

# DABCO-POCl<sub>3</sub>, A mild dehydrating agent for the preparation of nitriles from aldoximes

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DABCO-POCl<sub>3</sub> was found to be an efficient reagent for the dehydration of aldoximes to nitriles under mild reaction conditions in excellent yields.

**Keywords:** aldoximes, nitriles, DABCO, POCl<sub>3</sub>

Nitriles are versatile functional groups. They are classified as carboxylic acid derivatives because they can be converted to carboxylic acids on hydrolysis under acidic and basic conditions. They can also be converted to amides via nucleophilic addition of water and ketones via hydrolysis of the imine formed by the nucleophilic addition of a Grignard reagent.<sup>1</sup>

Nitriles can be prepared from the corresponding oximes via dehydration by a variety of methods employing as reagent 1-chlorosulfinyl-4-dimethylaminopyridinium chloride,<sup>2</sup> H<sub>2</sub>SO<sub>4</sub>/SeO<sub>2</sub> under microwave irradiation,<sup>3</sup> clays,<sup>4</sup> TiCl<sub>3</sub>(OTf),<sup>5</sup> polymeric reagent,<sup>6</sup> *p*-toluenesulfonyl chloride on a solid support using microwave<sup>7</sup> indium trifluoromethanesulfonate,<sup>8</sup> phthalic anhydride,<sup>9</sup> tetrachloropyridine,<sup>10</sup> Na<sub>2</sub>SO<sub>3</sub>/SOCl<sub>2</sub>,<sup>11</sup> iodine,<sup>12</sup> zeolite,<sup>13</sup> silica gel,<sup>14</sup> and DABCO/thionyl chloride.<sup>15</sup> These methods have their own merits and drawbacks.

Recently we have demonstrated the one pot conversion of aldoximes into nitriles via aldoxime tosylates under microwave irradiation.<sup>7b</sup> In this communication we wish to report that a complex of DABCO-POCl<sub>3</sub> serves as an efficient and excellent leaving group for conversion of aldoximes into nitriles.

The reagent was easily prepared as a white solid by the reaction of DABCO with a stoichiometric amount of POCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. We were unable to obtain a single-crystal or a mass spectrum in order to establish the structure. However, we expect it to be similar to that of the product of the reaction of polyvinylpyrrolidone and thionyl chloride.<sup>6</sup>

Representative aldoximes were then slowly added to this mixture. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> to give the pure nitrile.

To establish the applicability of method, various aldoximes were converted to the corresponding nitrile using DABCO/POCl<sub>3</sub> complex. The results obtained are recorded in Table 1. Although POCl<sub>3</sub> can be considered as a dehydrating agent, it did not convert aldoxime to nitrile alone.

In summary we have developed a new, simple efficient and high yielding method for conversion of aldoximes to nitriles using an inexpensive reagent.

The reaction proceeded probably via O-substituted aldoxime (II) which undergoes cleavage to afford the corresponding nitriles (Scheme 1).

## Experimental

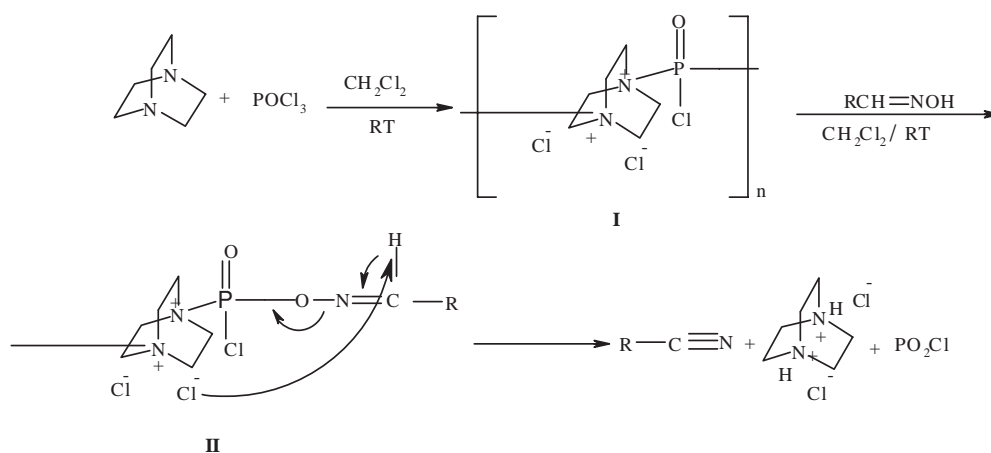
DABCO and POCl<sub>3</sub> were purchased from Merck. Aldoximes were prepared according to the known procedures. All products were known and their physical and spectroscopic data were compared with those of authentic samples.

