

## Michael Addition Reaction without Catalyst: The Synthesis of 2-Amino-5, 6, 7, 8-tetrahydro-5-oxo-4-aryl-7, 7-dimethyl- 4H-benzo-[b]-pyran Derivatives

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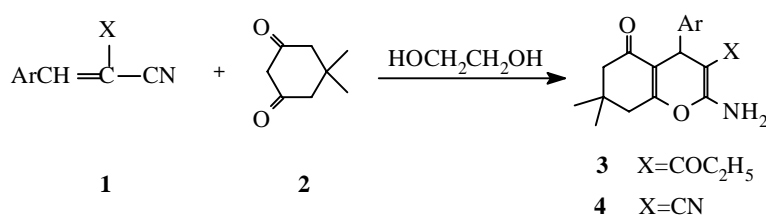
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**Abstract:** A series of tetrahydrobenzo-[b]-pyran derivative was synthesized by the reaction of arylmethylene malononitrile or arylmethylene cyanoacetate with dimedone in ethylene glycol at 80°C without catalyst. The structures of the two products were characterized by X-ray diffraction.

**Keywords:** Benzo-[b]-pyran, dimedone, ethylene glycol.

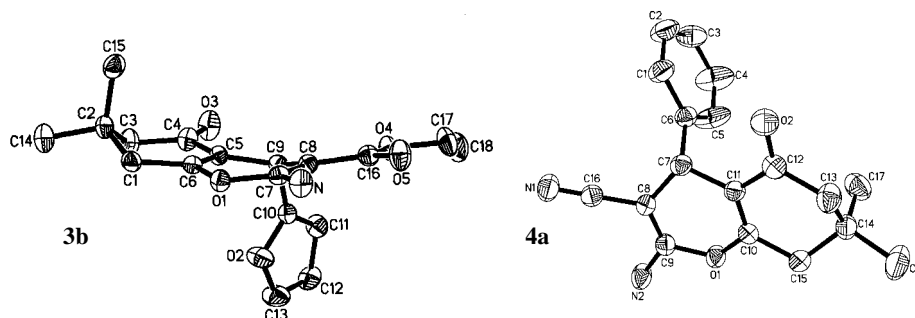
Michael addition reaction is one of the most important reactions in organic chemistry. Usually the acetic or basic catalyst was used<sup>1-3</sup>. For example, compound **3a** or **4a** was obtained by Michael addition reaction of **1** and **2**, HOAc was used as catalyst. But we found when arylmethylene cyanoacetate or arylmethylene malononitrile **1** was heated with dimedone **2** for 2 hours at 80°C in ethylene glycol, the Michael addition could take place without any catalyst, the addition cyclodehydration products **3a-g** or **4a-g** were obtained (**Scheme 1**). The crystal structures of **3b** and **4a** were presented in **Figure 1**.

Scheme 1



### General procedure

Arylmethylene cyanoacetate or arylmethylene malononitrile (5 mmol), dimedone(5 mmol) and ethylene glycol (15 mL) were heated at 80°C for 2 hours, then cooled to room temperature. The reaction mixture was poured into 150 mL of water. The solid product was filtered, washed with ether, recrystallized from 95% EtOH to give **3a-g** or **4a-g**.

**Figure 1** The crystal structure of **3b**, **4a****Table 1** The mp and yield of **3a-g** and **4a-g**

Compd.	Ar	Yield (%)	mp(°C) (lit)	Compd.	Ar	Yield (%)	mp(°C) (lit)
<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	61	146-148 (138)	<b>4a</b>	C <sub>6</sub> H <sub>5</sub>	91	232-233 (218)
<b>3b</b>	2-furyl	87	128-129	<b>4b</b>	2-BrC <sub>6</sub> H <sub>4</sub>	92	150-152
<b>3c</b>	2-ClC <sub>6</sub> H <sub>4</sub>	90	166-168	<b>4c</b>	4-BrC <sub>6</sub> H <sub>4</sub>	80	160-162
<b>3d</b>	4-ClC <sub>6</sub> H <sub>4</sub>	75	149-150	<b>4d</b>	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	96	196-198
<b>3e</b>	3,4-OCH <sub>2</sub> OC <sub>6</sub> H <sub>3</sub>	62	142-144	<b>4e</b>	4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	89	220-222
<b>3f</b>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	86	172-174	<b>4f</b>	4-HOC <sub>6</sub> H <sub>4</sub>	88	206-208
<b>3g</b>	3,4-(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	80	155-157	<b>4g</b>	3-HO-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>3</sub>	93	228-230

