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## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

# MICHAEL ADDITIONS OF ACTIVE METHYLENE COMPOUNDS TO CHALCONES PROMOTED BY SAMARIUM(III) IODIDE

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Published online: 16 Aug 2006.

To cite this article: Yongmin Ma & Yongmin Zhang (2002) MICHAEL ADDITIONS OF ACTIVE METHYLENE COMPOUNDS TO CHALCONES PROMOTED BY SAMARIUM(III) IODIDE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:6, 819-823, DOI: <u>10.1081/SCC-120002689</u>

To link to this article: http://dx.doi.org/10.1081/SCC-120002689

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### MICHAEL ADDITIONS OF ACTIVE METHYLENE COMPOUNDS TO CHALCONES PROMOTED BY SAMARIUM(III) IODIDE

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#### ABSTRACT

Promoted by SmI<sub>3</sub>,  $\alpha$ , $\beta$ -unsaturated ketones reacted with malononitrile, ethylcyanoacetate, diethylmalonate,  $\beta$ -ketoester or nitromethane to give the 1,4-adducts in moderate to good yields.

In the last decades the application of lanthanoid compounds in organic synthesis has been of great interest.<sup>1</sup> Recently carbon–carbon bond formation reactions mediated by trivalent lanthanoid have rapidly increased. For example, lanthanoid trichlorides were used in combination with NaBH<sub>4</sub>,<sup>2</sup> LiAlH<sub>4</sub>,<sup>3</sup> or Grignard reagent<sup>4</sup> for selective reduction or alkylation of carbonyl compounds; and CeI<sub>3</sub> or CeI<sub>3</sub>/NaI was used in the carbon–carbon bond formation between  $\alpha$ -haloketones and aldehydes.<sup>5</sup>

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We reported that, promoted by SmI<sub>3</sub>,  $\alpha$ -haloketones can react with aldehydes to give  $\alpha$ , $\beta$ -unsaturated ketones.<sup>6</sup> We also reported that, mediated by SmI<sub>3</sub>,  $\beta$ -diketones or  $\beta$ -ketoesters can condense with aldehydes to form benzylidene-substituted  $\beta$ -diketones or  $\beta$ -ketoesters in good yield.<sup>7</sup>

The Michael reaction is one of the most useful methods for forming carbon–carbon bond and has wide synthetic applications. The reaction is usually carried out in the presence of a strong base (such as barium hydroxide<sup>8a</sup>) or weak base (such as piperidine<sup>8b</sup>), but in these reaction conditions, some side reactions will occur. Certainly many other methods have been reported in fitting with this important reaction.<sup>9</sup> Here, we wish to report that, mediated by SmI<sub>3</sub>, active methylene compounds can condense with chalcones to form 1,4-adducts in moderate to good yields (Scheme 1).



The results were summarized in Table 1. We found that when, malononitrile,  $\beta$ -ketoester, diethylmalonate or nitromethane reacted with chalcones, usually the products were obtained in high yields, but when ethylcyanoacetate was ued as nucleophilic reagent, the yields were comparatively low. Unlike traditional base-promoted reactions, the reaction above mentioned was performed in neutral, mild conditions and some side reactions, which occurred in basic conditions, could be avoided.

#### **EXPERIMENTAL**

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer in KBr with absorptions in cm<sup>-1</sup>. <sup>1</sup>H-NMR spectra were determined on a Bruker AC 80 spectrometer as CDCl<sub>3</sub> solutions. Chemical shifts were expressed in ppm downfield from internal standard tetramethylsilane. Mass spectra were recorded on

*Table 1.* Michael Additions of Active Methylene Compounds with Chalcones Induced by  $SmI_3$ 

3a C <sub>6</sub> H <sub>5</sub> NCCH <sub>2</sub> CN	86
$p-ClC_6H_4$ NCCH <sub>2</sub> CN	80
$3c$ $C_6H_5$ NCCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	67
3d $p$ -ClC <sub>6</sub> H <sub>4</sub> NCCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	64
$C_6H_5$ $CH_3COCH_2COOC_2H_5$	88
$p-ClC_6H_4$ $CH_3COCH_2COOC_2H_5$	87
$C_6H_5$ $C_2H_5OOCCH_2COOC_2H_5$	88
$p-ClC_6H_4$ $C_2H_5OOCCH_2COOC_2H_5$	83
$C_6H_5$ CH <sub>3</sub> NO <sub>2</sub>	90
$_{3j}$ <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> NO <sub>2</sub>	81

\*Isolated yield.

