SHORT PAPER

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A novel tandem reaction of chalcone with malononitrile or ethylcyanoacetate promoted by samarium (III) iodide and followed by samarium (II) iodide

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Michael additions of active methylene compounds (for example: malononitrile, ethylcyanoacetate) to chalcones promoted by SmI_3 gave 1,4-adducts which, after intramolecular coupling reactions induced by SmI_2, furnished fine yields of cyclic products.

Keywords: chalcone, malononitriles, ethyl cyanoacetate

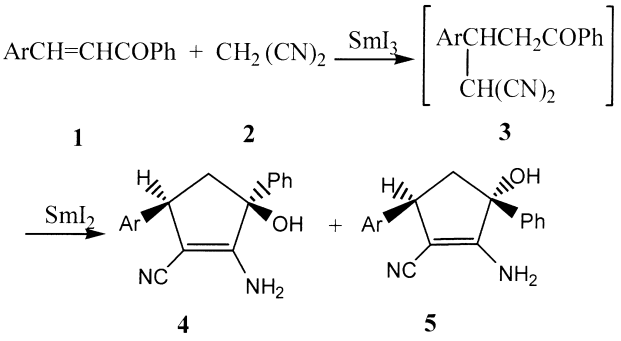
In the last decades the applications of lanthanoid compounds in organic synthesis have been of great interest.[1] Pioneering work performed by Kagan with SmI_2 has served to outline the uses of this reagent in synthetic organic chemistry.[2] Kagan's investigations have been followed by others, revealing that SmI_2 is an exceeding reliable, mild, neutral, selective and versatile single electron transfer reagent for promoting reductive coupling reactions difficult to accomplish by other existing methodologies. For example, Barbier reactions,[3] Reformatsky reactions,[4] pinacol coupling reactions[5] and ketyl–olefin coupling reactions[6] have been reported using SmI_2 as the reagent.

However, compared with the application of samarium diiodide in organic synthesis, little application of samarium triiodide has been developed[7] but it has rapidly increased recently. We have reported that promoted by SmI_3, α-haloketones can react with aldehydes to give α, β-unsaturated ketones.[8] Mori reported that in the presence of SmI_2 or SmI_3, α-haloketones can react with α-ketocarboxylates and α-diketone to form α-hydroxy-γ-ketocarboxylates and 2-hydroxy-1,4-diketones.[9] We have also reported that mediated by SmI_3, β-diketones or β-ketoesters can condense with aldehydes to form benzylidene-substituted β-diketones or β-ketoesters in fair yield.[10]

Carbonyl coupling reactions passing through a ketyl intermediate constitute an important class of reactions in organic chemistry. For instance, ketone–olefin couplings,[11] and intermolecular and intramolecular pinacol coupling reactions[12] have been conducted using SmI_2 as the reagent. It is well known that the carbonyl group can easily be reduced by SmI_2. However, the cyano or alkoxycarbonyl group is relatively stable to samarium diiodide. To the best of our knowledge, little attention has been concerned on the reductive coupling reaction of nitrile or ester with other functional groups. Molander reported the intramolecular ketone–nitrile coupling promoted by SmI_2 under irradiation with a 250 W floodlamp.[13] It has been reported that low valent titanium could induce intermolecular or intramolecular reductive coupling of ketone with ester.[14] Recently, we have reported an intermolecular and intramolecular ketone-nitrile cross-coupling reaction promoted by SmI_2.[15]

Here, we wish to describe our preliminary results on novel one-pot synthesis of 2-amino-3-hydroxy-3,5-diaryl-1-cyclopenten-1-carbonitrile derivatives or 2,3-dihydroxy-3,5-diaryl-1-cyclopenten-1-carbonitrile directly from chalcone with malononitrle or ethylcyanoacetate through cascade reactions promoted by SmI_3 and SmI_2 in THF without isolating the intermediate product— -3-benzoyl-1,1-dicyano-2-arylpropanes or 3-benzoyl-1-cyano-1-ethoxycarboxy-2-arylpropanes from the reaction mixture.

When chalcones **1** (1mmol) and malononitrile **2** (1mmol) were treated with SmI_3 (1mmol) in dry THF at 65° under a nitrogen atmosphere, the intermediate products 3-benzoyl-1,1-dicyano-2-arylpropanes **3** were obtained. Then powdered samarium (0.8 mmol) was added to the flask and reacted with SmI_3 to form SmI_2, which induced the reductive cyclisation of the intermediate products **3** to afford the products 2-amino-3-hydroxy-3,5-diaryl-1-cyclopenten-1-carbonitriles **4** and their geometric isomers **5** (Scheme 1). The results were summarised in Table 1.



