

Domino Knoevenagel/Michael addition/C-acylation reactions. Synthesis of 1,3-cyclohexane-1,3-diones

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Abstract

The three component reactions of Meldrum's acid, 1,3-bis-(benzotriazol-1-yl)propan-2-one or 1-benzotriazol-1-ylpropan-2-one and an aldehyde, carried out in DMF at 60 °C gave rise to 2,4-bis-(benzotriazol-1-yl)cyclohexane-1,3-diones or 4-benzotriazol-1-ylcyclohexane-1,3-diones, respectively, in fairly high yields. Unlike similar reactions reported earlier with acetone, the reactions with 1,3-bis-(benzotriazol-1-yl)propan-2-one and 1-benzotriazol-1-ylpropan-2-one proceeded *via* an intramolecular acylation of the other methyl group of acetone.

Keywords: 1,3-Bis-(benzotriazol-1-yl)propan-2-one, 1-benzotriazol-1-ylpropan-2-one, 2,4-bis-benzotriazol-1-yl-cyclohexane-1,3-diones, 2,2-dimethyl-1,3-dioxane-4,6-dione, Meldrum's acid

Introduction

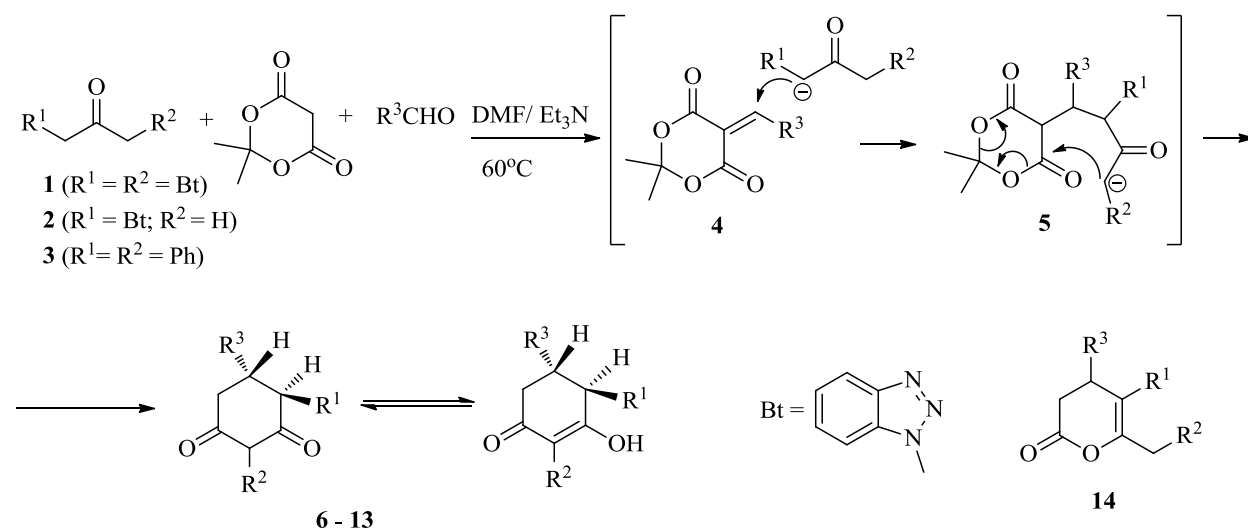
Domino reactions¹⁻³ are considered to be versatile synthetic tools and are used for the synthesis of structurally diverse compounds including biologically active natural products and drugs.²⁻⁵ As a strong CH-acid, Meldrum's acid readily enters into condensation reactions of the aldol⁶ and Knoevenagel^{3,7} type to yield 5-alkenyl-2,2-dimethyl-1,3-dioxane-4,6-diones which are widely used in organic synthesis. With a vast number of diverse synthetic applications Meldrum's acid may be considered a unique synthon. Its methylenedioxy derivatives, for instance, often are engaged as intermediates in multicomponent reactions (MCR) in which the Meldrum's acid moiety decomposes^{2,3,12-14} as it is the case with intra- and intermolecular Friedel-Crafts C-alkylations¹⁵ and NH-acylations of thioamides.¹⁶⁻¹⁸

