# A Simple Unusual One-Step Conversion of Aromatic Aldehydes into Nitriles

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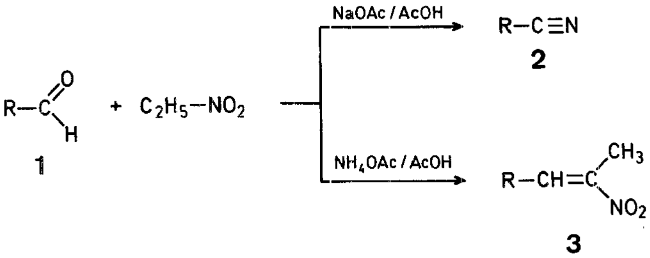
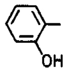
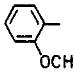
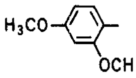
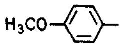
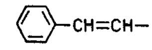
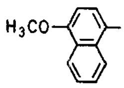
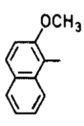
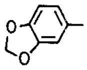
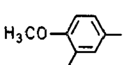
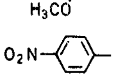
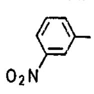
Several methods for the conversion of aldehydes into nitriles are known[1-8], among them are two recently published one-pot procedures[9,10]. We report here a somewhat unusual, high-yield method which is simple, general, and convenient and which does not use expensive reagents.

Refluxing of aldehydes **1** and nitroethane in glacial acetic acid in the presence of sodium acetate, followed by hydrolysis and ether extraction gives the corresponding nitriles **2** in pure form. The method affords high yields with aromatic aldehydes whereas the yields are only fair with alkanals and with cinnamaldehyde. The use of hydrated or fused sodium or potassium acetate in the reaction does not lead to markedly differing results as regards yield and purity of the product nitriles **2**.



Under similar conditions, the use of ammonium acetate in place of sodium or potassium acetate results in the formation of the expected[11-14] 1-aryl-2-nitropropenes **3**.

**Table.** Reaction of Aldehydes **1** with Nitroethane and Sodium Acetate or Ammonium Acetate in Acetic Acid

| 1, 2, 3 | R | Product 2 obtained using NaOAc | | | | Product 3 obtained using $NH_4OAc$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Yield [%] | | m.p. [°C] or b.p. [°C]/torr | | Yield [%] | | m.p. [°C] | |
| | | found[a] | reported[b] | found | reported | found[a] | reported[b] | found | reported |
| **a** |  | 90 | 80[7] | m.p. 95° | m.p. 97°[7] | 0[c] | | | |
| **b** |  | 80 | 90[7] | b.p. 107°/0.1 | b.p. 140°/20[7] | 64 | 59[7] | 50° | 51°[11] |
| **c** |  | 65 | 92[7] | m.p. 94° | m.p. 96°[7] | 40 | | 72° | |
| **d** |  | 92 | 79[6] | m.p. 60° | m.p. 61°[6] | 68 | 60[12] | 44° | 48°[12] |
| **e** |  | 48[d] | 81[6] | b.p. 102°/0.1 | b.p. 128°/10[6] | 0 | | | |
| **f** |  | 75 | 81[2] | m.p. 105° | m.p. 103°[2] | 59 | 29[13] | 86° | 85°[13] |
| **g** |  | 89 | 95[2] | m.p. 87° | m.p. 89°[2] | 54[e] | | | |
| **h** |  | 71 | 81[4] | m.p. 92° | m.p. 92°[4] | 65 | 80[12] | 94° | 98°[12] |
| **i** |  | 82 | 76[1] | m.p. 67° | m.p. 67°[1] | 70 | 35[14] | 68° | 68°[14] |
| **j** |  | 80 | 94[9] | m.p. 147° | m.p. 146°[9] | 40 | 32[17] | 113° | 114°[17] |
| **k** |  | 75 | 94[9] | m.p. 110° | m.p. 109°[9] | 0 | | | |
| **l** | $n$-$C_9H_{19}$— | 55 | 17[18] | b.p. 240°/710 | b.p. 109°/10[18] | | | | |

[a] Yield of isolated purified product.

[b] Best yields obtained by other methods.

[c] No nitrostyrene formation with $NH_4OAc$ even after 5 h reflux.

[d] Together with cinnamonitrile (**2e**), 22% of nitrostyrene (**3e**), m.p. 80°C is obtained.

[e] Mixture of the ($E$)- and ($Z$)-isomers.

Another noteworthy feature of the reaction is the observation that if nitromethane was used instead of nitroethane, the products were only 1-aryl-2-nitroethylenes ($\omega$-nitrostyrenes) even when sodium acetate was used. This result reveals the importance of the combination nitroethane/sodium acetate. It should be pointed out that in a recently described method[10] nitromethane/polyphosphoric acid is used to convert aromatic aldehydes into nitriles. It is also worthy of note that the use of nitromethane/pyridine hydrochloride[7] results in nitrile formation.

It has been reported[15] that nitroethane reacts with 36 normal sulfuric acid to give ethanehydroxamic acid. The presence of an intermediate of this type in the reaction mixture could presumably convert the aldehyde into an oxime derivative which could be cleaved to give the nitrile in the presence of sodium acetate. This assumption is supported by the observation that under the conditions used by us the oxime acetate prepared from 2-methoxy-1-naphthaldehyde is converted into the same nitrile which is obtained directly from the aldehyde. Further work on the mechanism in progress.

The structures of the nitriles prepared were proven by comparison of their physical and spectral data with those reported in the literature and by microanalyses. Another proof of the structure of nitriles **2** is provided by the fact that the nitrile **2e** (cinnamonitrile) obtained from cinnamaldehyde (**1e**) and nitroethane/sodium acetate according to our method was identical with cinnamonitrile (**2e**) prepared from benzaldehyde by base-catalyzed reaction with acetonitrile[16].

### Nitriles (2); General Procedure:

A mixture of the aldehyde **1** (0.05 mol), nitroethane (7.51 g, 0.1 mol), fused sodium acetate (8.21 g, 0.1 mol), and glacial acetic acid (10 ml) is refluxed for 3–4 h. The progress of the reaction is followed by T.L.C. After cooling, the mixture is poured onto ice (100 g) and extracted with ether (3 × 50 ml). The ether extract is washed with saturated sodium hydrogen carbonate solution (2 × 50 ml), dried with sodium sulfate, and evaporated. The solid product thus obtained is recrystallized from 1/4 benzene/$n$-hexane. In the case of cinnamonitrile (**2e**), 4-nitro-1-phenyl-1,3-pentadiene is formed as a side product; the two products can be separated by column chromatography on silica gel using $n$-hexane as eluent.

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