HP5989B Mass spectrometer. Elemental analyses were carried out on an EA 1110 instrument.

**General procedure:** Under anhydrous conditions, a mixture of powdered samarium (0.30 g, 2 mmol) and iodine (0.75 g, 3 mmol) in freshly distilled dry THF (20 ml) was stirred at room temperature under a N<sub>2</sub> atmosphere. After Samarium disappeared (ca. 0.5 h), a solution of chalcones 1 (2 mmol) and active methylene compounds 2 (2 mmol) in anhydrous THF (3 ml) was added. The mixture was stirred for 20–24 h at 65°C. The reaction mixture became dark red and homogeneous. Then the reaction mixture was quenched with 0.1 N HCl (5 ml) and extracted with diethyl ether  $(3 \times 15 \text{ ml})$ . The combined extracts were washed with a saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (15 ml) and a saturated solution of NaCl (15 ml) then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporating the solvent under reduced pressure, the crude product was purified by preparative TLC on silica gel using ethyl acetate-cyclohexane (1:6) as eluent.

**3-Benzoyl-1,1-dicyano-2-phenyl-propane (3a).** M.p. 122–125°C (lit.,<sup>10</sup> 125–126°C).  $v_{\text{max}}$  (cm<sup>-1</sup>): 2260 (CN), 1680 (CO).  $\delta_{\text{H}}$  (ppm) 3.60–3.68 (2H, d, J = 7.2 Hz, CH<sub>2</sub>), 3.85–4.18 (1H, m, CH), 4.60–4.66 (1H, d, J = 4.8 Hz, CH), 7.10–8.00 (10H, m, ArH).

**3-Benzoyl-2-(**4'-chlorophenyl)-1,1-dicyano-propane (3b). M.p. 114–116°C (lit.,<sup>10</sup> 115–116°C).  $v_{max}$  (cm<sup>-1</sup>): 2255 (CN), 1680 (CO).  $\delta_{\rm H}$  (ppm) 3.55–3.64 (2H, d, J=7.2 Hz, CH<sub>2</sub>), 3.78–4.20 (1H, m, CH), 4.58–4.64 (1H, d, J=4.8 Hz, CH), 7.10–8.13 (9H, m, ArH).

**3-Benzoyl-1-cyano-1-ethoxycarbonyl-2-phenyl-propane (3c).** Oil.  $v_{max}$  (cm<sup>-1</sup>): 2250 (CN), 1745 (COOC<sub>2</sub>H<sub>5</sub>), 1680 (CO).  $\delta_{\rm H}$  (ppm) 0.93 (3H, t, J = 6.4 Hz, CH<sub>3</sub>), 3.56–3.65 (2H, d, J = 7.2 Hz, CH<sub>2</sub>), 3.86–4.15 (3H, m, CH, OCH<sub>2</sub>), 4.52–4.56 (1H, d, J = 3.2 Hz, CH), 7.30–8.05 (10H, m, ArH). m/z: 321 (M<sup>+</sup>, 1.2), 248 (26.8), 209 (16.4), 119 (11.3), 105 (100), 77 (31.2).

**3-Benzoyl-1-cyano-1-ethoxycarbonyl-2-(4'-chlorophenyl)-propane (3d).** Oil.  $v_{max}$  (cm<sup>-1</sup>): 2250 (CN), 1740 (COOC<sub>2</sub>H<sub>5</sub>), 1685 (CO).  $\delta_{\rm H}$  (ppm) 0.99 (3H, t, J=6.4 Hz, CH<sub>3</sub>), 3.59–3.67 (2H, d, J=6.4 Hz, CH<sub>2</sub>), 3.86–4.24 (3H, m, CH, OCH<sub>2</sub>), 4.63–4.67 (1H, d, J=3.2 Hz, CH), 7.21–7.90 (9H, m, ArH). m/z: 355 (M<sup>-</sup>, 1.4), 282 (22.9), 243 (16.4), 119 (13.8), 105 (100), 77 (40.4).

**3-Benzoyl-1-acetyl-1-ethoxycarbonyl-2-phenyl-propane** (3e). M.p.  $120-122^{\circ}C$  (lit., <sup>8</sup>  $120-121^{\circ}C$ ).  $v_{max}$  (cm<sup>-1</sup>): 1745 (COOC<sub>2</sub>H<sub>5</sub>), 1710 (COCH<sub>3</sub>), 1680 (COPh).  $\delta_{\rm H}$  (ppm) 0.95 (3H, t, J=6.4 Hz, CH<sub>3</sub>), 2.16 (3H, s, CH<sub>3</sub>), 3.48–3.57 (2H, d, J=7.2 Hz, CH<sub>2</sub>), 3.80–4.28 (4H, m, 2CH, OCH<sub>2</sub>), 7.10–7.84 (10H, m, ArH).

