Benzonitriles from Benzaldoximes and an Ynamine

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Many types of reagents have been used for the synthesis of nitriles from aldoximes[1-7]. We wish to report the use of another reagent for this synthesis, namely 1-(*N*,*N*-diethylamino)-propyne (**1**). The reaction of **1** with benzaldoximes **2** is carried out at reflux for 2 h in acetonitrile and nitriles **4** are obtained in good yields (see Table).

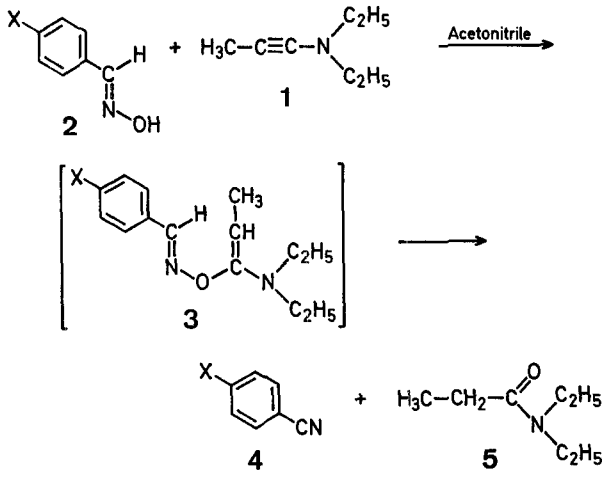

Table. Benzonitriles **4** from Benzaldoximes **2** and 1-Diethylamino-propyne **1**

X	Configuration of oxime	Yield [%]	m.p. or b.p./torr	Lit. m.p. or b.p./torr
H	*E*	69[a]	79°/15	69°/10[9]
H	*Z*	21[a]	79°/15	69°/10[9]
Cl	*E*	77	91°	94–96°[9]
O_2N	*E*	80	146°	149°[9]
H_3CO	*E*	73	60°	61–62°[9]

[a] Yield determined by N.M.R. spectrometry of mixture of **4** and **5**.

To explain the formation of the nitrile **4** and the diethyl propanamide (**5**), we must assume the formation of the intermediate **3** which fragments to give **4** and **5**. The existence of this intermediate can also explain the low yield of benzonitrile from *Z*-benzaldoxime. The *Z*-isomer, to form **3**, must at first be converted into the *E*-isomer, but reacts also directly with the guanine to give a mixture from which no identifiable product could be isolated.

Preparation of Nitriles 4 from Benzaldoximes 2; General Procedure:

A solution of 1-diethylaminopropyne[8] (**1**; 2.22 g, 0.022 mol) in acetonitrile (10 ml) is added to a stirred solution of he oxime (0.02 mol) in acetonitrile (50 ml). The temperature of the mixture is maintained at 20° during the addition. The reaction mixture is then refluxed for 2 h and a slight excess of **1** (0.22 g) is added after 1 h. Acetonitrile is evaporated and the residue distilled in vacuo; in the case of benzonitrile, distillation is unable to affect a separation of the product from diethylpropanamide. In this case the yield was determined by N.M.R. spectrometry.

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