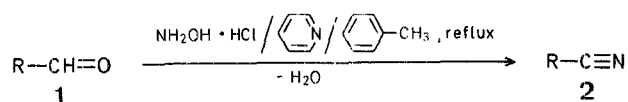


One-Flask Conversion of Aldehydes into Nitriles

Akbar SAEDNYA


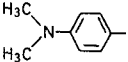

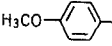

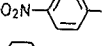
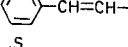


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There are only a few methods known for the one-step or one-flask conversion of aldehydes into nitriles without separation of the aldoxime formed¹⁻⁹. The hydroxylammonium chloride/pyridine/toluene system with azeotropic separation of water has now been applied for converting aldehydes **1** into nitriles **2**. The pyridinium chloride formed participates in the aldoxime-nitrile conversion; thus, the presence of a dehydrating agent is not necessary. Also, all materials used are readily available and inexpensive. It should be noted that the prepared nitriles must have higher boiling points than either toluene or pyridine. Obviously, the method is not applicable to the preparation of low-boiling nitriles.



In this study, two methods have been applied. In Method A, a stoichiometric amount of pyridine is used, the pyridinium chloride formed gradually sublimes to the head of the trap and condenser. The Method B is modified to prevent this sublimation of the salt by using a 1 molar excess of pyridine for each litre of toluene present.

Table. Conversion of Aldehydes 1 to Nitriles 2

Product ^a No.	R	Reaction conditions Method/time	Yield ^b [%]	b.p. [°C]/torr or m.p. [°C]		I.R. (neat or CCl ₄) ν [cm ⁻¹]
				found	reported	
2a		A/3 h; B/6 h	83 ^c ; 68	56°/5	192°/760 ²	2230
2b		A/8 h; B/1.25 h	86; 83	75° (C ₂ H ₅ OH/H ₂ O)	69-70° ¹ , 74-75° ¹⁰	2215
2c		A/6 h; B/6 h	83; 81	93-94°/11	90-92°/11 ²	2230
2d		A/3.5 h; B/4 h	91; 89	59-60° (PE/C ₆ H ₆) ^f	58-59° ² , 61° ¹	2230
2e		A/8 h; B/10 h	80 ^d ; 70	94-95° (PE/C ₆ H ₆) ^f	91° ¹ , 94-96° ²	2235
2f ^c		A/3 h; B/24 h	75; 54	146-147° (95% C ₂ H ₅ OH)	147° ¹ , 147-150° ⁴	2230
2g		A/3 h; B/3 h	92; 85	88-89°/1	128-129°/10 ¹	2230
2h		A/3 h; B/6 h	78° ^c ; 73° ^c	99-100°/39-40	192°/760 ¹¹	2225
2i		A/4.5 h; B/22 h	85; 78	106-107°/1	148°/12 ¹³	2220
2j	<i>n</i> -C ₇ H ₁₅ -	A/3 h; B/4 h	83; 82° ^c	79-81°/10	79°/10 ¹² , 82°/12 ¹²	2245
2k	<i>n</i> -C ₉ H ₁₉ -	A/4 h; B/5 h	52; 50° ^c	77-80°/1-2	106°/10 ¹³	2250

^a Products characterised by comparison of m.p., T.L.C., G.L.C., I.R., and ¹H-N.M.R. data.

^b Yield of pure product after distillation or recrystallisation.

^c Purity ≥98% by G.L.C. (conditions: 15% Carbowax on Chromosorb W, 190°C, Perkin-Elmer F-30, N₂ 20 ml/min).

^d Purified by column chromatography (silica gel/dichloromethane) and recrystallisation.

^e Slightly soluble in toluene at room temperature.

^f Or ligroin or petroleum ether (PE).

Cinnamitrile 2g; Typical Procedure for Method A:

To a mixture of hydroxylammonium chloride (7 g, 0.1 mol) and pyridine (8 g, 0.101 mol), stirred by a magnetic bar, in a 500 ml flask, is added redistilled *trans*-cinnamaldehyde (1g; 13.2 g, 0.1 mol) in one portion. An increase in temperature is observed. After the reaction mixture has been stirred for 5-10 min, toluene (100 ml) is added. The flask content is refluxed and water is separated using a Dean-Stark water trap. The amount of water to be obtained from the oxime formation is collected within the first hour of reflux. Generally, the pyridinium chloride formed, after oxime formation, sublimes slowly to the head of the trap. Thus, the collected water contains some of the salt and when the reaction is completed, its volume amounts to something between 5-6 ml. The reaction is monitored by T.L.C. (silica gel/dichloromethane). After completion of the reaction (see Table), the flask contents are left to cool down. The cooled mixture is filtered from the unsublimed salt (if any). The filtrate is separated from toluene by distillation. The remaining filtrate is distilled through a short column under reduced pressure; yield: 12 g.

The sublimed pyridinium chloride in reaction vessel can be washed down with the chloroform (50 ml) by refluxing. As the volume of chloroform is decreased by distillation, the pyridinium chloride is precipitated by the addition of dry ether.

4-(*N,N*-Dimethylamino)-benzonitrile (2b); Typical Procedure for Method B:

4-(*N,N*-Dimethylamino)-benzaldehyde (1b; 14.9 g, 0.1 mol) is added in one portion to a 500 ml flask containing a solution of hydroxylammonium chloride (7 g, 0.1 mol) in pyridine (15.8 g, 0.2 mol) with stirring by a magnetic bar. After 3-5 min stirring, toluene (100 ml) is added and the mixture is heated under reflux with separation of water by means of a Dean-Stark water trap. After 0.5 h, the theoretical amount of water from oxime formation is collected. Heating is continued until no more water is collected (1.25 h). The cooled solution is filtered from the pyridinium chloride, the filtrate is washed with water (2 × 50 ml), dried with anhydrous sodium sulphate, and the toluene is removed by distillation. The residue solidifies on cooling. It is purified by recrystallization from aqueous ethanol; yield: 12.2 g.

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