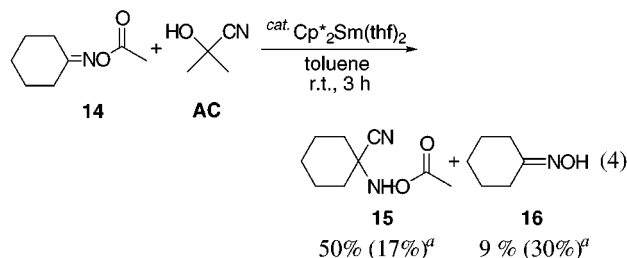


along with cyclohexanoneoxime (**16**) (eq 4). However,  $\text{Sm}(\text{O}^i\text{Pr})_3$  promoted the hydrolysis of oxime acetate **14** to oxime **16** rather than the addition of hydrogen cyanide. Compound **15** is an attractive precursor of an  $\alpha$ -amino acid. The present lanthanide-catalyzed hydrocyanation of oxime ester provides an alternative route for the synthesis of  $\alpha$ -acetylaminonitrile, although the optimum reaction conditions must be further investigated.



<sup>a</sup> Parenthesis shows the yield by  $\text{Sm}(\text{O}^i\text{Pr})_3$  in THF.

In conclusion, we found a direct acetylcyanation method of aldehydes with AC in the presence of IPA catalyzed by  $\text{Cp}^*_2\text{Sm}(\text{thf})_2$  under mild conditions.  $\alpha,\beta$ -Unsaturated carbonyl compounds produced Michael addition products under neutral conditions.

### Experimental Section

**General Procedure.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured at 270 and 67.5 MHz, respectively, in  $\text{CDCl}_3$  with TMS as the internal standard. IR spectra were measured as thin films on NaCl plates or KBr pressed disks. GLC analysis was performed with a flame ionization detector using a 1 mm  $\times$  30 m capillary column (OV-1). Mass spectra were determined at an ionizing voltage of 70 eV. Isopropenyl acetate and acetone cyanohydrin were purchased from a commercial origin and distilled prior to use.  $\text{Cp}^*_2\text{Sm}(\text{thf})_2$ ,<sup>13</sup>  $\text{Cp}^*_2\text{Yb}(\text{thf})_2$ ,<sup>13</sup>  $\text{Sm}(\text{O}^i\text{Pr})_3$ ,<sup>14</sup>

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$\text{Sm}(\text{OTf})_3$ ,<sup>15</sup>  $\text{SmI}_2$ ,<sup>16</sup> and  $\text{SmI}_3$ <sup>17</sup> were prepared according to literature procedures.

**General Procedure for the  $\text{Cp}^*_2\text{Sm}(\text{thf})_2$ -Catalyzed Acetylcyanation of Aldehydes with Acetone Cyanohydrin and Isopropenyl Acetate.** To a Schlenk tube containing a toluene solution (1 mL) of  $\text{Cp}^*_2\text{Sm}(\text{thf})_2$  (0.1 mmol) were added aldehydes (1 mmol), acetone cyanohydrin (1 mmol), and isopropenyl acetate (2 mmol). The reaction mixture was stirred at room temperature for 15 h under argon. After the reaction, wet diisopropyl ether was added to the solution, and the catalyst was removed by filtration. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (10/1 v/v) as eluent to give the corresponding acetates.

**2-Acetoxybutyronitrile (2b):**<sup>18</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.11 (t,  $J = 7.4$  Hz, 3H), 1.89–2.05 (m, 2H), 2.14 (s, 3H), 5.28 (t,  $J = 6.6$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.9, 20.3, 25.8, 62.2, 116.7, 169.2.

**2-Acetoxyisovaleronitrile (2c):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.08 (d,  $J = 6.8$  Hz, 3H), 1.12 (d,  $J = 6.8$  Hz, 3H), 2.10–2.25 (m, 1H), 2.16 (s, 3H), 5.18 (d,  $J = 5.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  17.3, 17.7, 20.3, 31.0, 66.3, 116.0, 169.2.

**2-Acetoxy-4-methylvaleronitrile (2d):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.98 (d,  $J = 6.5$  Hz, 3H), 0.99 (d,  $J = 6.5$  Hz, 3H), 1.76–1.90 (m, 3H), 2.13 (s, 3H), 5.36 (t,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.3, 22.0, 22.1, 24.4, 40.7, 59.8, 117.0, 169.1.

**2-Acetoxy-3,3-dimethylbutyronitrile (2e):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.15 (s, 9H), 2.22 (s, 3H), 5.12 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.1, 25.0, 34.5, 69.2, 115.9, 169.1.

**2-Acetoxy-2-cyclohexylacetoneitrile (2f):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.12–1.32 (m, 5H), 1.67–1.93 (m, 6H), 2.14 (s, 3H), 5.18 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.3, 25.2, 25.3, 25.7, 27.8, 28.0, 40.0, 65.5, 116.1, 169.2.

**2-Acetoxy-2-phenylacetoneitrile (2g):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.16 (s, 3H), 6.41 (s, 1H), 7.44–7.53 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.4, 62.8, 116.1, 127.8, 129.2, 130.3, 131.7, 168.9.

**2-Hydroxy-4-cyanoheptanenitrile (2i):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.99 (t,  $J = 6.8$  Hz, 3H), 1.36–1.78 (m, 4H), 2.05–2.14 (m, 2H), 2.88–3.02 (m, 1H), 3.15–3.22 (m, 1H), 4.65–4.80 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.3, 20.1, 27.1, 33.7, 36.9, 58.0, 119.2, 120.7.

**1-Cyano-N-cyclohexylhydroxyamine O-acetate (15):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.18–2.08 (m, 10H), 2.11 (d,  $J = 2.7$  Hz, 3H), 7.58 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.7, 21.7, 27.1, 24.6, 32.9, 59.4, 119.9, 169.9.

**Acknowledgment.** This work is supported by a Grant-in-Aid for Scientific Research (No. 10132262) on Priority Areas (No. 283), "Innovative Synthetic Reactions" from Monbusho.

**Supporting Information Available:**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and MS spectral for compounds **2b–g**, **2i**, **4**, **6**, **8**, **10**, and **15** and IR and MS spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Additions and Corrections

Vol. 64, 1999

**Bruno Linclau, Ashvani K. Sing, and Dennis P. Curran\***. Organic-Fluorous Phase Switches: A Fluorous Amine Scavenger for Purification in Solution Phase Parallel Synthesis.

Page 2835. Ashvani K. Sing's surname should be spelled Singh.

JO9949873

10.1021/jo9949873

Published on Web 05/04/1999