, 72.50; H, 4.89; N, 6.79%.

5-{1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3g: Pink white solid. Yield 38%; m.p. 248-50°C; R_f 0.25; UV-Vis: 253 (π→π* of C=O), 210 (π→π* of C=C); IR (KBr): 3450, 3220 (OH, NH), 1740, 1700, 1690 (C=O), 1600, 1580, 1505 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.06 (s, 1H, NH, H-1)$^{\tau}$, 11.02 (s, 1H, NH, H-3)$^{\tau}$, 8.0 (d, *J*=8.5, 2H, H-2´´, 6´´), 7.60 (d, *J*=8.5, 2H, H-2´, 6´), 7.06 (d, *J*=9.0, 2H, H-3´, 5´), 6.82 (d, *J*=8.5, 2H, H-3´´, 5´´), 4.11 (m, 1H, H-7), 4.00 (dd, J_{vic}=8.25, J_{gem}=18.25, 1H, H-8), 3.75 (d, *J*=3.5, 1H, H-5), 3.56 (dd, J_{vic}=6.5, J_{gem}=18.0, 1H, H-8), 3.70 (s, 3H, Ar-OCH_3); ^{13}C NMR (DMSO-d_6): δ 197.35 (C-9), 170.21 (C-4)‡, 169.80 (C-6)‡, 150.44 (C-2), [158.32, 138.15, 135.31, 131.10, 129.77, 128.83, 113.68 (aromatic)], 51.75 (C-5), 41.75 (C-7), 40.92 (C-8), 54.94 (Ar-OCH_3); MS: m/z 400 (M^+), 401, 402, 261, 246, 272, 166, 154, 139 (100%), 134, 132, 128, 111, 107, 103, 91, 65, 43. Anal. Found: C, 59.79; H, 4.22; N, 7.01. Calcd. for $C_{20}H_{17}N_2O_5Cl$: C, 59.93; H, 4.27; N, 6.99%.

5-{1-(4-Methylphenyl)-3-(4-methoxyphenyl)-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3h: Yellow solid. Yield 6%; m.p. 261-63°C; R_f 0.28; UV-Vis: 257 (π→π* of C=O), 209 (π→π* of C=C);

IR (KBr): 3450, 3200 (OH, NH), 1750, 1700 (C=O), 1640, 1600, 1590, 1510 cm^{-1} ($^{\tau}$C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.05 (s, 1H, NH, H-3)$^{\tau}$, 11.01 (s, 1H, NH, H-1)$^{\tau}$, 7.88 (d, *J*=8.0, 2H, H-2´´, 6´´), 7.34 (d, *J*=8.0, 2H, H-2´, 6´), 7.07 (d, *J*=8.5, 2H, H-3´, 5´), 6.83 (d, *J*=9.0, 2H, H-3´´, 5´´), 4.12 (m, 1H, H-7), 3.96 (dd, J_{vic}=8.0, J_{gem}=18.0, 1H, H-8), 3.75 (d, *J*=4.0, 1H, H-5), 3.54 (dd, J_{vic}=6.75, J_{gem}=18.0, 1H, H-8), 3.70 (s, 3H, Ar-OCH_3), 2.38 (s, 3H, Ar´-CH_3); ^{13}C NMR (DMSO-d_6): δ 197.75 (C-9), 170.27 (C-4)‡, 169.83 (C-6)‡, 150.46 (C-2), [158.29, 143.60, 134.21, 131.21, 127.93, 113.67 (aromatic)], 51.87 (C-5), 41.06 (C-7), 40.72 (C-8), 54.93 (Ar-OCH_3), 21.09 (Ar´-CH_3); MS: m/z 380 (M^+), 381, 382, 261, 253, 252, 247, 246, 134, 132, 128, 119 (100%), 107, 103, 91, 65. Anal. Found: C, 66.26; H, 5.34; N, 7.34. Calcd. for $C_{21}H_{20}N_2O_5$: C, 66.31; H, 5.30; N, 7.36%.

5-{1,3-Di(4-methoxyphenyl)-1-oxopropyl}pyrimidine (1*H*, 3*H*, 5*H*)-2,4,6-trione, 3i: Light orange solid. Yield 37%; m.p. 296-98°C; R_f 0.38; UV-Vis: 346 (n→π* of C=O), 268 (π→π* of C=O), 220, 207 (π→π* of C=C); IR (KBr): 3440, 3200 (OH, NH), 1740, 1700, 1670 (C=O), 1600, 1560, 1510 cm^{-1} (C=C, C=N); ^{1}H NMR (DMSO-d_6): δ 11.05 (s, 1H, NH, H-1)$^{\tau}$, 11.01 (s, 1H, NH, H-3)$^{\tau}$, 7.96 (d, *J*=9.0, 2H, H-2´´, 6´´), 7.07 (d, *J*=8.5, 2H, H-2´, 6´), 7.05 (d, *J*=8.5, 2H, H-3´, 5´), 6.83 (d, *J*=9.0, 2H, H-3´´, 5´´), 4.12 (m, 1H, H-7), 3.94 (dd, J_{vic}=8.5, J_{gem}=18.0, 1H, H-8), 3.75 (d, *J*=4.0, 1H, H-5), 3.50 (dd, J_{vic}=6.75, J_{gem}=17.75, 1H, H-8), 3.70 (s, 3H, Ar-OCH_3), 3.84 (s, 3H, Ar´-OCH_3); ^{13}C NMR (DMSO-d_6): δ 196.59 (C-9), 170.30 (C-4)‡, 169.85 (C-6)‡, 150.47 (C-2), [163.16, 158.27, 131.36, 113.88, 113.67 (aromatic)], 51.92 (C-5), 41.18 (C-7), 40.42 (C-8), 54.94 (Ar-OCH_3), 55.51 (Ar´-OCH_3); MS: m/z 396 (M^+), 397, 398, 261, 247, 268, 162, 150, 135 (100%), 134, 128, 107, 103, 91, 77. Anal. Found: C, 63.59; H, 5.13; N, 6.96. Calcd. for $C_{21}H_{20}N_2O_6$: C, 63.63; H, 5.09; N, 7.06%.

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