**3-Benzoyl-1-acetyl-1-ethoxycarbonyl-2-(**4'**-chlorophenyl)-propane (3f).** M.p. 109–111°C (lit.,<sup>8</sup> 110–111°C).  $v_{max}$  (cm<sup>-1</sup>): 1740 (COOC<sub>2</sub>H<sub>5</sub>), 1710 (COCH<sub>3</sub>). 1680, (COPh).  $\delta_{\rm H}$  (ppm) 1.00 (3H, t, J=6.4 Hz, CH<sub>3</sub>), 2.30 (3H, s, CH<sub>3</sub>), 3.45–3.55 (2H, d, J=8.0 Hz, CH<sub>2</sub>), 3.76–4.23 (4H, m, 2CH, OCH<sub>2</sub>), 7.19–7.79 (9H, m, ArH).

**3-Benzoyl-1,1-diethoxycarbonyl-2-phenyl-propane (3g).** M.p. 63–65°C (lit.,<sup>8</sup> 65–67°C).  $v_{max}$  (cm<sup>-1</sup>): 1740 (COOC<sub>2</sub>H<sub>5</sub>), 1680 (COPh).  $\delta_{H}$  (ppm) 0.90 (3H, t, J=7.2 Hz, CH<sub>3</sub>), 3.38–3.47 (2H, d, J=7.2 Hz, CH<sub>2</sub>), 3.95–4.19 (5H, m, CH, 2OCH<sub>2</sub>), 4.40–4.43 (1H, d, J=2.4 Hz, CH), 7.14–7.94 (10H, m, ArH).

**3-Benzoyl-1,1-diethoxycarbonyl-2-(**4'**-chlorophenyl)-propane (3h).** M.p. 93–95°C (lit.,<sup>8</sup> 96–98°C).  $v_{max}$  (cm<sup>-1</sup>): 1740 (COOC<sub>2</sub>H<sub>5</sub>), 1680 (COPh).  $\delta_{\rm H}$  (ppm) 0.98 (3H, t, J=7.2 Hz, CH<sub>3</sub>), 3.36–3.46 (2H, d, J=8.0 Hz, CH<sub>2</sub>), 4.00–4.21 (5H, m, CH, 2OCH<sub>2</sub>), 4.42–4.45 (1H, d, J=2.4 Hz, CH), 7.14–8.13 (9H, m, ArH).

**4-Nitro-1,3-diphenyl-1-butanone (3i).** M.p. 98–100°C (lit.,<sup>8</sup> 100–101°C).  $v_{max}$  (cm<sup>-1</sup>): 1685 (COPh), 1545 (NO<sub>2</sub>), 1375 (NO<sub>2</sub>).  $\delta_{H}$  (ppm) 3.40–3.48 (2H, d, J=6.4 Hz, CH<sub>2</sub>), 4.00–4.34 (1H, m, CH), 4.66–4.77 (2H, d, J=8.8 Hz, CH<sub>2</sub>), 7.14–7.90 (10H, m, ArH).

**4-Nitro-1-phenyl-3-(4'-chlorophenyl)-1-butanone (3j).** M.p. 110–111°C.  $v_{max}$  (cm<sup>-1</sup>): 1680 (COPh), 1550 (NO<sub>2</sub>), 1360 (NO<sub>2</sub>).  $\delta_{\rm H}$  (ppm) 3.44–3.52 (2H, d, J=6.4 Hz, CH<sub>2</sub>), 4.08–4.37 (1H, m, CH), 4.68–4.79 (2H, d, J=8.8 Hz, CH<sub>2</sub>), 7.14–8.01 (9H, m, ArH). m/z: 257 (M-46, 0.8), 256 (1.9), 105 (100), 77 (26.7). Anal. Calcd for C<sub>20</sub>H<sub>18</sub>ClNO<sub>3</sub>: C, 63.27; H, 4.65; N, 4.61. Found: C, 63.10; H, 4.64; N, 4.63.

#### MICHAEL ADDITIONS

#### ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (Project No. 29872010) and the NSF of Zhejiang Province, China for financial support.

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Received in the UK November 17, 2000

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