Scheme 1

Table 1 Synthesis of 2-amino-3-hydroxy-3,5-diaryl-1-cyclopenten-1-carbonitriles **4** and **5**

Entry	Ar	Isolated yield/%	
		4	**5**
a	C_6H_5	18	40
b	4-ClC_6H_4	20	47
c	4-$CH_3C_6H_4$	15	51
d	4-$CH_3OC_6H_4$	20	48
e	3,4-$OCH_2OC_6H_3$	18	41
f	2-ClC_6H_4	16	48

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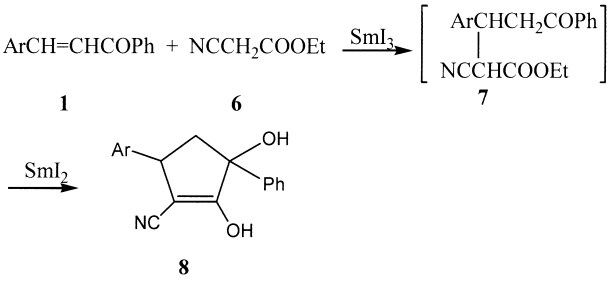
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Similarly, when chalcone **1** and ethylcyanoacetate **6** were treated by SmI_3, the intermediate products 3-benzoyl-1-cyano-1-ethoxycarbonyl-2-arylpropanes **7** were obtained. However, when the intermediate products **7** were treated by addition of powdered samarium, we did not obtain similar reductive cyclisation products ethyl 2-amino-3-hydroxy-3,5-diaryl-1-cyclopenten-1-ester, but the ketone-ester reductive cyclisation products 2,3-dihydroxy-3,5-diaryl-1-cyclopenten-1-carbonitriles **8** was afforded (Scheme 2). The results were summarised in Table 2.



Scheme 2

Table 2 Synthesis of 2,3-dihydroxy-3,5-diaryl-1-cyclopenten-1-carbonitriles **8**

Entry	Ar	Isolated yield/%
a	C_6H_5	42
b	4-ClC_6H_4	48
c	4-$CH_3C_6H_4$	50
d	4-$CH_3OC_6H_4$	44
e	3,4-$OCH_2OC_6H_3$	45

Tables 1 and 2 summarise the results on the tandem reaction of a number of substrates. All products were obtained in moderate yields. From Table 1, we could see that two isomers were obtained. The yield of product **5** was much higher than that of **4**. As to the product **8**, the reaction was highly chemoselective and only one isomer was obtained.

In conclusion, we have provided a new route to 2-hydroxy cyclopentenamine and 2-hydroxy cyclopentenol derivatives. The advantages of the method are the accessibility of the starting materials, simple and mild reaction conditions. Further studies to develop other new uses of SmI_3 and SmI_2 promoted cascade reactions are now in progress.

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^{-1}. ^1H NMR spectra were determined on a Bruker AC 80 or AC 400 spectrometer as $CDCl_3$ or DMSO-d_6 solutions. Chemical shifts were expressed in ppm downfield from internal standard tetramethylsilane. Mass spectra were recorded on HP5989B Mass spectrometer. Elemental analyses were carried out on an EA 1110 instrument.

General procedure for the synthesis of compounds **4** *or* **5:** A solution of chalcone **1** (1 mmol) and malononitrile **2** (1mmol) in THF (2 ml) was added to SmI_3 (1 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred 20–24h at 65°, then the reaction temperature was reduced to room temperature and Sm powder (0.8 mmol) was added to the flask, the colour of the reaction mixture gradually changed into pale-green. After the solution was stirred for another 20 minutes at room temperature, the reaction was quenched with dilute HCl (1M, 1 ml) and extracted with ether. After the usual work-up, the crude product was purified by preparative TLC on silica gel using ethyl acetate–cyclohexane (1:2) as eluent.

Cis-2-amino-3-cyano-1,4-diphenyl-2-cyclopentene-1-ol **(4a):** m.p. 167–168°C, lit.,[15] 168–170°C. ν_{max} (cm^{-1}): 3440, 3325, 2205, 1670, 1610, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.10–2.17 (1H, dd, *J* = 13.2, 7.5 Hz, CH), 2.62 (1H, br s, OH), 2.74–2.81 (1H, dd, *J* = 13.2, 7.5 Hz, CH), 3.88–3.92 (1H, t, *J* = 7.4 Hz, CH), 4.68 (2H, br s, NH_2), 7.25–7.49 (10H, m, ArH).