Results and Discussion

The three component proline-catalyzed reaction of acetone with aldehydes and Meldrum's acid has been reported to yield triketones with no change in the 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) ring.¹⁹ Analogous products have been noted in the piperidine-catalyzed

reaction starting with cyclohexanone.²⁰ Those results prompted us to investigate the reactions under conditions that could be favorable for inducing an intramolecular *C*-acylation of the other methyl group of benzotriazolo-acetone **1**, **2**. However, one could not rule out that the reaction may take another course and yield the enol form of the ketone **5** which subsequently may cyclize to give the corresponding lactone **14**.

The readily available acetone derivatives, namely 1,3-bis-benzotriazol-1-ylpropan-2-one **1**²¹ and 1-benzotriazol-1-ylpropan-2-one **2**²² were used in the present research as the active methylene compounds. All reactions were carried out at 60 °C in a DMF solution under inert gas with triethylamine added as the catalyst. As expected, methyldene derivatives **4** were formed in the first stage. Their subsequent Michael reaction with the ketone **1** or **2** anion yielded the addition product **5** which next underwent an intramolecular acylation with a concomitant decomposition of the Meldrum's acid fragment. An additional support to that mechanistic concept was gained in the reaction of **4** ($R^3 = \text{Ph}$) with **1**; under identical reaction conditions (DMF, TEA, 60 °C) only **6** was formed, its yield being twice that high as in the three component variant (60% vs. 30%). The formation of lactones **14** or keto-esters **5** was not observed in our



Cpd	R ¹	R ²	R ³	Yield (%)	Cpd	R ¹	R ²	R ³	Yield (%)
6	Bt	Bt	Ph	30(60)	10	Bt	H	3,4-(OCH ₂ O)C ₆ H ₃	92
7	Bt	Bt	4-CH ₃ C ₆ H ₄	52	11	Bt	H	Ph	51
8	Bt	Bt	CH ₃	86	12	Bt	H	CH ₃	81
9	Bt	Bt	3,4-(OCH ₂ O)C ₆ H ₃	85	13	H	H	3,4-(OCH ₂ O)C ₆ H ₃	10

Scheme 1. Formation of cyclohexanediones.

experiments. Since Knoevenagel condensation of aldehydes with benzotriazolo-acetone (**2**, R¹=Bt, R²=H) is known to require forced conditions (boiling DMF),²³ the initial formation of the methyldene derivatives of **4** and their subsequent addition to Meldrum's acid seems rather unlikely.

It is noteworthy that the benzotriazole substituent were markedly effective when the acetone derivatives **1** and **2** formed the corresponding carbanions.^{24,25} Under analogous conditions the reaction of Meldrum's acid with benzaldehyde and 1,3-diphenylacetone **3** yielded a 1.5:1 mixture of the product of **3** addition to the appropriate methyldene derivative **4** and triphenyl-1,3-cyclohexanedione **13**; the reaction rate was much lower and the yield did not exceed 25%. The ¹H – and ¹³C-NMR spectra confirmed the initial structural assignments and showed that in solutions the compounds **6-13** exist in the enol form.

The configurations at C-4 (substituent R¹) and at C-5 (substituent R³) were established by analysis of the vicinal coupling constants (¹H, ¹H COSY NMR spectra) and of the through-space interactions (¹H, ¹H NOESY NMR spectra) of compounds **8-10**. High values (8.2-10.5 Hz) of the coupling constants between the vicinal protons H-4 and H-5 indicated their *trans*-diaxial orientation.

