Journal of the Iranian Chemical Society, Vol. 1, No. 1, September 2004, pp. 28-32.

JOURNAL OF THE
Iranian
Chemical Society

An Efficient Solvent Free and One-Pot Conversion of Aldehydes into Nitriles Using $NH_2OH.HCl/CH_3COCl$/Charcoal System

H. Sharghi* and M. Hosseini Saravi
Department of Chemistry, Faculty of Science, Shiraz University, Shiraz 71454, I. R. Iran.

(Received 6 May 2003, Accepted 18 June 2003)

The high yield conversion of aldehydes into their corresponding nitriles using hydroxylamine hydrochloride/ CH_3COCl /charcoal system is presented. We have clearly shown the effectiveness of charcoal in these reactions.

Keyword: Charcoal, Nitrile, Aldehyde, Hydroxylamine hydrochloride

INTRODUCTION

Synthetic chemists continue to explore new methods to carry out chemical transformations. One of these new methods is to run reactions on the surface of solids. As the surfaces have properties that are not duplicated in the solution or gas phase, entirely new chemistry may appear. Even in the absence of new chemistry, a surface reaction may be more desirable than a solution counterpart, because the reaction is more convenient to run, or a high yield of product is attained. For these reasons, synthetic surface organic chemistry is a rapidly growing field of study.

Heterogenous reactions generally have the following features; *i)* it is often easy to isolate the products from the solid phase; *ii)* comparing the reaction conditions with those of related homogeneous reactions, they are usually milder and more specific; *iii)* selectivity and activity of the heterogeneous system are often comparable to those of enzymes [1]. Several classes of solids have commonly been used for surface organic chemistry including alumina, silica gel, clays and activated charcoal [2].

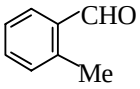
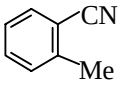
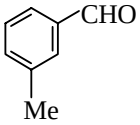
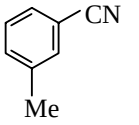
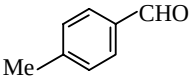
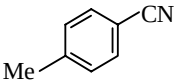
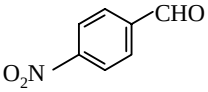
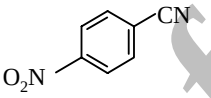
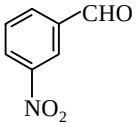
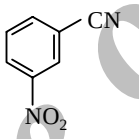
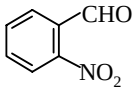
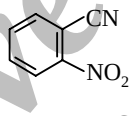
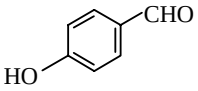
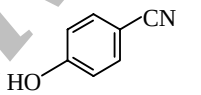
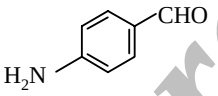
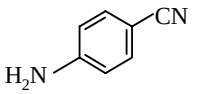
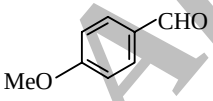
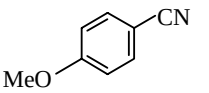
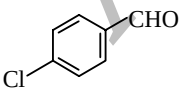
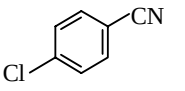
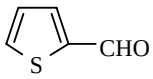
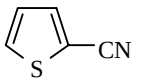
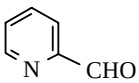
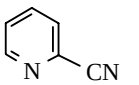
The conversion of aldehydes into nitriles is a useful transformation [3] and a topic of current interest to organic chemists. Among the plethora of available methods to prepare nitriles [4], the most simple and straightforward route are those based on the dehydration of the aldoximes, formed *in situ* by condensation of aldehydes and hydroxylamine hydrochloride, with several kinds of catalysts such as HY-Zeolite [5], silica gel supported $NaHSO_4$ [6], $HCONH_2$ [7], Burgess reagent [8] and etc. However, in spite of their inherent simplicity, these methods are not generally applicable to alkyl, aryl as well as heterocyclic aldehydes and often give unsatisfactory results. I in this report we have presented a useful heterogeneous system for the one-pot conversion of aldehydes into their corresponding nitriles.

EXPERIMENTAL

IR spectra were obtained on an Impact 400 D Nickolet FTIR spectrophotometer. NMR spectra were recorded on a Brucker Avance DPX-250 (90 MHz) in pure deuterated solvents. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on short columns of silica gel 60 (230-400 mesh) in glass columns (2-3 cm diameter) using 15-30 g of silica gel/g of crude mixture. Melting points were determined in open capillary tubes in a Buchi-510 circulating oil melting point apparatus and are uncorrected. Liquid aldehydes were purified by distillation

* Corresponding author. E-mail: shashem@chem.susc.ac.ir

Table 1. Nitriles Prepared from their Corresponding Aldehydes Using $NH_2OH.HCl/Charcoal/CH_3COCl$ System

