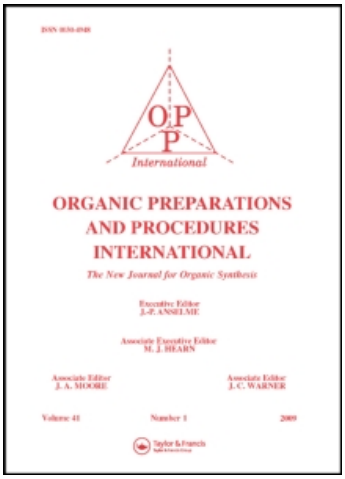

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A CONVENIENT LABORATORY NITRILE SYNTHESIS. THERMAL DECOMPOSITION OF O-(METHYLCARBAMOYL) ALDOXIMES

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A CONVENIENT LABORATORY NITRILE SYNTHESIS. THERMAL DECOMPOSITION OF O-(METHYLCARBAMOYL) ALDOXIMES

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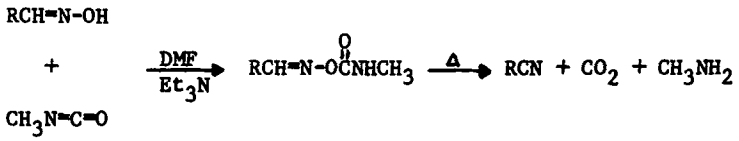
O-(Methylcarbamoyl) aldoximes constitute an important class of commercial insecticides.[2] Because of our interest in the mode of action and the fate of insecticides, we have studied the stability of various members of this class at elevated temperatures.

Payne, Stansbury, and Weiden have shown that the commercial insecticide, 2-methyl-2-(methylthio)-propionaldehyde-O-(methylcarbamoyl) oxime, decomposes to the corresponding nitrile.[3] We have found this to be a general reaction of N-methyl carbamates of aldoximes and have developed it into a convenient laboratory conversion of aldoximes to nitriles.

There are a number of known methods in the literature for the dehydration of aldoximes to nitriles.[4] Our method offers the advantages of being convenient, resulting in good to excellent yields and eliminating the use of acids or bases. In addition, the nitriles formed are easily separated from the gaseous reaction by-products. The conversion is outlined in the reaction below.



The aldoxime is dissolved in dimethylformamide and a 10% molar excess of methyl isocyanate is added along with triethylamine as a catalyst. After standing for 0.5 hr. (carbamate formation), the DMF solution is heated to reflux without isolation of the intermediate carbamate; decomposition takes place between 110-120° as indicated by gas evolution. Upon cooling, the product is isolated by dilution of the reaction mixture with water; the solid products are isolated directly and the liquid products are worked up in the usual manner.

Table I summarizes the yields and physical properties of the nitriles synthesized. The method appears to be a general one. Good to excellent yields have been obtained from aromatic aldoximes regardless of whether the benzene ring bears electron withdrawing, electron donating or sterically hindering substituents. Similarly, good yields have been obtained from both an aliphatic and an α,β-unsaturated aldoxime.

The substitution of methyl isothiocyanate for methyl isocyanate likewise results in the formation of the corresponding nitrile in good yield. Although this reagent offers the advantage of decomposition at lower temperatures (85-90°); the unpleasant odor of the starting material, intermediates, and reaction by-products does not make this reagent as convenient for laboratory use. Further work is now in progress to study in detail the mechanism and other applications of this reaction and will be reported elsewhere.

EXPERIMENTAL

All aldoximes were prepared by standard methods.[5] The structure of all nitriles was established by comparison of their IR, mp. or bp. with those of authentic materials.

Nitriles. General Procedure. - In a 250 ml flask equipped with a

TABLE I

$$R\text{-}CH{=}N\text{-}OH \longrightarrow R\text{-}C{\equiv}N$$

R	mp. or bp./mm	Lit. mp. or bp./mm	Yield %
4-Methoxyphenyl	60-62°	61-62°[d]	67
3,4-Methylenedioxyphenyl	93-94°	94-95°[e]	65[a] 69[b]
3,4-Dichlorophenyl	86-89°	92°[f]	85
2,4,6-Trimethylphenyl	50-52°	50-51°[g]	79
Phenyl	75-79°/20 mm	69/10 mm[h]	65[c]
2,6-Dimethyl-1-heptyl	75-77°/1.2 mm	119-120/30 mm[i]	88[c]
2,6-Dimethylhepta-1,5-dien-1-yl	80-83°/2.5 mm	78/2 mm[j]	99[c]

a) Methyl isocyanate method.
b) Methyl isothiocyanate method.
c) Yield determined by GLC of isolated reaction product.
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magnetic stirrer, reflux condenser and thermometer, a solution of 0.1 mole of the aldoxime in 35 ml of DMF is treated with 0.11 mole of methyl isocyanate. Two drops of triethylamine are added and the solution is allowed to stir at ambient temperature for 0.5 hr. In some cases the intermediate carbamate separates from the solution. The solution or mixture is then refluxed for 2 hrs. Evolution of the gaseous reaction products is observed between 110-120°. The solution is then cooled to room temperature and diluted with 200 ml of water. The solid products are filtered and recrystallized while the liquid products are extracted

3x100 ml with benzene, dried, concentrated and distilled.

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