A New Route to Nitriles. Dehydration of Aldoximes using 2,4,6-Trichloro-s-triazine (Cyanuric Chloride)

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Summary Nitriles are produced in good yields when aldoximes are treated with 2,4,6-trichloro-*s*-triazine in the presence of pyridine under mild conditions.

THE preparation of nitriles from aldehydes normally requires vigorous reaction conditions.[1] Recently there has been a growing interest in suitable methods by which such conversions can be efficiently carried out under mild conditions. Although a few mild procedures have been described for the dehydration of aldoximes to nitriles,[2] their application, in general, has not been widely established. We therefore report a dehydration sequence, which is a convenient and exceptionally mild preparative route to nitriles.

The dehydration of benzamide to benzonitrile using cyanuric chloride has been described[3] The conversion of aldoximes into nitriles by use of this reagent has not been reported. We have found that the reaction of some aldoximes with cyanuric chloride gives nitriles in very good yields.

The method involves addition of cyanuric chloride (0·36—0·5 mole) to a solution of the oxime (1 mole) in the presence of pyridine (1 mole) at room temperature. The reaction, in most cases, is nearly complete within an hour. The precipitate† is filtered off and the nitrile isolated by distillation or crystallization.

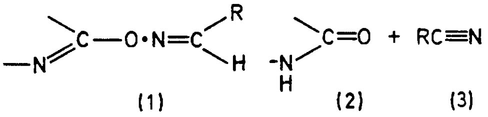
Table

Oxime[a]	Nitrile[b] yield %
Benzaldoxime, (*E*-)	82
4-Nitrobenzaldoxime, (*Z*-)[c]	92
3,4,5-Trimethoxybenzaldoxime	92
2-Pyridylaldoxime,[d] (*E*-)	63
1-Methyl-2-pyrrolealdoxime[e]	70
Butanal oxime, (*E*:*Z* = 1:1 mole)	64

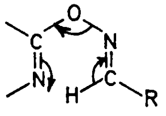
[a] The oximes were either obtained from commercial sources or prepared by standard procedures. The reaction, unless mentioned otherwise, was carried out in dichloromethane solution under N_2. [b] The yields refer to isolated and analytically pure (values within ± 0·3%) products (b.p./m.p., i.r., and n.m.r. identical with authentic specimens). [c] The adducts were kept stirring overnight for completion of the reaction. [d] The addition of the reagents was reversed, dichloromethane–dioxan (1:2 vol.) used as solvent. [e] Dioxan was used as solvent.

The process is quite general and particularly useful for acid-sensitive aldehydes. The results, shown in the Table, suggest that the stereochemistry of the oximes‡ has very little effect on the reaction.

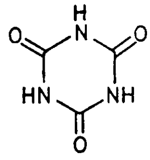
The reaction sequence can be rationalised by assuming the formation of an *O*-*s*-triazinyl intermediate (**1**), which undergoes a ready elimination[5] to the nitrile (**3**). The requisite driving force for such fragmentation,[6] derived from the transformation of (**1**) into (**2**), could be represented by a cyclic concerted process (**4**).



(1) (2) (3)



(4)



(5)

Trisubstitution on the triazine ring may occur simultaneously or in a stepwise process. The corresponding intermediate *O*-*s*-triazinylaldoxime then decomposes leading eventually to (**5**). The relative ease of such conversion is attributed to the fact that the triazinyl is a good leaving group. Similar features are also observed in the pyrolysis of iminoethers.[7]

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† Compound (**5**) was isolated from the precipitate by crystallization from water.

‡ The (*E*)-(*Z*) interconversions are well known[4] and it is likely that the oximes are isomerised under the reaction conditions.

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