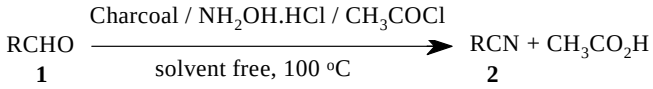
Entry	Reactant	Product[a]	Mp or bp/torr °C(lit)	Time(min)	Yield (%)[b]
1			205(205) [12]	15	90
2			210(213) [12]	5	98
3			216(218) [10]	10	95
4			148(148) [10]	5	95
5			117(117) [12]	7	98
6			109(109) [13]	10	87
7			112(112) [9]	5	95
8			86(86) [12]	5	94
9			62(62) [10]	6	98
10			90(91) [10]	5	94
11			190(192) [10]	10	90
12			78(79) [13]	10	90
13	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2CN$	118(118) [10]	10	92

[a]Products were characterized by their melting points, IR, and NMR spectra. [b]Yields refer to pure isolated products.

prior to use and other chemical materials were from Merck and Fluka Chemical Companies. Activated charcoal 35-50 mesh ASTM was also from Merck.

General Procedure for Conversion of Aldehydes into Nitriles

Aldehyde (1 mmol), $NH_2OH.HCl$ (0.3 g, 0.4 mmol), CH_3COCl (0.08 ml, 1 mmol) and charcoal (0.5 g) were thoroughly mixed with a mechanical stirrer. The resulting fine powder was transferred to a round-bottom flask (50 ml) and heated in an oil bath at 100 °C for appropriate time (Table 1). Then diethyl ether (10 ml) was added to the reaction mixture and charcoal was removed by filtration. The filtrate was extracted with water (2 × 10 ml), dried over Na_2SO_4 and the solvent evaporated in vacuum to give the crude product. Purification of solid products was achieved by crystallization from EtOH and the liquid products by distillation.



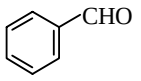
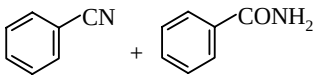
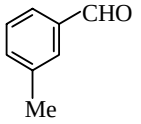
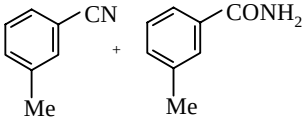
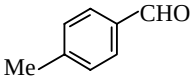
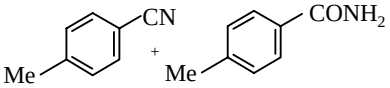
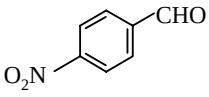
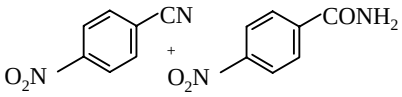
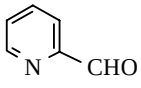
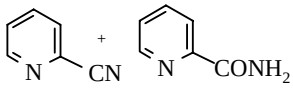
Scheme 1

RESULTS AND DISCUSSION

We report here a novel and clean synthesis of nitriles using hydroxylamine hydrochloride, charcoal and CH_3COCl under solvent free condition as shown in the scheme 1.

In a typical experiment, charcoal, hydroxylamine hydrochloride, acetyl chloride and aldehyde were mixed thoroughly together. The mixture was heated in an oil bath

Table 2. Conversion of Aldehydes into their Nitriles and Amides in the Absence of Charcoal

Entry	Reactant	Products[b]	Time(min)	Yield%[a] (ratio)
1			120	95 (1:1)
2			5	98 (1:1)
3			10	95 (1:1)
4			5	95 (1:1)
5			10	95 (1:1)
6	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2CN$ + $CH_3CH_2CH_2CONH_2$	10	90 (1:1)

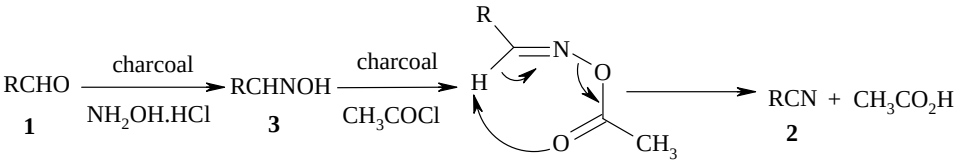
[a]Yields refer to pure isolated products. [b]Products were characterized by their melting points, IR, and NMR spectra and compared with the authentic samples in the literature.

at 100 °C in the absence of the solvent for the appropriate reaction times (Table 1). The products obtained were analyzed through melting points, IR and NMR spectroscopy through direct comparison with authentic samples [9-13].

Charcoal was shown to have a remarkable activity for the high yield conversion of alkyl, aryl and heterocyclic aldehydes into nitriles. We tried the reaction of benzaldehyde with $NH_2OH.HCl/CH_3COCl$ without using charcoal. This reaction was proceeded well and the corresponding benzonitrile and benzamide were produced in equal ratios with high yields. These results are summarized in Table 2.