Experimental Section

General. Melting points were determined on a digital apparatus Electrothermal model IA9300 and are uncorrected. NMR spectra were recorded on a Bruker DPX apparatus (400 MHz) spectrometer in deuteriochloroform and deuteriodimethyl sulfoxide with tetramethylsilane as internal standard. In some cases trifluoroacetic acid (TFFA) was added to the solvent. The IR spectra were taken with Specord M80 instruments in potassium bromide pellets or Nujol. Purity and molecular mass determinations were carried out by gas chromatography-mass spectrometry (GC/MS) on a Hewlett-Packard instrument model HP 6890 equipped with a mass detector HP 5973. The analytical procedure was developed for a 30 m long capillary column, 0.2 mm in diameter, with methylsiloxane modified with phenyl groups (5% Ph, Me siloxane) in the 0.25 μm thick active phase layer. Elemental analyses were performed on EuroEA 3000 series, Euro Vector CHNS-O Elemental Analyzer.

General procedure

A mixture of dibenzotriazolacetone²¹ or benzotriazolacetone²² (1 mmol), Meldrum's acid (0,144g, 1 mmol), appropriate aldehyde (1 mmol) and triethylamine (1 mL) in anhydrous DMF (5 mL) was stirred and heated under argon blanket at 60 °C for a few hours. The reaction progress was controlled by thin-layer chromatography (silica gel, hexane/ethyl acetate, 1:1). After cooling 10 mL of 10% aq. HCl was added to the reaction mixture. The semisolid residue was filtered, dissolved in ethyl acetate, and chromatographed on SiO₂ with hexane/ethyl acetate,

1:1. The filtrate was evaporated to dryness and the product left was recrystallized from toluene/hexane 6:4.

2,4-Bis-(1*H*-1,2,3-benzotriazol-1-yl)-5-phenylcyclohexane-1,3-dione (6). Light yellow oil, yield: 60%, IR: 1695, 1710 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.76-3.86 (m, 2H, C- CH_2), 4.11-4.33 (m, CH-Ph), 5.73 (s, CH-Bt), 5.91-6.01 (m, OCH_2), 7.11 (d, $J = 7.52$ Hz, 2H, Ph), 7.21-7.30 (m, 2H, Bt), 7.32-7.44 (m, 5H, Bt, Ph), 7.93-8.11 (m, 4H, Bt), 11.62 (s, 1H, OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 36.91 (d, CH-Ph), 53.42 (t, CH_2), 69.48 (d, CH-Bt), 125.19, 128.61, 132.18, 142.79 (Ph), 110.64, 113.72, 119.60, 122.55, 127.02, 127.33, 129.06, 130.17, 136.11, 140.82, 145.45, 146.86 (Bt), 172.15 (s, =C-OH), 196.34 (s, C=O), MS: m/z : 422 (9), 351 (8), 281 (16), 260 (11), 220 (100), 207 (24), 117 (32), 77 (39). Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_2$: C, 68.24; H, 4.29; N, 19.89. Found: C, 68.07; H, 4.28; N, 19.93%.

2,4-Bis-(1*H*-1,2,3-benzotriazol-1-yl)-5-(4-methylphenyl)cyclohexane-1,3-dione (7). Dark yellow oil, yield: 52%, IR: 1697, 1711 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.09 (s, 3H, CH_3), 3.86-3.99 (m, 2H, C- CH_2), 4.16-4.26 (m, CH-Ph), 5.59 (s, CH-Bt), 7.15 (d, $J = 7.66$ Hz, 2H, Ph), 7.19-7.23 (m, 2H, Bt), 7.24-7.42 (m, 4H, Bt, Ph), 7.91-8.08 (m, 4H, Bt), 11.75 (s, 1H, OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 21.11 (q, CH_3), 42.39 (d, CH-Ph), 45.89 (t, CH_2), 67.45 (d, CH-Bt), 124.47, 131.11, 135.95, 137.18 (Ph), 110.64, 114.58, 119.59, 122.25, 127.83, 128.45, 128.86, 129.64, 135.75, 140.39, 145.40, 147.11 (Bt), 172.33 (s, =C-OH), 197.25 (s, C=O), MS: m/z 436 (14), 351 (7), 281 (8), 260 (8), 220 (100), 207 (28), 117 (30), 77 (35). Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_2$: C, 68.80; H, 4.62; N, 19.25. Found: C, 68.91; H, 4.60; N, 19.29%.