### Preparation of DABCO-POCl<sub>3</sub> complex

POCl<sub>3</sub> (1 mmol) was gradually added to a stirred solution of DABCO (0.11 g, 1 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 ml) at room temperature to obtain a white precipitate. The reaction mixture was stirred for 5 min to affect the complete reaction. Anal calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>Cl, PO: C, 36.84; H, 6.1; N, 14.32. Found: C, 36.95; H, 6.0; N, 14.1%.

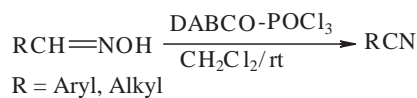
### Conversion of aldoximes to nitriles. General procedure

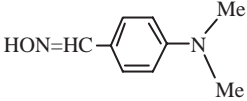
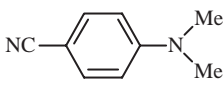
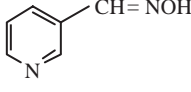
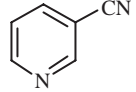
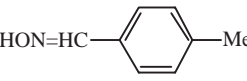
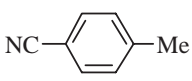
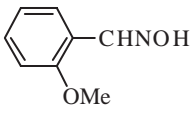
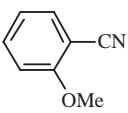
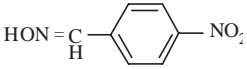
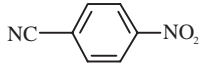
POCl<sub>3</sub> (2 mmol) was gradually added to a stirred solution of DABCO (0.22 g, 2 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 ml) at room temperature to obtain a white precipitate. The reaction mixture was stirred for 5 min to affect the complete reaction. To this reaction mixture an appropriate aldoxime (1 mmol) was added and the mixture was stirred at room temperature. The progress of reaction was monitored by TLC. Upon completion, the reaction mixture was poured into water (20 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over MgSO<sub>4</sub>, filtered and evaporated to afford the corresponding nitrile (Table 1).



Scheme 1

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**Table 1** Conversion of aldoximes to nitriles by DABCO-POCl<sub>3</sub>

Entry	Substrate	Time/min	Product	M.p./°C		B.p./°C		Yield/%
				Observed	Reported	Observed <sup>a</sup>	Reported	
1		2		67	69-71 <sup>16</sup>			96
2		5		51	50-52 <sup>17</sup>			94
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH=NOH	15	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CN			202	205.2 <sup>17</sup>	97
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH=NOH	15	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CN			241	243 <sup>17</sup>	95
5	PhCH=CH CHNOH	45	PhCH=CH-CN			260	263.8 <sup>17</sup>	98.3
6	PhCH <sub>2</sub> CH <sub>2</sub> CHNOH	60	PhCH <sub>2</sub> CH <sub>2</sub> CN			259	261 <sup>17</sup>	98
7		75				215	217.6 <sup>17</sup>	92
8		80				253	255-6 <sup>17</sup>	9
9		120		147	148 <sup>17</sup>			86

<sup>a</sup>At 698–699 mmHg.Received 24 October 2004; accepted 10 May 2005  
Paper 04/2835**References**

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