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## Organic Reactions in Water: Transformation of Aldehydes to Nitriles using NBS under Mild Conditions

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**Abstract:** Aliphatic, aromatic, heterocyclic, conjugated, and polyhydroxy aldehydes gave corresponding nitriles in high yields at 0°C using NBS and ammonia in water.

Keywords: Aldehydes, NBS, nitriles, organic reactions in water

Conversion of carbonyl compounds into nitriles is an important functional group transformation in organic synthesis,<sup>[1]</sup> which is achieved in majority of the cases via aldoxime dehydration in a two-step process. Direct conversion of aldehydes into nitriles without isolation of nitrogen-containing intermediates has also been explored.<sup>[2]</sup> Of the different one-pot preparative methods developed in recent years, many are mainly limited to aromatic aldehydes, which are preferably converted to aromatic nitriles, whereas the transformation of enolizable aliphatic aldehydes often give unsatisfactory yields of aliphatic nitriles. The problem can be somewhat circumvented by using less available reagents<sup>[3]</sup> and unconventional approaches<sup>[4]</sup> for direct conversion of aldehydes into nitriles that employ IR and microwave activation in the presence of inorganic solid

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Address correspondence to B. P. Bandgar, Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, India. Fax: 0091-2462-29245; E-mail: bnadgar\_bp@yahoo.com supports. In one such method reported by Villemin et al.,<sup>[4a]</sup> the intermediate dithiocarbonate generated by reacting the oximate with CS<sub>2</sub> is converted into nitrile by prolonged reaction in presence of Al<sub>2</sub>O<sub>3</sub>/KF. Recently aliphatic and aromatic nitriles were prepared in high yields in a direct one-pot process by heating corresponding aldehydes with hydroxylamine hydrochloride in N-methylpyrrolidone at a high temperature  $(100-115^{\circ}C)$  for a longer time (4 to 8 h).<sup>[5]</sup> Other methods<sup>[6]</sup> that are applicable to both aromatic and aliphatic aldehydes often involve expensive or hazardous reagents.

The use of ammonia combined with an appropriate oxidant is an expedient method for the transformation of aliphatic and aromatic aldehydes to their corresponding nitriles. Different reagents developed to effect this conversion are  $NH_3/O_2/CuCl_2 \cdot 2H_2O/MeONa$  in MeOH,<sup>[7a]</sup>  $NH_3/Pb(OAc)_4$ in dry benzene,<sup>[7b]</sup>  $NH_3/I_2/MeONa$  in MeOH,<sup>[7c]</sup>  $NH_3/S_8/NaNO_2$ ,<sup>[7d]</sup>  $NH_3/KI/MeONa$  in MeOH on electrooxidation,<sup>[7e]</sup>  $NH_3/H_2O_2/CuCl$  in 2-propanol,<sup>[7f]</sup>  $NH_3/I_2$  in THF–water.<sup>[7g]</sup>

The development of a method that allows the reaction under essentially mild and neutral conditions should heighten the synthetic potential of the conversion. In this communication we report preliminary results of direct conversion of aldehydes to corresponding nitriles in excellent yields using NBS and aq.  $NH_3$  under mild conditions (Equations 1–3 and Table 1).

$$R - C \xrightarrow{0}_{H} \frac{NBS, aq, NH_{3}, 0^{\circ}C}{R - C \equiv N} \qquad (1)$$

### **RESULTS AND DISCUSSION**

The aldehydes examined in this study included aliphatic aldehydes, aromatic aldehydes, heterocyclic aromatic aldehydes,  $\alpha$ , $\beta$ -unsaturated aldehydes, and saccharide aldehydes. It is also important to note that the dialdehyde, terephthalaldehyde, smoothly converted into corresponding dicyanide in excellent yield. The preparations of p-nitrobenzonitrile (93%), furonitrile (90%), cinnamononirile (87%), and aliphatic nitriles (88–94%) from the corresponding aldehydes in the presence of NBS–NH<sub>3</sub> were successfully accomplished. The water-soluble 2-deoxy-D-ribose with NBS in ammonia–water at 0°C for 15 min gave (3,4,5-tri-acetoxy)pentane-nitrile **14** (97%) after isolated acetylation (Ac<sub>2</sub>O/water). Similarly D-glucose furnished the corresponding nitrile isolated after acetylation to yield (2,3,4,5,6-pentaacetoxy)-D-glucononitrile **15** in 85% yield (Equation 3).