2,4-Bis-(1*H*-1,2,3-benzotriazol-1-yl)-5-methylcyclohexane-1,3-dione (8). Light brown solid, yield: 86%, mp. 148-150 $^\circ\text{C}$, IR: 1694, 1706 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.67 (s, 3H, CH_3), 2.09 (s, 1H, CH-CH_3), 2.75 (s, 1H, CHH), 2.91 (s, 1H, CHH), 5.70-5.85 (m, 1H, CH-Bt), 7.41 (t, $J = 6.94$ Hz, 2H, Bt), 7.57 (t, $J = 7.90$ Hz, 2H, Bt), 7.88 (d, $J = 7.94$ Hz, 2H, Bt), 7.99-8.11 (m, 2H, Bt), 11.65 (s, 1H, OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 17.39 (q, CH_3), 34.74 (d, CH-CH_3), 45.87 (t, CH_2), 67.43 (d, CH-Bt), 111.26, 114.06, 119.54, 122.36, 127.90, 128.72, 128.83, 129.63, 134.11, 140.51, 145.46, 147.19 (Bt), 173.41 (s, C-OH), 197.22 (s, C=O), MS: m/z 360 (16), 261 (10), 207 (8), 184 (19), 166 (15), 144 (99), 123 (17), 104 (30), 77 (100), 51 (19). Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_6\text{O}_2$: C, 63.32; H, 4.48; N, 23.32. Found: C, 63.26; H, 4.47; N, 23.36%.

5-(1,3-Benzodioxol-5-yl)-2,4-bis-(1*H*-1,2,3-benzotriazol-1-yl)cyclohexane-1,3-dione (9). Yellow solid, yield: 85%, mp. 167-170 $^\circ\text{C}$, IR: 1690, 1715 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.51-2.62 (m, 2H, C- CH_2), 3.24-3.44 (m, 1H, $\text{CH-3,4-(OCH}_2\text{O)C}_6\text{H}_3$), 6.16 (s, 2H, OCH_2), 6.98 (d, $J = 7.81$ Hz, 2H, 3,4-($\text{OCH}_2\text{O)C}_6\text{H}_3$), 7.38 (t, $J = 6.81$ Hz, 1H, Bt), 7.51 (t, $J = 7.37$ Hz, 1H, Bt), 7.61 (d, $J = 7.81$ Hz, 2H, Bt), 7.78 (d, $J = 7.36$ Hz, 1H, 3,4-($\text{OCH}_2\text{O)C}_6\text{H}_3$), 7.95-8.06 (m, 4H, Bt), 11.26 (s, 2H, 2OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 30.98 (d, CH-3,4-($\text{OCH}_2\text{O)C}_6\text{H}_3$), 54.33 (t, C- CH_2), 102.40 (t, OCH_2), 103.89 (s, =C-Bt), 108.34 (s, =C-Bt), 110.44, 111.45, 111.69, 119.13, 123.81, 125.99, 127.31, 133.69, 134.05, 145.24, 147.86, 152.84, 157.00 (Bt, 3,4-($\text{OCH}_2\text{O)C}_6\text{H}_3$), 159.91 (s, =C-OH), 163.10 (s, =C-OH), MS: decomposition. Anal. Calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_6\text{O}_4$: C, 64.37; H, 3.89; N, 18.02. Found: C, 64.52; H, 3.88; N, 18.05%.

