Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Version of record first published: 23 Aug 2006.

To cite this article: Jun-Cai Feng , Bin Liu , Li Dai & Ning-Sheng Bian (1998): One-Step Conversion of Aldehydes Into Nitriles in Dry Media Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:20, 3765-3768

To link to this article: http://dx.doi.org/10.1080/00397919808004928

SYNTHETIC COMMUNICATIONS, 28(20), 3765-3768 (1998)

ONE-STEP CONVERSION OF ALDEHYDES INTO NITRILES IN DRY MEDIA UNDER MICROWAVE IRRADIATION

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ABSTRACT: *Aldehydes undergo rapid reaction with hydroxylammonium chloride using $HCOOH/SiO_2$ as solid support catalyst, under microwave irradiation without solvent to affords nitriles in 60-90% yields.*

Organic synthesis under dry condition is a topic that is drawing many recent research interest. In our laboratory, we have been continually working on developing new synthetic methods for nitriles by taking advantage of both microwave irradiation and dry reaction conditions.[1]

The conversion of aldehydes into the corresponding nitriles is an important organic chemical transformation. Several methods have been described, but only a few are known for one-step conversion of aldehydes into nitriles without the need of separation of the aldoxime intermediate formed.[2-5] Almost all of these methods were carried out by using large amounts of hazardous solvent or special catalysts which

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are not readily available.[2-7] Although Villemin et al. reported, [8] that the synthesis of nitriles from aldehydes could be accelerated by the use of microwave irradiation, the actual application of microwave in his experiment was limited to the synthesis of the intermediate oximate. Here we would like to report an effective one-step method to convert both alkyl and aryl aldehydes to the corresponding nitriles in dry media under microwave irradiation, using $HCOOH/SiO_2$ as catalyst. Under the described conditions (see Table), reactions are generally completed in less than 3 minutes.

This mild and versatile method, which results in yields of 60-90%, can also be applied to aldehydes containing other reactive functional groups, such as double bond and hydroxy group. As to furaldehyde, the yield is very low (about 5%), partly because it is easy to undergo ring-opening reaction or carbonization under microwave irradiation.

The synthetic route is shown as following:

$$RCHO + NH_2OH{\cdot}HCl \xrightarrow[\text{1-3min}]{\text{HCOOH/SiO}_2,\ \text{microwave irradiation}} RCN + H_2O$$

R=alkyl or aryl

The results obtained are shown in Table I:

Table I: Syntheses of nitriles from aldehydes under microwave irradiation

entry	R	Time (min)	yield (%)[a]	mp. or bp. (°C)/mmHg	Lit. mp. or bp. (°C)/mmHg
1	*p*-$CH_3OC_6H_4$	2	88	59-60	61-2
2	*p*-$O_2NC_6H_4$	1	85	144-6	149
3	*o*-C_6H_4	2	72	38-40	42-3
4	3,4-$(CH_3O)_2C_6H_3$	2	90	62-4	67-8
5	3,4,5-$(CH_3O)_3C_6H_2$	2	80	90-2	91-4
6	*p*-$CH_3C_6H_4$	2	61	28	30
7	*p*-HOC_6H_4	1	72	112-4	113-4

(*continued*)

Table I. Continued

8	3,4-$(CH_2O_2)C_6H_3$	1	92	92-4	95
9	*p*-BrC_6H_4	2	85	110-2	113
10	3,4-$(HO)_2C_6H_3$	1	70	153-4	156
11	*m*-C_6H_4	2	80	114-6	117-8
12	C_6H_5	3	75	190/760	69/10
13	*P*-ClC_6H_4	3	79	90-2	92-4
14	C_6H_5CH=CH	2	78	126-8/10	134/12
15	C_5H_{11}	3	75	162/760	160/760
16	C_7H_{15}	3	70	200/760	198/760

a. Yields are determined by HPLC.[column/Hypersil ODS 5μm (4.6×200mm). column temperature: 35°C; mobil phase: mothanol:water=70:30 (v/v); flow rate: 1mL/min.; λ=270nm]

Experimental:

All reagents were commercially available and used without further purification. Microwave irradiation was carried out with a commercial microwave oven (2450 MHz, 500W) under atmospheric pressure. IR spectra were obtained on a Nicolet FT-IR50DX instrument. ^{1}HNMR spectra were recorded on a JEOL JNM-PMX 60DI spectrometer with TMS as internal standard. HCOOH/SiO_2 was prepared from chromatography grade (Merck,70-130 mesh, 60Å) silica gel.

General procedure:

Aldehyde (10 mmol) and hydroxylamine hydrochloride (13 mmol) were thoroughly mixed with HCOOH/SiO_2 catalyst (5g) in an agate mortar. The resulting fine power was transferred to a flask (50ml) connected with refluxing equipment. After irradiated by microwave for1-3 minutes, the mixture was cooled to room temperature. The inorganic support was separated by filtration after extracting the product with proper solvent. The filtrate was washed with saturated aqueous sodium bisulfite solution, dried with magnesium sulfate, and evaporated to give the crude product, which was purified by crystallization, distillation or column chromatography.

Anhydrous formic acid (20g) was stirred with a suspension of silica gel (Merk, 70-130 mesh, 60A) in acetone (150 ml) for 1 hour. The catalyst obtained was flowing power after the acetone was removed.

Acknowledgments: We would like to thank the Nanjing University for financial support of our work. The analyses work was partially supported by the Center of Materials Analysis, Nanjing University.

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(Received in the USA 27 April 1998)