## References and Notes

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- Spectral data for compounds **3** and **4**: **3b**: mp 128-129°C. Y=87%. IR(KBr, v, cm<sup>-1</sup>): 3452, 3321, 1696, 1660. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.02 (s, 3H, CH<sub>3</sub>), 1.09(s, 3H, CH<sub>3</sub>), 1.21 (t, 3H, J=7.11Hz, CH<sub>3</sub>), 2.25 (s, 2H, CH<sub>2</sub>), 2.41 (s, 2H, CH<sub>2</sub>), 4.10 (q, 2H, J=7.05Hz, CH<sub>2</sub>), 4.98 (s, 1H, CH), 6.27 (brs, 2H, NH<sub>2</sub>), 6.05-7.17 (m, 3H, furan H). Anal. calcd.(%) for C<sub>18</sub>H<sub>21</sub>NO<sub>5</sub>, C 65.24, H 6.39, N 4.22; found: C 65.32, H 6.44, N 3.99. **3c**: mp 166-168°C. Y=90%. IR(KBr, v, cm<sup>-1</sup>): 3400, 3300, 1680, 1654. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 0.99 (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 1.12 (t, 3H, J=7.11Hz, CH<sub>3</sub>), 2.19 (m, 2H, CH<sub>2</sub>), 2.41 (s, 2H, CH<sub>2</sub>), 4.01 (q, 2H, J=7.12Hz, CH<sub>2</sub>), 5.00 (s, 1H, CH), 6.27 (brs, 2H, NH<sub>2</sub>), 7.04-7.32 (m, 4H, ArH). Anal. calcd.(%) for C<sub>20</sub>H<sub>22</sub>ClNO<sub>4</sub>, C 63.91, H 5.90, N 3.72; found: C 63.80, H 6.12, N 3.83. **3d**: mp 149-150°C. Y=75%. IR(KBr, v, cm<sup>-1</sup>): 3438, 3304, 1680, 1658. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 0.98 (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 1.14 (t, 3H, J=7.11Hz, CH<sub>3</sub>), 2.14 (m, 2H, CH<sub>2</sub>), 2.43 (s, 2H, CH<sub>2</sub>), 4.06 (q, 2H, J=7.11Hz, CH<sub>2</sub>), 4.68 (s, 1H, CH), 6.21 (brs, 2H, NH<sub>2</sub>), 7.16-7.30 (m, 4H, ArH). Anal. calcd.(%) for C<sub>20</sub>H<sub>22</sub>ClNO<sub>4</sub>, C 63.91, H 5.90, N 3.72; found: C 63.79, H 6.10, N 3.90. **3e**: mp 142-144°C. Y=62%. IR(KBr, v, cm<sup>-1</sup>): 3402, 3300, 1683, 1657. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.00 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 1.17 (t, 3H, J=7.14Hz, CH<sub>3</sub>), 2.18 (m, 2H, CH<sub>2</sub>), 2.43 (s, 2H, CH<sub>2</sub>), 4.08 (q, 2H, J=7.14Hz, CH<sub>2</sub>), 4.64 (s, 1H, CH), 5.93 (s, 2H, OCHO), 6.17 (brs, 2H, NH<sub>2</sub>), 6.71-6.76 (m, 3H, ArH). Anal. calcd.(%) for C<sub>21</sub>H<sub>23</sub>NO<sub>6</sub>, C 65.44, H 6.01, N 3.63; found: C 65.32, H 5.92, N 3.78. **3f**: mp 172-174°C. Y=86%. IR(KBr, v, cm<sup>-1</sup>): 3500, 3310, 1698, 1679. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 0.98 (s, 3H, CH<sub>3</sub>), 1.11 (s, 3H, CH<sub>3</sub>), 1.15 (t, 3H, J=7.11Hz, CH<sub>3</sub>), 2.18 (m, 2H, CH<sub>2</sub>), 2.47 (s, 2H, CH<sub>2</sub>), 4.04 (q, 2H, J=7.14Hz, CH<sub>2</sub>), 4.79 (s, 1H, CH), 6.33 (brs, 2H, NH<sub>2</sub>), 7.35-8.10 (m, 4H, ArH). Anal. calcd.(%) for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>, C 62.16, H