5-(1,3-Benzodioxol-5-yl)-4-(1H-1,2,3-benzotriazol-1-yl)cyclohexane-1,3-dione (10). Brown oil, yield: 92%, IR: 1695, 1712 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.95-4.10 (m, 2H, C- CH_2), 4.26-4.42 (m, 1H, CH -3,4-(OCH_2O) C_6H_3), 5.68 (s, 1H, CH-Bt), 5.80-5.93 (m, 2H, OCH_2), 6.46 (s, 1H, $=\text{CH}-\text{C}=\text{O}$), 6.70 (t, $J = 9.72$ Hz, 2H, 3,4-(OCH_2O) C_6H_3), 7.25 (s, 1H, Bt), 7.29-7.40 (m, 2H, Bt), 7.47 (t, $J = 7.67$ Hz, 1H, 3,4-(OCH_2O) C_6H_3), 7.96-8.04 (m, 1H, Bt), 11.84 (br. s., 1H, OH). ^{13}C NMR (100 MHz, CDCl_3): δ 28.50 (d, CH -3,4-(OCH_2O) C_6H_3), 60.40 (t, C- CH_2), 70.59 (d, CH-Bt), 100.85 (t, OCH_2), 107.99 (d, $\text{O}=\text{C}-\text{CH}=\text{O}$), 109.75, 110.31, 120.00, 121.51, 124.45, 124.64, 127.9, 132.48, 145.21, 154.53, 158.40 (Bt, 3,4-(OCH_2O) C_6H_3), 171.24 (s, C-OH), 190.43 (s, C=O), MS: m/z 349 (17), 293 (24), 274 (19), 250 (100), 220 (25), 192 (11), 147 (66), 89 (21), 77 (12), 63 (9), 43 (31). Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4$: C, 65.32; H, 4.33; N, 12.03. Found: C, 65.26; H, 4.35; N, 12.06%.

4-(1H-1,2,3-Benzotriazol-1-yl)-5-phenylcyclohexane-1,3-dione (11). Red oil, yield: 51%, IR: 1692, 1715 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.86-3.99 (m, 2H, C- CH_2), 4.16-4.35 (m, 1H, CH-HT), 5.87 (s, 1H, CH-Bt), 6.46 (s, 1H, $=\text{CH}-\text{C}=\text{O}$), 7.25 (s, 2H, Ph), 7.31-7.52 (m, 6H, Bt, Ph), 8.06 (d, $J = 8.65$ Hz, 1H, Bt), 11.66 (br. s., 1H, OH). ^{13}C NMR (100 MHz, CDCl_3): δ 31.94 (d, CH-Ph), 60.95 (t, C- CH_2), 71.51 (d, CH-Bt), 100.68 (d, $\text{O}=\text{C}-\text{CH}=\text{O}$), 110.50, 118.52, 124.56, 125.72, 126.31, 131.27, 133.86, 142.72, 145.66 (Bt, Ph), 172.34 (s, C-OH), 195.43 (s, C=O), MS: m/z 305(2), 263(8,7), 235(14,5), 206(71), 131(100), 103(61), 77(85), 51(23). Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_2$: C, 70.81; H, 4.95; N, 13.76. Found: 70.71; H, 4.95; N, 13.72%.

4-(1H-1,2,3-Benzotriazol-1-yl)-5-methylcyclohexane-1,3-dione (12). Light brown solid, yield: 81%, IR: 1695, 1725 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.75 (s, 3H, CH_3), 2.07 (s, 1H, CH - CH_3), 2.84 (s, 1H, CHH), 2.96 (s, 1H, CHH), 5.93 (s, 1H, CH-Bt), 6.65 (s, 1H, $=\text{CH}-\text{C}=\text{O}$), 7.50 (d, $J = 5.66$ Hz, 1H, Bt), 7.58-7.78 (m, 1H, Bt), 7.81 (d, $J = 7.37$ Hz, 1H, Bt), 8.13 (d, $J = 6.94$ Hz, 1H, Bt), 11.57 (br. s., 1H, OH). ^{13}C NMR ($\text{DMSO}-d_6$): δ 14.62 (q, CH_3), 31.13 (d, $\text{CH}-\text{CH}_3$), 56.86 (t, CH_2), 69.41 (d, CH-Bt), 106.01 (d, $\text{O}=\text{C}-\text{CH}=\text{O}$), 111.20, 119.46, 124.39, 127.79, 134.01, 145.79 (Bt), 166.23 (C-OH), 201.62 (s, C=O), MS: m/z 243 (5), 200 (10), 186 (6), 172 (43), 158 (9), 144 (100), 130 (17), 124 (10), 117 (10), 104 (19), 91 (18), 77 (31), 50 (27), 43 (77), 29 (8). Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.31; H, 5.36; N, 17.30%.