Trans-2-amino-3-cyano-1,4-diphenyl-2-cyclopentene-1-ol **(5a):** m.p. 165–167°C, lit.,[15] 164–165°C. ν_{max} (cm^{-1}): 3480, 3360, 2200, 1665, 1610, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.20-2.23 (1H, dd, *J* = 14.2, 7.5 Hz, CH), 2.52 (1H, br s, OH), 2.67–2.73 (1H, dd, *J* = 14.2, 7.5 Hz, CH), 4.28-4.32 (1H, t, *J* = 7.3 Hz, CH), 4.40 (2H, br s, NH_2), 7.25–7.49 (9H, m, ArH).

Cis-2-amino-3-cyano-1-phenyl-4-(4-chlorophenyl)-2-cyclopentene-1-ol **(4b):** m.p. 177–180°C, lit.,[15] 178–180°C. ν_{max} (cm^{-1}): 3490, 3420, 3360, 2180, 1685, 1620, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.05–2.13 (1H, dd, *J* = 13.2, 7.3 Hz, CH), 2.60 (1H, br s, OH), 2.72–2.79 (1H, dd, *J* = 13.0, 7.5 Hz, CH), 3.84–3.88 (1H, t, *J* = 7.4 Hz, CH), 4.73 (2H, br s, NH_2), 7.25–7.50 (9H, m, ArH).

Trans-2-amino-3-cyano-1-phenyl-4-(4-chlorophenyl)-2-cyclopentene-1-ol **(5b):** m.p. 191–193°C, lit.,[15] 191–193°C. ν_{max} (cm^{-1}): 3500, 3385, 2205, 1660, 1610, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.15–2.18 (1H, dd, *J* = 14.0, 7.4 Hz, CH), 2.55 (1H, br s, OH), 2.73–2.80 (1H, dd, *J* = 14.0, 7.5 Hz, CH), 4.25–4.29 (1H, t, *J* = 7.4 Hz, CH), 4.37 (2H, br s, NH_2), 7.20–7.45 (9H, m, ArH).

Cis-2-amino-3-cyano-1-phenyl-4-(4-methylphenyl)-2-cyclopentene-1-ol **(4c):** m.p. 172–174°C. ν_{max} (cm-1): 3440, 3370, 3260, 2200, 1670, 1620, 1520. ^1H NMR (400 MHz, $CDCl_3$) δ 2.09–2.12 (1H, dd, *J* = 14.2, 7.2 Hz, CH), 2.32 (3H, s, CH_3), 2.73–2.78 (1H, dd, *J* = 14.2, 7.1 Hz, CH), 2.81 (1H, br s, OH), 3.81–3.87 (1H, t, *J* = 7.4 Hz, CH), 4.70 (2H, br s, NH2), 7.11–7.47 (9H, m, ArH). *m/z*: 290 (M^+, 37), 272 (100). Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.60; H, 6.25; N, 9.65. Found: C, 78.25; H, 5.93; N, 9.91.

Trans-2-amino-3-cyano-1-phenyl-4-(4-methylphenyl)-2-cyclopentene-1-ol **(5c):** m.p. 164–166°C, lit.,[15] 166-168°C. ν_{max} (cm^{-1}): 3440, 3370, 3260, 2200, 1670, 1620, 1520. ^1H NMR (400 MHz, $CDCl_3$) δ 2.12–2.17 (1H, dd, *J* = 14.4, 7.0 Hz, CH), 2.32 (3H, s, CH_3), 2.62–2.68 (1H, dd, *J* = 14.2, 7.4 Hz, CH), 2.93 (1H, br s, OH), 4.23–4.26 (1H, t, *J* = 7.3 Hz, CH), 4.41 (2H, br s, NH_2), 7.12–7.46 (9H, m, ArH).

Cis-2-amino-3-cyano-1-phenyl-4-(4-methoxyphenyl)-2-cyclopentene-1-ol **(4d):** m.p. 146–148°C. ν_{max} (cm^{-1}): 3440, 3365, 3260, 2205, 1670, 1610, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.14–2.20 (1H, dd, *J* = 13.9, 6.8 Hz, CH), 2.49–2.55 (1H, dd, *J* = 14.1, 7.7 Hz, CH), 3.62–3.74 (2H, t, *J* = 7.1 Hz, CH, OH), 3.78 (3H, s, OCH_3), 5.38 (2H, br s, NH_2), 6.82–6.86 (2H, m, ArH), 7.16–7.51 (7H, m, ArH). *m/z*: 306 (M^+, 34), 288 (100). Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.25; H, 5.78; N, 9.31.

