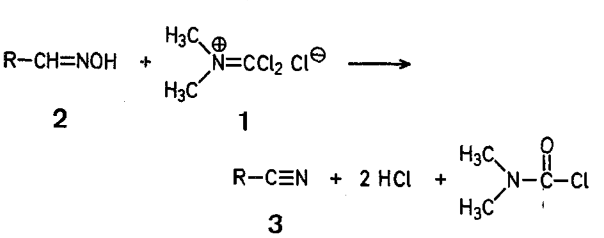
Nitriles from Aldoximes and *N*,*N*-Dimethyldichloromethaniminium Chloride

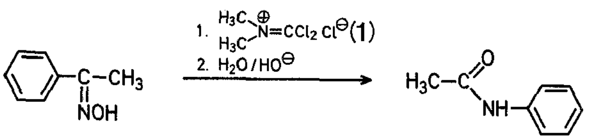
V. P. Kukhar and V. I. Pasternak

Institute of Organic Chemistry, Academy of Science of the Ukrainian SSR, Kiev-252660, USSR

Many types of reagents have been used for the synthesis of nitriles from aldoximes. We wish to report a new reagent for this synthesis, *N*,*N*-dimethyldichloromethaniminium chloride[1] ("phosgeneimmonium chloride") **1**. The reaction of **1** with aldoximes is carried out at reflux for 2–4 h in chloroform or dichloromethane and nitriles are obtained in high yields (see Table).



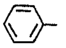
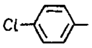
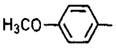
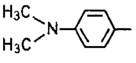
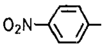
Ketoximes undergo the Beckmann rearangement upon reaction with **1**; for example, acetophenone oxime is converted into acetanilide.



Acetonitrile:

To a mixture of **1** (0.03 mol) and dichloromethane (50 ml), a solution of acetaldoxime (0.03 mol) in dichloromethane (30 ml) is added with stirring at 0°. The reaction mixture is then refluxed until the evolution of hydrogen chloride ceases (~2 h). Dichloromethane and acetonitrile are distilled at atmospheric pressure; yield of *acetonitrile*: 92%; b.p. 81°. The residue is distilled under reduced pressure to give *dimethylcarbamoyl chloride*; yield: 65%; b.p. 53°/15 torr.

Table. Nitriles (**3**) from Aldoximes (**2**) and *N*,*N*-Dimethyldichloromethaniminium Chloride (**1**)

R	Reaction time (h)	Yield[a] (%)	m.p. or b.p.
H_3C-	2	92	b.p. 81°/760 torr
	2	97	b.p. 68–70°/12 torr
	3–4	90	m.p. 77–79°
	3–4	96	m.p. 57–59°
	2–3	82	m.p. 74–75°
	3–4	98	m.p. 146–148°

[a] The nitriles were identified by their physical properties and by elemental analyses (good accordance with theoretical values).

Benzonitrile:

The solution of benzaldoxime (0.04 mol) in chloroform (50 ml) is added with stirring to a suspension of **1** (0.04 mol) in chloroform (70 ml). The reaction mixture is refluxed until the evolution of hydrogen chloride ceases (~2 h), chloroform is evaporated, and the residue is distilled in vacuo.

4-Chlorobenzonitrile:

A suspension of 4-chlorobenzaldoxime (0.01 mol) in chloroform (30 ml) is added with stirring to a mixture of **1** (0.01 mol) and chloroform (30 ml). The reaction mixture is refluxed for 3–4 h until evolution of hydrogen chloride ceases. Chloroform is evaporated at reduced pressure, the crystaline product is washed with petroleum ether, and recrystallized from hexane.

4-Methoxybenzonitrile and *4-nitrobenzonitrile* are obtained similarly.

4-Dimethylaminobenzonitrile:

A solution of 4-dimethylaminobenzaldoxime (0.04 mol) in chloroform (50 ml) is added to a stirred solution of **1** (0.04 mol) in chloroform (70 ml). The reaction mixture is refluxed for 2–3 h. Chloroform and dimethylcarbamoyl chloride are evaporated in vacuo (12 torr). The residue is dissolved in water (100 ml), cooled (5°), and the precipitated 4-dimethylaminobenzonitrile is isolated by filtration and recrystallized from water.

Acetanilide:

A solution of acetophenone oxime (0.04 mol) in chloroform (50 ml) is added to a stirred solution of **1** (0.04 mol) in chloroform (70 ml). The mixture is refluxed for 2 h and then evaporated in vacuo (10–15 torr). The residue is dissolved in water (100 ml) and the solution is neutralized with 10% sodium carbonate solution. The precipitate is collected, dried, and crystallized from water; yield: 86%; m.p. 112–114°. The identity of the product was confirmed by comparison with an authentic sample.

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[1] H. G. Viehe, Z. Janousek, *Angew. Chem.* **85**, 837 (1973); *Angew. Chem. Internat. Edit.* **12**, 806 (1973).
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