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A novel and convenient transformation of nitriles to aldehydes

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Abstract—Various aromatic nitriles are reduced to the corresponding aldehydes by platinum(IV) oxide in aqueous formic acid with yields ranging from 76 to 94%. This mild method may be generally applied to multi-step organic synthesis. © 2002 Elsevier Science Ltd. All rights reserved.

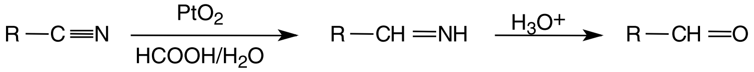
Aldehydes are important intermediates in organic synthesis due to their reactivity. Three principal methods can be used for the reduction of nitriles to aldehydes: (1) Stephen reduction,[1] in which nitriles are reduced to aldehydes by stannous chloride and hydrogen chloride under anhydrous conditions; (2) using metal hydrides such as $LiAlH_4$, $LiAlH(OEt)_3$,[2] DIBAL,[3] NaH_2AlEt_2;[3] (3) reduction by 150% (w/w) Raney nickel, first reported by Backeberg and Staskun.[4–6] A comprehensive reagent list for this transformation has been compiled by Larock.[7]

In this communication, we wish to report a convenient method to reduce nitriles to aldehydes by platinum(IV) oxide under mild conditions. A typical procedure is illustrated by the preparation of *p*-methoxybenzaldehyde: a mixture of 4-methoxybenzonitrile (10 mmol) and platinum oxide (1 mmol) in 15 mL of 80% aqueous formic acid was stirred at 55–60°C for 7 h. Platinum was removed by filtration. Water (15 mL) was added to the filtrate and the product was extracted with ether (3×20 mL). The ether extract was washed with water (3×4 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford crude product with above 90% purity. Purification of the crude product by a silica gel chromatographic column with a mixed solvent of methylene chloride and methanol (95:5) gave a colorless liquid product.

Formic acid not only serves as a solvent, but also as a hydrogen source in the reaction. Reaction of formic acid with platinum oxide liberates hydrogen and carbon dioxide[8] and leads to formation of more reactive platinum species capable of reducing nitriles to the corresponding aldimines. The aldimines are rapidly hydrolyzed to aldehydes (Scheme 1).

Representative reaction times and yields are given in Table 1. It should be noted that better yields are achieved with shorter reaction times when platinum is added portionwise at certain intervals. In addition, the double bond in entry 4 remains unreacted when treated with PtO_2 under these reaction conditions, the same observation were reported by Staskun and van Es when Raney nickel used.[5,9] Attempted reduction of an aliphatic nitrile (entry 9) gave a yield of only 9%. An improved yield might be achieved under amended reaction conditions, but such studies have not been conducted.

In conclusion, a simple method for the transformation of aromatic nitriles to the corresponding aldehydes is described herein. The reaction can be carried out under mild conditions and proceeds with good to excellent yield. This method may find application in multi-step organic synthesis of complex compounds.



$$R-C\equiv N \xrightarrow[HCOOH/H_2O]{PtO_2} R-CH=NH \xrightarrow{H_3O^+} R-CH=O$$

Scheme 1. Proposed pathway of reduction of nitrile to aldehyde.

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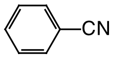
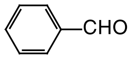
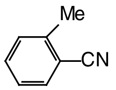
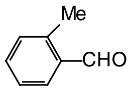
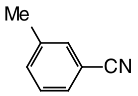
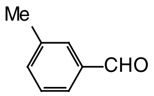
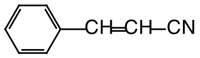
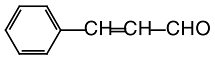
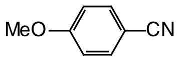
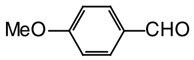
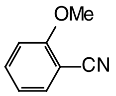
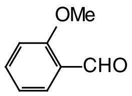
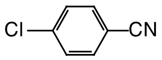
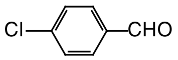
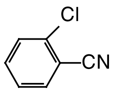
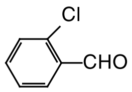
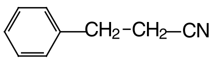
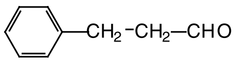
Table 1. Reaction time and yields of products

Entry	Nitrile	Aldehyde	Reaction Time (hr)	Yield (%)
1			3	94
2			3	90
3			3	92
4			12-20	42-56
5			7	86
6			8.5	83
7			7-19	80-89
8			10-15	76-84
9			20	9

Acknowledgements

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