

## Selective Deoxygenation of Nitrones Mediated by Sm/CoCl<sub>2</sub>·6H<sub>2</sub>O Reductive System

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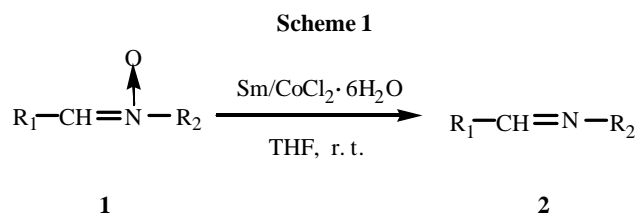
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**Abstract:** In the presence of metallic samarium–cobalt (II) chloride hexahydrate, the nitrones can be reduced to the corresponding imines in moderate to high yields under mild and neutral conditions.

**Keywords:** Nitrone, samarium, cobalt (II) chloride hexahydrate.

Aldimines are an important class compounds<sup>1</sup> which can be prepared by selective deoxygenation of nitrones. Thus more attention was paid to the selective deoxygenation of nitrones in organic synthesis. The reducing reagents, include low-valent titanium<sup>2</sup>, acetic formic anhydride<sup>3</sup>, sodium hydrogen telluride<sup>4</sup>, tributyltin hydride<sup>4</sup>, terathiomolybdate<sup>5</sup>, metallic indium in aqueous media<sup>6</sup>, zinc-aluminum trichloride<sup>7</sup>, aluminum iodide<sup>8</sup>, triphenylphosphine<sup>9</sup>, *etc.* However, there are various limitations to their general utilities: (1) drastic reaction conditions which affect the substituents, and cause uncontrolled reduction of nitrones to amines rather than expected imines<sup>4</sup>, (2) not readily available or expensive reagents. (3) low temperature and dry reaction conditions<sup>2</sup>, (4) long reaction time<sup>5</sup>. Therefore, search for a more efficient, cheap and readily available reagent is required. In connection with our ongoing interest in developing new synthetic application of Sm/MCl<sub>n</sub> system<sup>10</sup>, we found Sm/CoCl<sub>2</sub>·6H<sub>2</sub>O is an efficient reducing reagent in the reduction of nitro compounds or azides<sup>11</sup>. To expand its uses, we apply Sm/CoCl<sub>2</sub>·6H<sub>2</sub>O reductive system to the deoxygenation of nitrones under mild and neutral conditions in THF (as shown in **Scheme 1**).



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The results are listed in **Table 1**. The selective deoxygenation of nitrones mediated by Sm/CoCl<sub>2</sub>·6H<sub>2</sub>O reductive system proceeded very smoothly to give the corresponding imines with satisfactory yields under mild conditions. Interestingly, the carbon-carbon double bond (entry 7), furan (entry 6), which are susceptible to saturation, remain intact. Moreover, aromatic methoxyl (entry 3 and 10) or chloro (entry 2, 5) substituted nitrones were selectively reduced to the corresponding imines.

**Table 1** Selective deoxygenation of nitrones with Sm/CoCl<sub>2</sub>·6H<sub>2</sub>O reductive system

Entry	R <sub>1</sub>	R <sub>2</sub>	Compd.	Time (h)	Yield (%) <sup>a</sup>
1	Ph	Ph	<b>2a</b>	1	91
2	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	<b>2b</b>	1	93
3	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Ph	<b>2c</b>	1	82
4	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	<b>2d</b>	1	81
5	2-ClC <sub>6</sub> H <sub>4</sub>	Ph	<b>2e</b>	1	73
6	Furyl	Ph	<b>2f</b>	1	82
7	Ph-CH=CH	Ph	<b>2g</b>	1	84
8	Ph	4-ClC <sub>6</sub> H <sub>4</sub>	<b>2h</b>	1.5	88
9	Ph	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>2i</b>	1.5	75
10	Ph	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>2j</b>	1.5	81

<sup>a</sup>The structures of all products are confirmed by IR, <sup>1</sup>H NMR.

### General procedure

To a mixture of Sm powder (2 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (2 mmol) was added THF (10 mL), then nitrone (1 mmol) was added under nitrogen atmosphere at room temperature. The mixture was allowed to react at room temperature for 1-1.5 hours. On completion of the reaction (monitored by TLC), the mixture was poured into saturated NH<sub>4</sub>Cl aqueous solution (50 mL) and extracted with diethyl ether (3×20 mL). The combined extracts were washed with saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL), saturated brine (20 mL), successively 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 thin layer chromatography using ethyl acetate and cyclohexane (1:4) as eluant.

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