Synthetic Methods and Reactions; 83[1]. Sulfuryl Chloride Fluoride, a Mild Dehydrating Agent in the Preparation of Nitriles from Aldoximes

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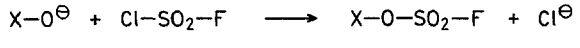
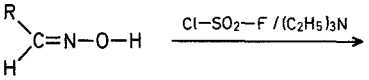
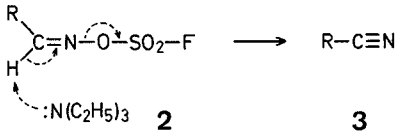
Sulfuryl chloride fluoride has found extensive use as a solvent in the preparation of stable carbocations[2]. Recently, a simplified, easy preparation from sulfuryl chloride and hydrogen fluoride/pyridine[3] has made it readily available. Sulfuryl chloride fluoride has not yet been utilized as a reagent in organic synthesis, although it should be highly reactive toward nucleophiles. It is expected that the reaction of sulfuryl chloride fluoride with oxygen-containing nucleophiles should result in the displacement of chloride ion while forming the fluorosulfonate group, one of the most efficient leaving groups in solvolysis-cleavage reactions.



We consequently tested the expected reactivity of sulfuryl chloride fluoride and the good leaving group ability of the resulting fluorosulfonate group and report the efficient preparation of nitriles **3** from the corresponding aldoximes **1** in excellent yield (Table), when the aldoximes were treated with sulfuryl chloride fluoride in the presence of triethylamine at room temperature.



1



2 **3**

The reaction is applicable to alkyl, aralkyl and aryl aldoximes. The present method constitutes one of the mildest methods, among those available[4,5], for the dehydration of aldoximes to nitriles under neutral conditions and should also be applicable to other dehydrations.

Table. Dehydration of Aldoximes **1** to Nitriles **3**

R	Yield [%][a,b]	m.p. [°C] or b.p. [°C]/torr	
		found	Ref.[6]
C_6H_5	97	49°/3.5	69°/10
4-H_3CO—C_6H_4	85	59.6°	61–62°
4-H_3C—C_6H_4	81	97°/15	103–106°/20
1-naphthyl	95	119°/4	148°/12
2-furyl	70	42°/10	146°/738
C_6H_5—CH=CH	88	95°/1.5	134°/12
n-C_5H_{11}	92	44°/8	47.3°/10
n-C_6H_{11}	73	45–51°/3	70–72°/10

[a] Yield of pure, isolated product.
[b] Purity determined by I.R. and ^{1}H-N.M.R. spectroscopy.

General Procedure for the Dehydration of Aldoximes:
Sulfuryl chloride fluoride (2.5 ml) condensed in dichloromethane (5 ml) at −78 °C (Dry Ice/acetone) is slowly added with good stirring to a solution of the aldoxime **1** (10 mmol) and triethylamine (30 mmol) in dichloromethane (50 ml), under a dry nitrogen atmosphere at room temperature. The reaction mixture is stirred for 8 h (or alternatively for 1 h at room temperature and then heated under reflux for 3 h) and then quenched with ice/water (50 ml). The organic layer is separated from the aqueous layer which is further extracted with dichloromethane (2 × 25 ml). The combined organic extract is washed successively with cold water and saturated sodium chloride solution. The organic extract is dried with anhydrous magnesium sulfate and the solvent evaporated. The crude products are purified by distillation or recrystallization and their purity determined by comparison of physical and spectral characteristics with those of authentic samples.

Support of our work by the National Science Foundation is gratefully acknowledged. One of us (A. G. L.) wishes to thank Consejo Nacional de Ciencia y Technologia (Government of Mexico) for financial support.

Received: February 11, 1980

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