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A Useful Method for the Conversion of Aldehyde Oximes into Nitriles Using 1,1′-Oxalyldiimidazole

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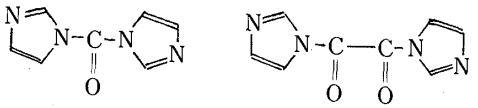
Under neutral conditions, aliphatic, alicyclic, aromatic, and heteroaromatic aldehyde oximes (**3**) react with 1,1′-oxalyldiimidazole (**2**) in an appropriate solvent such as benzene, acetonitrile, chloroform, or tetrahydrofuran at 65—70 °C within 1 h to give the corresponding nitriles (**4**) in good yield.

Keywords——dehydration; 1,1′-carbonyldiimidazole; 1,1′-oxalyldiimidazole; oxime; nitrile

Foley and Dalton have reported that 1,1′-carbonyldiimidazole (CDI; **1**)[1] is an effective dehydrating reagent for the conversion of aldehyde oximes (**3**) into nitriles (**4**) at, or slightly above, room temperature in dichloromethane solution.[2] Recently, Iizuka and co-workers have also shown that carboxamide (**5**) reacts with CDI (**1**) in the presence of a reactive halide such as allyl bromide to give the corresponding nitrile (**4**).[3] CDI (**1**), though commercially available, is too expensive for application on a large scale.[4] Furthermore, toxic phosgene[1b] used for the preparation of CDI (**1**) requires very careful handling. Thus, we were prompted to examine the possibility that 1,1′-oxalyldiimidazole (ODI; **2**) may be generally effective as a dehydrating reagent in the transformation of aldehyde oximes (**3**) into nitriles (**4**). Incidentally, the critical reagent, ODI (**2**), is a known compound,[5] which is easily prepared on a laboratory scale by the reaction of 1-(trimethylsilyl)imidazole[6a] with oxalyl chloride in benzene at room temperature.[6b]



(CDI) **1** (ODI) **2**

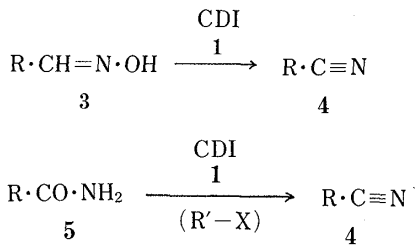


Chart 1

We now report another simple and convenient method for the preparation of nitriles (**4**) from aldehyde oximes (**3**) under neutral conditions utilizing ODI (**2**). For instance, the reaction of *n*-heptaldehyde oxime (**3a**) with an equimolar amount of ODI (**2**) in benzene solution at 65—70 °C for 10 min occurred smoothly to afford *n*-heptanenitrile (**4a**) in 80%

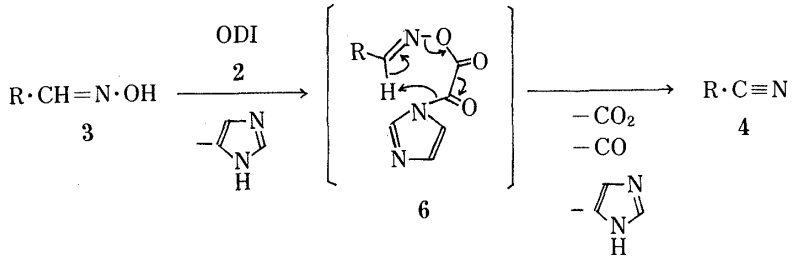


Chart 2

TABLE I. Preparation of Nitriles (**4**) from Aldehyde Oximes (**3**) Using 1,1′-Oxalyldiimidazole (ODI; **2**)

Compd. No.	R	Reaction time[a] (min)	Yield[b] (%)	bp/mmHg (mp)[c] (°C)	
				Found	Reported
4a	$CH_3(CH_2)_5$–	10	80	77—80/20	182—182.5/757[7]
4b	Cyclohexyl–	60	81	70—73/18	64—66/12[8]
4c	Cl–C$_6$H$_4$–	50	83	(91—93)[d]	(93—94)[9]
4d	CH_3–C$_6$H$_4$–	30	78	102—104/20	214—216/760[9]
4e	CH_3O–C$_6$H$_4$–	30	83	(57—59)[d]	(58—61)[9]
4f	O_2N–C$_6$H$_4$–	30	79	(145—147)[e]	(146—147)[9]
4g	2-furyl–	5	73	82—83/100	139—140/640[9]
4h	CH_3–2-furyl–	10	77	74—75/27	65—67/15[10]
4i	O_2N–2-furyl–	10	84	(60—61)[f]	(61—62)[11]
4j	2-thienyl–	5	80	95—97/25	72—73/10[9]
4k	O_2N–2-thienyl–	10	80	(44—45)[f]	(45)[12]

a) Heating time at 65—70 °C. *b*) Yields of the products (**4a**—**k**) after purification. Compounds (**4a**—**k**) were characterized by comparison of their mp (bp) and IR data with those of authentic samples. *c*) All melting points are uncorrected. *d*) Purified by column chromatography on silica-gel with benzene as an eluent. *e*) Recrystallized from ethanol–benzene (4 : 1). *f*) Recrystallized from ethanol.

yield after distillation. Similarly, 3-methoxybenzaldehyde oxime (**3e**) was successfully converted to 3-methoxybenzonitrile (**4e**) in 83% yield. A heteroaromatic nitro compound, 5-nitro-2-furancarboxaldehyde oxime (**3i**), was likewise dehydrated with ODI (**2**) to give 5-nitro-2-furancarbonitrile (**4i**) in 84% yield after recrystallization from ethanol. Acetonitrile, chloroform, and tetrahydrofuran were equally effective as reaction solvents. The results of representative cases are summarized in Table I.

As shown in Chart 2, the reaction described in this short communication probably proceeds *via* the formation of an *o*-[2-(1-imidazolyl)oxalyl]oxime intermediate (**6**) between the

aldehyde oxime (**3**) and ODI (**2**) at room temperature, and subsequently concerted eliminations of CO_2, CO, and imidazole take place under heating to afford the corresponding nitrile (**4**).

Thus, it has been demonstrated that 1,1′-oxalyldiimidazole (ODI; **2**) can be conveniently used in the transformation of aldehyde oximes (**3**) into nitriles (**4**) under mild and neutral conditions.

Experimental[13]

Nitriles (4) from Aldehyde Oximes (3)——General Procedure (Using Benzene as the Reaction Solvent): ODI (**2**) (5 mmol) was added to a solution of an aldehyde oxime (**3**) (5 mmol) in benzene (30 ml). The mixture was stirred at room temperature for 15 min, and then heated at 65—70 °C for the time listed in Table I. The resultant mixture was filtered to remove oily materials. The filtrate was washed with 1% hydrochloric acid and water, then the benzene layer was dried over anhydrous sodium sulfate. The organic solvent was evaporated under reduced pressure to give the crude nitrile (**4**), which was further purified by distillation or recrystallization.

References and Notes

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