Entry	Substrate	Product	Reaction time (min)	Yield (%)
1 2 3 4	H <sub>3</sub> CCH <sub>2</sub> CHO H <sub>3</sub> C(CH <sub>2</sub> ) <sub>2</sub> CHO H <sub>3</sub> C(CH <sub>2</sub> ) <sub>4</sub> CHO H <sub>3</sub> C(CH <sub>2</sub> ) <sub>5</sub> CHO	H <sub>3</sub> CCH <sub>2</sub> CN H <sub>3</sub> C(CH <sub>2</sub> ) <sub>2</sub> CN H <sub>3</sub> C(CH <sub>2</sub> ) <sub>4</sub> CN H <sub>3</sub> C(CH <sub>2</sub> ) <sub>5</sub> CN	10 10 15 20	88 94 90 88
5	СНО	CN O	15	86
6	СНО	CN OH	10	96
7	СНО	CN CI	25	93
8			30	93
9	CHO	CN OMe	90	78
10	СНО		60	80
11	CHO CN		40	85
12	O CH	CN CN	40	90
13		CH=CHCN	30	87

Table 1. Transformation of aldehydes to nitriles using NBS in ammonia water

The plausible mechanism of the reaction are shown in Equations (2) and (3).



In conclusion, this method is general, as a variety of aldehydes (Table 1) were successfully transformed into nitriles by treatment with NBS and ammonia in water. This simple, economic, and environmentally benign method is especially useful for the transformation of water-soluble aldehydes such as carbohydrates (Equations 2 and 3).

#### **EXPERIMENTAL**

IR spectra were recorded on Bomem MB 104 FT-IR spectrometer, and <sup>1</sup>H NMR spectra were recorded on an AC 300F NMR spectrometer (300 MHz).

#### **General Procedure**

A suspension of an aldehyde (5 mmol) in ammonia water (10 ml of 30%) was stirred for 2 to 3 min at room temperature, which resulted in the

#### **Organic Reactions in Water**

formation of a turbid solution. To this turbid solution NBS (5 mmol) was added slowly with constant stirring at 0°C. The yellowish-brown solution immediately becomes colorless with precipitation of the product, which indicates completion of the reaction (TLC). Solid products are collected by simple filtration, whereas liquid products are obtained by usual workup after extraction with ethyl acetate.

(3,4,5-Triacetoxy)pentanenitrile (14):  $[\alpha]_D^{25} = 7.25$  (c = 2.6, CHCl<sub>3</sub>); IR (neat) = 22 65 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.1 (s, 3H, COCH<sub>3</sub>), 2.15 (s, 3H, COCH<sub>3</sub>), 2.18 (s, 3H, COCH<sub>3</sub>), 2.6–2.7 (m, 2H, CH<sub>2</sub>CN), 4.15 (dd, J = 12.2 and 4.5 Hz, 1H), 4.35 (dd, J = 12.2 and 3.3 Hz, 1H), 5.2–5.3 (m, 2H, CH<sub>2</sub>O; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 17 (CH<sub>2</sub>), 21 (2 × CH<sub>3</sub>), 22.5 (CH<sub>3</sub>), 62.3 (CH<sub>2</sub>), 65.7 (CH), 72.1 (CH), 123.2 (C), 171.4 (C), 171.8 (C), 172.1 (C). Anal. calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>6</sub>: C, 51.36; H, 5.84; N, 5.45. Found: C, 51.42; H, 5.77; N, 5.38.

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