



## A Very Efficient Cerium (IV) Ammonium Nitrate (CAN) Mediated Thiocyanation of Aralkenes: Formation of Dithiocyanates

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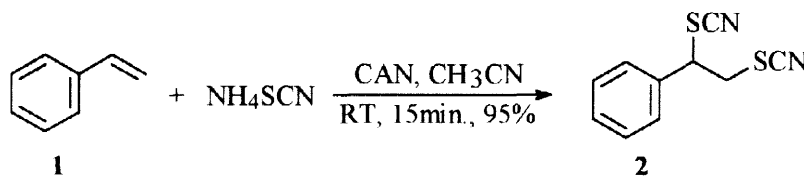
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**Abstract:** A facile dithiocyanation of aralkenes mediated by Cerium (IV) ammonium nitrate is described.  
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In the context of our recent work on carbon-carbon bond forming reactions<sup>1-3</sup> mediated by the Cerium (IV) ammonium nitrate (CAN), we have been exploring the potential application of the latter in oxidative addition of soft bases like thiocyanate to alkenes. Although CAN induced generation of azido radical and the addition of the latter to alkenes have been reported,<sup>4,5</sup> there has been no such work involving thiocyanate. Very recently, however, the addition of thiocyanate to alkenes and arenes mediated by iodosobenzene diacetate and NBS have been reported.<sup>6-8</sup> In view of this, herein we disclose our preliminary results on the thiocyanation of aralkenes.

The initial work involved the reaction of ammonium thiocyanate with styrene. A solution of styrene **1** and ammonium thiocyanate on treatment with CAN in acetonitrile afforded the product **2** in 95% yield (Scheme 1).<sup>9,10</sup>



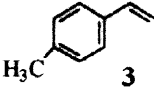
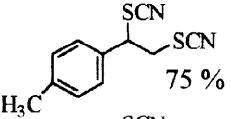
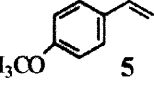
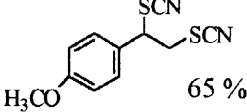
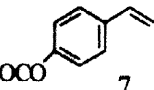
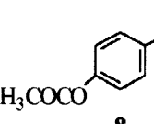
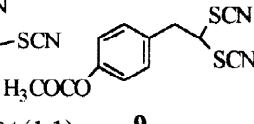
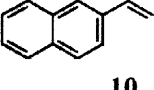
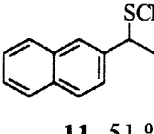
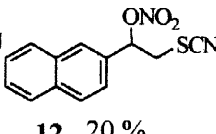
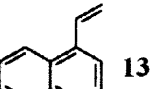
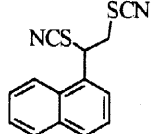
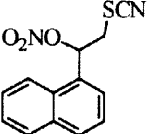
The reaction mixture on processing afforded **2** as a colorless crystalline solid. The IR spectrum showed the characteristic peak of  $-\text{SCN}$  at  $2160\text{ cm}^{-1}$  and the  $-\text{C-S}$  stretching appeared at  $703\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR, the benzylic proton appeared as double doublet at  $\delta$  4.67-4.61 ( $J = 6.01\text{ Hz}, 9.595\text{ Hz}$ ). The two protons attached to the terminal carbon bearing  $-\text{SCN}$  also gave two double doublets at  $\delta$  3.817 ( $J = 6.012\text{ Hz}, 13.72\text{ Hz}$ ) and at  $\delta$  3.659 ( $J = 6.738\text{ Hz}, 13.662\text{ Hz}$ ).  $^{13}\text{C}$  NMR spectrum showed two peaks at  $\delta$  109.808 and 109.455 which are characteristic of  $-\text{SCN}$ . Analytical data was also in agreement with the assigned structure.

A number of substituted styrenes afforded similar products and the results are summarized in Table 1.

In conclusion, we have uncovered a very efficient route to the synthesis of dithiocyanates. Preliminary results indicate that the reaction is applicable to alkenes other than styrenes. Further work is in progress.

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Table 1. Thiocyanation of aralkenes.

Entry	Substrate	Time	Products / Yield*
1.		15 min.	 <b>4</b> 75 %
2.		10 min.	 <b>6</b> 65 %
3.		15 min.	 <b>8</b> 58 % (1:1)  <b>9</b>
4.		30 min.	 <b>11</b> 51 %  <b>12</b> 20 %
5.		30 min.	 <b>14</b> 52 %  <b>15</b> 40 %

Reaction conditions: RT, CAN (2.3 equiv), NH<sub>4</sub>SCN (2 equiv), CH<sub>3</sub>CN; \* isolated yield.

## References and Notes

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- Typical experimental procedure: The styrene **1** (0.5 mmol) and ammonium thiocyanate (1 mmol) were dissolved in 2 mL methanol at room temperature and treated with CAN (1.15 mmol) in methanol (8 mL). The reaction mixture was stirred for 15 minutes. It was then diluted with water (100 mL) and extracted with dichloromethane (4 x 20 mL). The solvent was evaporated and the residue was purified by column chromatography (ethyl acetate / hexane as eluent) to afford **2** (95 %) as colorless crystals. MP: 102-105 °C.
- Spectral data for **2**: IR (KBr): 2955, 2160, 1640, 1506, 703 cm<sup>-1</sup>. <sup>1</sup>HNMR: (300 MHz, CDCl<sub>3</sub>) δ 7.452-7.363 (m, 5H, Aromatic), 4.670-4.618 (dd, 1H, -CHSCN), 3.817-3.751 (dd, 1H, CH<sub>2</sub>SCN), 3.659-3.581 (dd, 1H, CH<sub>2</sub>SCN). <sup>13</sup>CNMR: (75 MHz, CDCl<sub>3</sub>) δ 134.13, 130.23, 129.64, 129.29, 127.49, 109.808 (SCN), 109.455 (SCN), 51.399, 38.177.