samples.

References

1. J.L. Luche, J.C. Damiano, *J. Am. Chem. Soc.*, 1980, **102**, 7926.
2. K.S. Suslick, P.F. Schubert, and J.N. Goodale, *J. Am. Chem. Soc.*, 1981, **103**, 7342.
3. S. Raucher, and P. Klein, *J. Org. Chem.*, 1981, **46**, 3558.
4. B.H. Han, and P. Boudizouk, *Tetrahedron Lett.*, 1981, **22**, 2757.
5. J.V. Cooney, *Tetrahedron Lett.*, 1979, 3917.
6. P. Boudzouk, and B.H. Han, *Tetrahedron Lett.*, 1981, **22**, 3813.
7. F.H.C. Stewart, *Chem. Rev.*, 1964, **64**, 129.
8. J.C. Earl, and A.W. Mackney, *J. Chem. Soc.*, 1935, 899.
9. W.D. Ollis, and V.D. Poole, *J. Chem. Soc.*, 1949, 307.
10. R.A. Eade, and J.C. Earl, *J. Chem. Soc.*, 1946, 591.
11. V.G. Yashunskii, and L.E. Kholodav, *Zh. Obsch. Khim.*, 1962, **32**, 3661.
12. J.K. Stille, and F.W. Harris, *J. Heterocyclic. Chem.* 1966, **3**, 155.

New Methods for the Preparation of Nitriles and Isothiocyanates Using Di-2-pyridyl Carbonate

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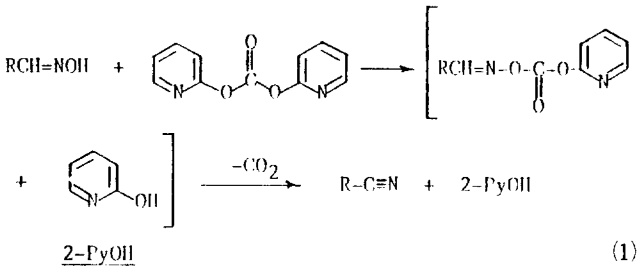
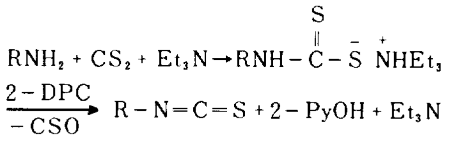
In connection with our ongoing research program on the synthetic utility of 2-pyridyl related active esters and carbonates, we have reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling reagent for the direct esterification of carboxylic acids[1,2] and a carbonyl transfer reagent for the formation of cyclic carbonates from 1,2- and 1,3-diols[3]. We now wish to report that nitriles can be prepared from aldoximes in high yields under mild conditions (eq. 1) and triethylammonium dithiocarbanates, easily prepared from amines, carbon disulfide, and triethylamine, are cleanly converted into the corresponding isothiocyanates (eq. 2) by the use of 2-DPC, respectively.

Conversion of aldoximes into nitriles using 2-DPC was carried out in the presence of bases such as triethylamine, 4-dimethylaminopyridine (DMAP), and 1,8-diazabicyclo-



(1)



$$RNH_2 + CS_2 + Et_3N \rightarrow RNH-\overset{\overset{S}{\|}}{C}-\overset{-}{S}\ \overset{+}{N}HEt_3 \xrightarrow[-CSO]{2-DPC} R-N=C=S + 2-PyOH + Et_3N \qquad (2)$$

Table 1. Preparation of Nitriles from Aldoximes

Aldoxime	Method[a]	Time, h	Yield, %	b.p./torr or m.p.	
				found[b]	reported
$C_6H_5CH=NOH$	A	3	83	68-69/9	190/760[10]
$p-CH_3C_6H_4CH=NOH$	A	2	95	62-64/1.5	91/11[10]
$p-CH_3O-C_6H_4CH=NOH$	A	5	82	60	60[6]
	B	0.5	94		
$p-Cl-C_6H_4CH=NOH$	A	0.5	91	92-93	91-92[6]
	B	0.7	90		
$p-NO_2-C_6H_4CH=NOH$	A	0.1	93	145-146	146-147[6]
	B	0.5	90		
$c-C_6H_{11}CH=NOH$	A	12	87	65-67/9	66/9[6]
	B	2	88		
$CH_3(CH_2)_7CH=NOH$	A	12	84	60-62/1	224/760[15]
	B	2	84		
$C_6H_5CH=CH-CH=NOH$	A	12	85	90-91/1.1	136-138/19[7]
	B	1.5	89		

[a] Method A: with 0.1 equiv of DBU in CH_2Cl_2 at room temperature. Method B: in refluxing toluene. [b] All nitriles obtained here are known compounds identified by physical and spectral data (m.p., b.p., IR, and ^1H-NMR).