5.74, N 7.25; found: C 62.07, H 5.90, N 7.38. **3g**: mp 155-157°C. Y=80%. IR(KBr, v, cm<sup>-1</sup>): 3448, 3346, 1698, 1662. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 0.98 (s, 3H, CH<sub>3</sub>), 1.09 (s, 3H, CH<sub>3</sub>), 1.18 (t, 3H, J=7.11Hz, CH<sub>3</sub>), 2.19 (m, 2H, CH<sub>2</sub>), 2.41 (s, 2H, CH<sub>2</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 4.05 (q, 2H, J=7.08Hz, CH<sub>2</sub>), 4.65 (s, 1H, CH), 6.21 (brs, 2H, NH<sub>2</sub>), 6.70-6.86 (m, 3H, ArH). Anal. calcd.(%) for C<sub>22</sub>H<sub>27</sub>NO<sub>6</sub>, C 65.82, H 6.78, N 3.49; found: C 65.93, H 6.70, N 3.50. **4b**: mp 150-152°C. Y=92%. IR(KBr, v, cm<sup>-1</sup>): 3394, 3282, 2197, 1649. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.07 (s, 3H, CH<sub>3</sub>), 1.11 (s, 3H, CH<sub>3</sub>), 2.16-2.24 (m, 2H, CH<sub>2</sub>), 2.45 (s, 2H, CH<sub>2</sub>), 4.64 (s, 2H, NH<sub>2</sub>), 4.90 (s, 1H, CH), 7.03-7.52 (m, 4H, ArH). Anal. calcd.(%) for C<sub>18</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>2</sub>, C 57.91, H 4.56, N 7.51; found: C 57.98, H 4.47, N 7.48. **4c**: mp 196-198°C. Y=96%. IR(KBr, v, cm<sup>-1</sup>): 3394, 3282, 2191, 1682. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.02 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 2.15-2.25 (m, 2H, CH<sub>2</sub>), 2.46 (s, 2H, CH<sub>2</sub>), 4.31 (s, 1H, CH), 5.84 (s, 2H, NH<sub>2</sub>), 7.11-7.40 (m, 4H, ArH). Anal. calcd.(%) for C<sub>18</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>2</sub>, C 57.91, H 4.56, N 7.51; found: C 57.99, H 4.48, N 7.48. **4d**: mp 220-222°C. Y=89%. IR(KBr, v, cm<sup>-1</sup>): 3471, 3332, 2192, 1685. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 0.97 (s, 3H, CH<sub>3</sub>), 1.08 (s, 3H, CH<sub>3</sub>), 2.08-2.20 (m, 2H, CH<sub>2</sub>), 2.46 (s, 2H, CH<sub>2</sub>), 5.16 (s, 1H, CH), 5.67 (s, 2H, NH<sub>2</sub>), 7.31-7.77 (m, 4H, ArH). Anal. calcd.(%) for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>, C 63.71, H 5.01, N 12.39; found: C 63.82, H 5.00, N 12.32. **4e**: mp 208-210°C. Y=92%. IR(KBr, v, cm<sup>-1</sup>): 3382, 3321, 2191, 1681. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.03 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 2.15-2.23 (m, 2H, CH<sub>2</sub>), 2.44 (s, 2H, CH<sub>2</sub>), 2.89 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>N), 4.26 (s, 1H, CH), 5.42 (s, 2H, NH<sub>2</sub>), 6.62-7.06 (m, 4H, ArH). Anal. calcd.(%) for C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>, C 71.21, H 6.82, N 12.46; found: C 71.27, H 6.77, N 12.28. **4f**: mp 206-208°C. Y=88%. IR(KBr, v, cm<sup>-1</sup>): 3651, 3327, 3163, 2191, 1664. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.05 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 2.14-2.23 (m, 2H, CH<sub>2</sub>), 2.43 (s, 2H, CH<sub>2</sub>), 4.26 (s, 1H, CH), 5.34 (s, 2H, NH<sub>2</sub>), 6.72-7.03 (m, 4H, ArH). Anal. calcd.(%) for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>, C 69.68, H 5.81, N 9.03; found: C 69.72, H 5.90, N 9.00. **4g**: mp 228-230°C. Y=93%. IR(KBr, v, cm<sup>-1</sup>): 3496, 3308, 3255, 2192, 1678. <sup>1</sup>HNMR(CDCl<sub>3</sub>): δ 1.04 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 2.20-2.22 (m, 2H, CH<sub>2</sub>), 2.40 (s, 2H, CH<sub>2</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 4.29 (s, 1H, CH), 5.25 (s, 2H, NH<sub>2</sub>), 6.59-6.78 (m, 3H, ArH), 6.80 (s, 1H, OH). Anal. calcd.(%) for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>, C 67.06, H 5.88, N 8.28; found: C 67.00, H 5.80, N 8.30.

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