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HYDROXYLAMINE-O-SULFONIC ACID: A CONVENIENT REAGENT FOR THE OXIDATIVE CONVERSION OF ALDEHYDES INTO NITRILES

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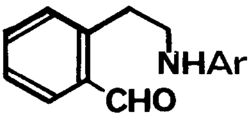
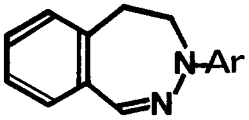
In an attempt to introduce a second nitrogen atom into δ-aminoaldehyde 1 by a nitrogen-nitrogen coupling reaction (1,2), we used hydroxylamine-O-sulfonic acid NH_2-O-SO_3H 2. The expected benzodihydrodiazepine 3 was obtained in poor yield only(3); the major product proved to be δ-aminonitrile 4.

From these results we conclude that the expected oxaziridine intermediate(2,4) did not form; instead one gets condensation to the corresponding oximino-O-sulfonic acid from which sulfuric acid is eliminated to yield the nitrile.



1



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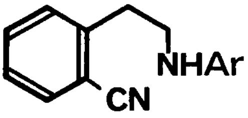

4

Ar = $p\text{-}NO_2\text{-}C_6H_4\text{-}$

Although the standard procedure for the conversion of aldehydes into nitriles is by dehydrating the corresponding oximes(5), it seemed desirable to generalize this oxidative one-batch reaction, which had been mentioned only briefly by Sommer(6) and by Cambi(7). Cambi for instance described the formation of hydrocyanic acid from the reaction of formaldehyde with 2.

In a standard run a solution, or a suspension in water of the aldehyde, is treated with 30% excess of hydroxylamine-O-sulfonic acid. Aliphatic aldehydes yield directly the corresponding nitriles at room temperature (method A). Aromatic aldehydes lead at room temperature to the oximino derivatives $R-CH=N-O-SO_3H$ which decompose to the corresponding nitriles at 65° (method A'); alternatively the oximino-intermediates are cleaved at room temperature by adding sodium hydroxide (method B). Formylpyridines and formylpyrroles, which are either unstable in solution or acid sensitive, are successively treated at 0° with 2, thence with sodium hydroxide, to yield the corresponding nitriles (Table 1).

Nitriles	yield %	Method	Nitriles	yield %	Method
EtCN	80	A	o,o'-Cl_2-C_6H_3-CN	68	A';B
nPrCN	90	A	2-cyanopyridine	75	B
HO-CH_2-CN	60	A	3-cyanopyridine	76	B
C_6H_5-CN	85	A'	4-cyanopyridine	70	B
m-OH-C_6H_4-CN	93	A'	2-cyanopyrrole	88	A'
p-OH-C_6H_4-CN	80	A'	2-cyano 3-methoxy pyrrole	60	A'
p-$NO_2C_6H_4$-CN	95	A'			
o-Cl-C_6H_4-CN	85	A';B			

Table 1

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