Trans-2-amino-3-cyano-1-phenyl-4-(4-methoxyphenyl)-2-cyclopentene-1-ol **(5d):** m.p. 131–132°C. ν_{max} (cm^{-1}): 3460, 3390, 3270, 2205, 1655, 1600, 1500. ^1H NMR (400 MHz, $CDCl_3$) δ 2.05–2.10 (1H, dd, *J* = 13.9, 6.9 Hz, CH), 2.67–2.73 (1H, dd, *J* = 14.1, 7.5 Hz, CH), 3.66 (1H, br s, OH), 3.77 (3H, s, OCH_3), 4.24–4.27 (1H, t, *J* = 7.2 Hz, CH) 5.38 (2H, br s, NH_2), 6.83–6.86 (2H, m, ArH), 7.17–7.51 (7H, m, ArH). *m/z*: 306 (M^+, 45), 288 (100). Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.20; H, 5.75; N, 9.22.

Cis-2-amino-3-cyano-1-phenyl-4-(3,4-methylenedioxyphenyl)-2-cyclopentene-1-ol **(4e):** m.p. 164–165°C, lit.,[15] 164–166°C. ν_{max} (cm^{-1}): 3470, 3385, 3260, 2205, 1660, 1610, 1510. ^1H NMR (400 MHz, $CDCl_3$) δ 2.05–2.12 (1H, dd, *J* = 13.1, 7.5 Hz, CH), 2.49 (1H, br s, OH), 2.65-2.74 (1H, dd, *J* = 13.1, 7.2 Hz, CH), 3.76–3.80 (1H, t, *J* = 7.3 Hz, CH), 4.70 (2H, br s, NH_2), 5.95 (2H, s, OCH_2O), 6.75–6.80 (3H, m, ArH), 7.37–7.61 (5H, m, ArH).

Trans-2-amino-3-cyano-1-phenyl-4-(3,4-methylenedioxyphenyl)-2-cyclopentene-1-ol **(5e):** m.p. 161–163°C, lit.,[15] 162–164°C. ν_{max} (cm^{-1}): 3500, 3375, 3260, 2205, 1660, 1610, 1490 1450. ^1H NMR (400 MHz, $CDCl_3$) δ 2.12–2.19 (1H, dd, *J* = 14.1, 7.5 Hz, CH), 2.56 (1H, br s, OH), 2.58–2.67 (1H, dd, *J* = 14.1, 7.2 Hz, CH), 3.14–3.19 (1H, t, *J* = 7.3 Hz, CH), 4.45 (2H, br s, NH_2), 5.95 (2H, s, OCH_2O), 6.75–6.78 (3H, m, ArH), 7.33–7.51 (5H, m, ArH).

Cis-2-amino-3-cyano-1-phenyl-4-(2-chlorophenyl)-2-cyclopentene-1-ol **(4f):** m.p. 169–170°C, lit.,[15] 171–172°C. ν_{max} (cm^{-1}): 3430, 3375, 3250, 2185, 1675, 1610, 1455. ^1H NMR (400 MHz, $CDCl_3$) δ 1.99–2.06 (1H, dd, *J* = 13.4, 6.4 Hz, CH), 2.44 (1H, br s, OH), 2.85–2.94 (1H, dd, *J* = 13.5, 7.4 Hz, CH), 4.40–4.48 (1H, t, *J* = 7.0 Hz, CH), 4.71 (2H, br s, NH_2), 7.19–7.51 (9H, m, ArH).

Trans-2-amino-3-cyano-1-phenyl-4-(2-chlorophenyl)-2-cyclopentene-1-ol **(5f):** m.p. 181–182°C, lit.,[15] 183–185°C. ν_{max} (cm^{-1}): 3460, 3375, 3250, 2185, 1660, 1610, 1460. ^1H NMR (400 MHz, $CDCl_3$) δ 2.04–2.11 (1H, dd, *J* = 14.4, 6.8 Hz, CH), 2.61 (1H, br s, OH), 2.76–2.86 (1H, dd, *J* = 14.5, 7.5 Hz, CH), 4.63 (2H, br s, NH_2), 4.70–4.80 (1H, t, *J* = 7.0 Hz, CH), 7.19–7.42 (9H, m, ArH).

General procedure for the synthesis of compounds **8:** A solution of chalcone **1** (1 mmol) and ethylcyanoacetate **6** (1mmol) in THF (2 ml) was added to SmI_3 (1 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred 20–24h at 65°, then the reaction temperature was reduced to room temperature and Sm powder (0.8 mmol) was added to the flask, the colour of the reaction mixture gradually changed into pale-green. After the solution was stirred for another 20 minutes at room temperature, the reaction was quenched with dilute HCl (1M, 1 ml) and extracted with ether. After the usual work-up, the crude product was purified by preparative TLC on silica gel using ethyl acetate-cyclohexane (1:1.5) as eluent.