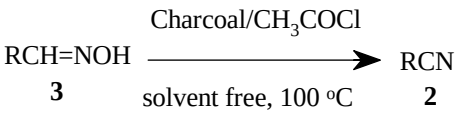
Therefore, we propose a mechanism for the reaction as follows: the first step involves the formation of aldoxime **3** followed by its reaction with CH_3COCl/charcoal to generate **4** as the key intermediate. The compound **4** subsequently undergoes thermal elimination reaction to produce the nitrile **2** with the liberation of acetic acid (Scheme 2).

We have also tried dehydration of various aldoximes into nitriles in the presence of charcoal with excellent yields. The results are summarized in Table 3.



Scheme 2

Table 3. Nitriles Prepared from their Corresponding Aldoximes Using Charcoal/CH_3Col System



Entry	R	Time(min)	Yield (%)[a]
1	$CH_3CH_2CH_2$-	5	97
2	2-Thiophyl	3	95
3	2-Pyridyl	4	95
4	2,6-$Cl_2C_6H_4$	5	96
5	C_6H_4	2	90
6	2-HOC_6H_4	6	90
7	3-HOC_6H_4	3	98
8	4-HOC_6H_4	5	98
9	2-$NO_2C_6H_4$	8	90
10	3-$NO_2C_6H_4$	2	93
11	4-$NO_2C_6H_4$	3	96
12	4-ClC_6H_4	2	97

[a]isolated yields.

CONCLUSION

We have presented here a simple, one-step and efficient method for direct conversion of aldehydes into the corresponding nitriles using $NH_2OH.HCl/CH_3COCl$/charcoal, as a heterogeneous system for the solvent-free and high yield preparation of nitriles from aldehydes.

ACKNOWLEDGEMENT

We gratefully acknowledge the support for this work by the Shiraz University Research Council.

REFERENCES

[1] R.M. Pagni, G.W. Kabalka, R. Boothe, K. Gaetano, L.J. Stewart, R. Conawaya, J. Org. Chem. 53 (1998) 4477.

[2] For review on Surface Organic Chemistry, see: a) G.H. Posner, Angew Chem. Int. Ed. Engl. 17 (1978) 487; b) A. McKillop, D.W. Young, Synthesis 401 and 408 (1979); c) A. Cornelis, P. Laszlo, Synthesis (1985) 909. d) P. Laszlo, Acc. Chem. Res. 19 (1986) 121; e) A. Cornelis, P. Laszlo, In Chemical Reactions in Organic and Inorganic Constrained Systems; R. Setton, Ed.; Reider: Dordrecht, (1986) 212.

[3] K. Friedrich, K. Wallenfels, The Chemistry of the Cyano Group; Z. Rappoport, Ed., Interscience, New York, 1970.

[4] a) H.G. Forey, D.R. Dalton, J. Chem. Soc., Chem. Commun. (1973) 628; b) J.G. Krauseand, S. Shaikh, Synthesis (1974) 563. c) H. Shinogaki, M. Imaizumi, M. Tajima, Chem. Lett. (1983) 929; d) G.A. Olah, T. Keumi, Synthesis (1979) 112; e) E. Vohwinkei, Bartel, J. Chem. Ber. 107 (1974) 1221; f) G. Rosini, G. Baccolini, S. J. Cacchi, J. Org. Chem. 38 (1973) 1061; g) T.J. Van E S, Chem. Soc. (1965) 1564; h) G. Sosnovsky, J.A. Krogh, S.G. Umhoefer, Synthesis (1979) 722; i) S.N. Karmarker, S.L. Kelkar, M.S. Waia Synthesis (1985) 510; j) H.M. Meshram, Synthesis (1992) 943; k) F.E. Chen, H. Fu, G. Meng, Y. Cheng, Y.X. Lu, Synthesis (2000) 1519.

[5] K.V.N.S. Srinivas, E.B. Reddy, B. Das, Synlett (2002) 625.

[6] B. Das, P. Madhusudhan, B. Venkataiah, Synlett (1999) 1569.

[7] A.S. Paraskar, H.S. Jagtap, A. J. Sudalai, J. Chem. Res. (s) (2000) 30.

[8] D.H. Kaufman, C.P. Miller, Synlett (2000) 1169.

[9] S.L. Ali, M.D. Nikalje, G.K. Dewkar, A.S. Paraskar, M.D. Nikalje, A. Sudalai, J. Chem. Res. (s) (2000) 30.

[10] H.M. Sampath Kumar, B.V. Subba Reddy, P. Tirupathi Reddy, J.S. Yadav, Synthesis (1999) 586.

[11] H.M. Sampath Kumar, P.K. Mohanty, M. Suresh Kumar, J.S. Yadav, Synth. Commun. 27 (1997) 1327.

[12] CRC, Handbook of Table for Organic Compounds Identification, 3rd Ed. & 54th Ed. (1991).

[13] F. Juncai, L. Bin, L. Yang, L. Changchuan, Synth. Commun. 26 (1996) 4545.