Table 2. Preparation of Isothiocyanates from Triethylammonium Dithiocarbamates

Isothiocyanates	Time, h[a]	Yield, %	b.p./torr or m.p.	
			found	reported
C_6H_5-N=C=S	1.5	90	65-68/3	105-108/14[11]
p-Cl-C_6H_4-N=C=S	1.5	91	45-46	46.5[11]
p-CH_3O-C_6H_4-N=C=S	1.5	91	120-122/2.2	167-168/18[11]
$C_6H_5CH_2$-N=C=S	1	86[b]	73-75/1.5	105-110/10[12]
c-C_6H_{11}-N=C=S	1	85[b]	55-57/0.9	109/10[12]
$CH_3(CH_2)_6CH_2$-N=C=S	1	84[b]	86-88/3	123/12[14]

[a] Reaction time for conversion of triethylammonium dithiocarbamates to isothiocyanates. [b] The reaction was carried out by two-step, one pot procedure and the yields are based on the amine.

[5.4.0]undec-7-ene (DBU) to find out an optimum condition. Reaction of 4-methylbenzaldoxime with an equimolar amount of 2-DPC and triethylamine in dichloromethane at room temperature in 8 h gave 4-methylbenzonitrile in 90% yield, whereas the reaction using 1 equiv of DMAP required 24 h for completion of the reaction. We have found that the use of DBU as a catalyst is very effective in the conversion of aldoximes into nitriles. In the case of 4-methylbenzaldoxime, the reaction was complete within 2 h at room temperature using 0.1 equiv of DBU. Thus, remaining reactions were carried out with an equimolar amount of 2-DPC and aldoximes in the presence of 0.1 equiv of DBU in dichloromethane at room temperature (Method A). Using this procedure, several aromatic aldoximes were cleanly converted into the corresponding nitriles within 5 h as shown in Table 1. However, conversion of aliphatic aldoximes into nitriles proceeded slowly, as compared to that of aromatic aldoximes and required 12 h for completion of the reaction.

Furthermore, we have found that conversion of aldoximes into nitriles smoothly proceeds in refluxing toluene (Method B). Using method B, various aldoximes were dehydrated to afford nitriles in high yields within 2 h. Since neutral, water-soluble 2-hydroxypyridine (2-PyOH) is produced as a byproduct from the reaction, it is of synthetic significance that the present reaction occurs under an essentially neutral condition. For instance, the use of N,N′-carbonyldiimidazole for this conversion produces basic imidazole, although the reaction occurs relatively at low temperature without adding a base[4].

We feel that the present method, because of its simplicity, effectiveness, and mildness, might become the method of choice for the conversion of aldoximes into nitriles, although a number of methods are available for this conversion[4-10].

The preparation of isothiocyanates from triethylammonium dithiocarbamates using 2-DPC was briefly studied. First, reaction of triethylammonium phenyl dithiocarbamate with an equimolar amount of 2-DPC in dichloromethane at room temperature for 1.5 h gave phenyl isothiocyanate in 90% yield. Similarly, several triethylammonium aryl dithiocarbamates[11] were cleanly converted into the corresponding isothiocyanates in high yields as shown in Table 2. In the case of aliphatic amines, the reaction was carried out by a two-step, one pot procedure without isolation of triethylammonium alkyl dithiocarbamates. Thus, treatment of amines with an equimolar amount of carbon disulfide and triethylamine in dichloromethane at room temperature for 1 h, followed by the addition of 2-DPC and subsequent stirring for 1 h gave the corresponding alkyl isothiocyanates in high yields.

In conclusion, the present method offers several advantages over previously known methods in terms of the mildness, effectiveness, and simple workup[11-14].

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References

1. S. Kim, J.I. Lee, and Y.K. Ko, *Tetrahedron Lett.*, 4943 (1984).
2. S. Kim and Y.K. Ko, *J. Chem. Soc. Chem. Commun.*, 473 (1985).
3. S. Kim and Y.K. Ko, *Heterocycles*, **24**, 1625 (1986).
4. H.G. Foley and D.R. Barton, *J. Chem. Soc., Chem. Commun.*, 628 (1973).
5. M. Shiono, Y. Echigo, and T. Mukaiyama, *Chem. Lett.*, 1397 (1976).
6. G. Sosnovsky and J.A. Krogh, *Synthesis*, 703 (1978).
7. H. Suzuki, T. Fuchita, A. Iwasa, and T. Mishina, *Synthesis*, 905 (1978).
8. G.A. Olah and K. Keumi, *Synthesis*, 112 (1979) and references cited therein.
9. G. Sosnovsky, J.A. Krogh, and S.G. Umhoefer, *Synthesis*, 722 (1979) and references cited therein.
10. T. Keumi, T. Yamamoto, H. Saga, and H. Kitajima, *Bull. Chem. Soc. Jpn.*, **54**, 1579 (1981).
11. J.E. Hodgkins and W.P. Reeves, *J. Org. Chem.*, **29**, 3098 (1964).
12. S. Sakai, T. Aizawa, and T. Fujinami, *J. Org. Chem.*, **39**, 1970 (1974).
13. T. Shibaunuma, M. Shiono, and T. Mukaiyama, *Chem. Lett.*, 573 (1977) and references cited therein.
14. G. Blotny, *Liebigs Ann. Chem.*, 1927 (1982).
15. Handbook of Chemistry & Physics, 53th Ed., Chemical Rubber Co., Inc. Cleveland, Ohio, 1972-1973.