Vol.3 Nol. 1,2
Winter&Spring 1992

J.Sci.I.R.Iran

3, 5- DINITROBENZOYL CHLORIDE. A USEFUL REAGENT FOR THE DEHYDRATION OF ALDOXIMES AND CARBOXAMIDES UNDER MILD CONDITIONS

A. Abhari [1], M. Bolourtchian[2], A. Saednya*[1]

[1] *Department of Organic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Islamic Republic of Iran.*

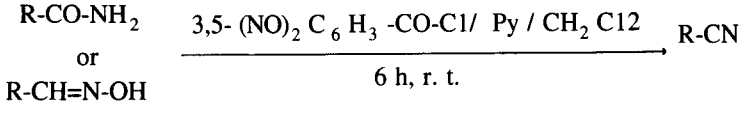
[2] *Chemistry and Chemical Engineering Research Center of Iran, P. O. Box 14335-186 Tehran, Islamic Republic of Iran.*

Abstract

3,5- dinitrobenzoyl chloride-pyridine system has been used for dehydration of aldoximes and carboxamides at room temperature.

Introduction

Since we have reported a convenient method for converting carboxamides and aldoximes to nitriles [1], other dehydrating reagents; aluminium iodide [2] di-2-pyridyl sulphite [3] 1,1-sulfinyl-bis -1,2,4-triazole [4] thiophthalylium salts [5] trichloromethyl chloroformate [6] and N,N- dimethylchlorosulphitemethaniminium-chloride [7], have been developed. In most cases, the reagents used are not easily available and should be prepared before the dehydration is done. Now we wish to report 3,5- dinitrobenzoyl chlorie as an easily available and handling reagent for preparation of nitriles from aldoximes and carboxamides under mild conditions.



R= alkyl, aryl

Result

To a stirred solution of aldoxime or carboxamide (50 mmol) and pyridine (100 mmol) in dichloromethane (30 ml), a solution of 3, 5-dinitrobenzoyl chloride (50 mmol) in dichloromethane (50 ml) is added dropwise at 0°C under anhydrous condition. The stirring is continued for 6 hours. After evaporating the solvent, ether (200 ml) is added, the salts are filtered and the filtrate is washed with water (3 × 20 ml). The residue is chromatographed over neutral aluminium oxide (type I, Brockmann) with petroleum ether-ethyl acetate mixtures. The results are listed in Table 1.

Keywords: Dehydration, aldoximes, carboxamides

Table 1.

Substrate	Product [a]	Yield[b]	mp or bp [c]/torr
C_6H_5-CH=N-OH	C_6H_5-CN	80	69/10
4-Me-C_6H_4-CH=N-OH	4-Me-C_6H_4-CN	77	107-109/6
C_6H_5-CH=CH-CH=N-OH	C_6H_5-CH=CH-CN	87	97/2
n-C_7H_{15}-CH=N-OH	n-C_7H_{15}-CN	84	79/10
C_6H_5-CO-NH_2	C_6H_5-CN	84	69/10
4-Me-C_6H_4-CO-NH_2	4-Me-C_6H_4-CN	82	107-109/6
C_6H_5-CH=CH-CO-NH_2	C_6H_5-CH=CH-CN	90	97/2
n-C_7H_{15}-CO-NH_2	n-C_7H_{15}-CN	93	79/10

a) Yield of isolated pure product. b) Products were characterized by comparison of their mp, tlc. IR, ^{1}H-nmr data with those of authentic samples.

References

1. a) A. Saednya, *Synthesis*, 784 (1983). b) A. Saednya, *Synthesis*, 184, (1985).
2. D. Konwar, R. C. Boruah, J. S. Sandhu, *Tetrahedron Lett.*, 1063, (1990) and references cited therein.
3. S. Kim, K. Y. Yi, *ibid.*, 1925, (1986).
4. S. Kim, S. Yang , J. R. Cho, Bull. *Korean Chem. Soc.* 9(4), 268, C. A. 110: 212698y, (1988).
5. D. A. Oparin, V. A. Shalygina, *Zh. Org. Khim*, 22 (4) . 886. C. A. 106: 138036e, (1986).
6- K. Maj, G. Patil, *Tetrahedron Lett.*, 2203 (1986).
7. A. Arrieta, J. M. Aizpurua, C. Palomo, *ibid*, 3365. (1984).