2-hydroxy-3-cyano-1,4-diphenyl-2-cyclopentene-1-ol **(8a):** m.p. 130–132°C. ν_{max} (cm^{-1}): 3355, 3220, 2180, 1620, 1560. ^1H NMR (400 MHz, DMSO-d_6) δ 1.85–1.90 (1H, dd, *J* = 14.3, 5.9 Hz, CH), 2.57–2.63 (1H, dd, *J* = 14.3, 8.4 Hz, CH), 4.21–4.24 (1H, dd, *J* = 8.4, 5.9 Hz, CH), 4.82 (1H, br s, OH), 7.20–7.48 (10H, m, ArH). *m/z*: 277 (M^+, 4.4), 259 (13.9), 105 (100). Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.58; H, 5.28; N, 5.31.

2-hydroxy-3-cyano-1-phenyl-4-(4-chlorophenyl)-2-cyclopentene-1-ol **(8b):** m.p. 168–170°C. ν_{max} (cm^{-1}): 3365, 3230, 2180, 1635, 1560. ^1H NMR (400 MHz, DMSO-d_6) δ 1.83–1.91 (1H, dd, *J* = 14.0, 5.5 Hz, CH), 2.59–2.66 (1H, dd, *J* = 13.6, 8.2 Hz, CH), 4.06–4.10 (1H, dd, *J* = 7.7, 6.0 Hz, CH), 4.85 (1H, br s, OH), 7.14–7.46 (9H, m, ArH). *m/z*: 311 (M^+, 2.4), 293 (23.7), 120 (100). Anal. Calcd. for $C_{18}H_{14}ClNO_2$: C, 69.35; H, 4.53; N, 4.49. Found: C, 68.96; H, 4.42; N, 4.62.

2-hydroxy-3-cyano-1-phenyl-4-(4-methylphenyl)-2-cyclopentene-1-ol **(8c):** m.p. 168–170°C. ν_{max} (cm^{-1}): 3355, 3215 2180, 1625, 1560. ^1H NMR (400 MHz, DMSO-d_6) δ 1.84–1.92 (1H, dd, *J* = 14.2, 6.0 Hz, CH), 2.53–2.62 (1H, dd, *J* = 13.9, 8.0 Hz, CH), 4.05–4.10 (1H, dd, *J* = 7.5, 6.0 Hz, CH), 4.91 (1H, br s, OH), 7.04–7.44 (9H, m, ArH). *m/z*: 311 (M^+, 2.4), 293 (23.7), 120 (100). Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.99; H, 5.78; N, 5.24.

2-hydroxy-3-cyano-1-phenyl-4-(4-methoxyphenyl)-2-cyclopentene-1-ol **(8d):** m.p. 141–143°C. ν_{max} (cm^{-1}): 3355, 3215, 2185, 1625, 1560. ^1H NMR (400 MHz, DMSO-d_6) δ 1.93–2.02 (1H, dd, *J* = 14.1, 5.9 Hz, CH), 2.65–2.72 (1H, dd, *J* = 13.6, 8.0 Hz, CH), 3.77 (3H, s, OCH_3), 4.11–4.17 (1H, dd, *J* = 7.8, 6.2 Hz, CH), 4.87 (1H, br s, OH), 6.81–6.83 (2H, d, ArH), 7.14–7.48 (7H, m, ArH). *m/z*: 307 (M^+, 3.8), 289 (19.7), 159 (100). Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.20; H, 5.48; N, 4.70.

2-hydroxy-3-cyano-1-phenyl-4-(3,4-methylenedioxyphenyl)-2-cyclopentene-1-ol **(8e):** m.p. 164–166°C. ν_{max} (cm^{-1}): 3355, 3210, 2185, 1620, 1555. ^1H NMR (400 MHz, DMSO-d_6) δ 1.81–1.90 (1H, dd, *J* = 14.4, 6.0 Hz, CH), 2.50–2.58 (1H, dd, *J* = 13.9, 8.2 Hz, CH), 4.05–4.13 (1H, dd, *J* = 8.3, 5.7 Hz, CH), 4.95 (1H, br s, OH), 5.90 (2H, s, CH_2), 6.69–6.79 (3H, m, ArH), 7.16–7.45 (6H, m, ArH). *m/z*: 321 (M^+, 17.0), 293 (23.9), 173 (100). Anal. Calcd. for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.65; H, 4.78; N, 4.61.

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