5-(1,3-Benzodioxol-5-yl)-2,4-diphenylcyclohexane-1,3-dione (13). Yellow solid, yield: 10%, mp 181-183 $^\circ\text{C}$, IR: 1690 (C=O). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.56-2.72 (m, 2H, C- CH_2), 3.69-3.79 (m, 1H, CH -3,4-(OCH_2O) C_6H_3), 3.98 (d, $J = 6.54$ Hz, 1H, CH-Ph), 4.30 (s, 1H, CH-Ph), 5.99 (s, 2H, OCH_2), 6.92 (d, $J = 7.75$ Hz, 2H, 3,4-(OCH_2O) C_6H_3), 6.99-7.08 (m, 1H, 3,4-(OCH_2O) C_6H_3), 7.11-7.24 (m, 4H, Ph), 7.25-7.32 (m, 4H, Ph), 7.35-7.42 (m, 2H, Ph). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 30.23 (d, CH -3,4-(OCH_2O) C_6H_3), 45.45 (t, C- CH_2), 54.63 (d, CH-Ph), 68.46 (d, CH-Ph), 101.53 (t, OCH_2), 108.98, 110.73, 121.53, 126.17, 127.93, 127.97, 128.04, 128.15, 130.48, 135.40, 137.35, 139.63, 146.03, 148.88 (2Ph, 3,4-(OCH_2O) C_6H_3), 203.11 (s, C=O), 205.29 (s, C=O), MS: m/z 384 (3), 320 (11), 292 (8), 274 (11), 216 (26), 188 (37), 131 (9), 104 (100), 42 (9). Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{O}_4$: C, 78.11; H, 5.24. Found: C, 77.99; H, 5.23%.

3-(1,3-Benzodioxol-5-yl)-5-hydroxy-4,6-diphenylcyclohexa-1,5-dien-1-one (5). Orange oil, yield: 15%, IR 1685 (C=O). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.75 (d, *J* = 8.65 Hz, 1H, CH=C=O), 3.38-3.49 (m, 1H, CH-3,4-(OCH₂O)C₆H₃), 4.36 (d, *J* = 7.74 Hz, 1H, CH-Ph), 6.10 (s, =CH-Ph), 6.00 (s, 2H, OCH₂), 6.81-6.92 (m, 3H, 3,4-(OCH₂O)C₆H₃), 7.19-7.34 (m, 8H, Ph), 7.59-7.65 (m, 2H, Ph), 13.89 (s, 1H, C-OH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 40.72 (s, C=C=C), 41.26 (d, CH-3,4-(OCH₂O)C₆H₃), 53.97 (d, CH-Ph), 101.10 (t, OCH₂), 106.03 (=CH-Ph), 109.50, 110.13, 123.16, 125.64, 126.65, 128.31, 128.34, 128.35, 128.56, 134.68, 135.70, 142.54, 146.12, 149.65 (2Ph, 3,4-(OCH₂O)C₆H₃). 170.09 (s, C-OH), 197.81 (s, C=O), MS: decomposition, Anal. Calcd. for C₂₅H₂₀O₄: C, 78.11; H, 5.24. Found: C, 78.06; H, 5.26%.

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