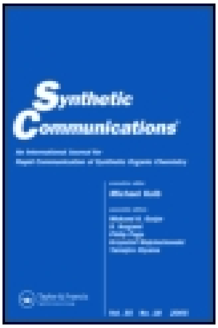

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Microwave-Assisted Methods for Conversion of Aldehydes into Nitriles

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MICROWAVE-ASSISTED METHODS FOR CONVERSION OF ALDEHYDES INTO NITRILES

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Abstract: A rapid conversion of aldehydes to corresponding nitriles has been achieved under microwave irradiation using hydroxylamine and phthalic anhydride or hydroxylamine and Envirocatalyst EPZG^{R} in solvent free conditions.

The nitriles are very important reagents for organic synthesis. Many standard synthetic procedures for preparing of nitriles require hard reaction conditions and have also some limitations (corrosive, toxic, expensive or commercially unavailable reagents)[1-5].

It is well know that dramatic reduction in reaction time can be achieved when the reactions have been carried out in microwave oven, especially when the reactions are performed in solvent free conditions [6]. There are just few publications describing the use of microwave irradiation for preparations of nitriles from aldehydes[7,8].

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In the present work we report two rapid, giving high yields, one-pot procedures for the synthesis of nitriles under microwave irradiation.

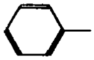
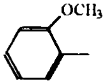
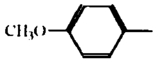
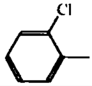
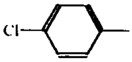
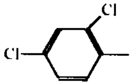
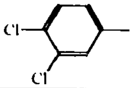
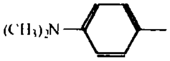
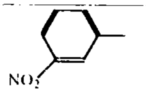
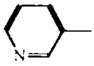
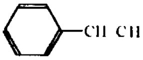
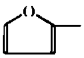
$$\mathrm{RCHO} \xrightarrow[\text{MWI, 3 min}]{\text{Method A, B}} \mathrm{RCN}$$

Method A: $NH_2OH.HCl$ / Et_3N / phthalic anhydride
Method B: $NH_2OH.HCl$ / Et_3N / EPZG^{R}

The first method consists of a short exposure of the mixture of aldehyde, hydroxylamine hydrochloride and phthalic anhydride in the presence of triethylamine (method A). From the results given in Table follows that high isolated yields of nitriles can be obtained and that the final temperature of the reaction mixture reached above 200 °C. Simmilar procedure was described recently, but reaction was carried out in acetonitrile[9]. Long (7 – 8 h) classical heating was necessary to reach the comparable yields. Our experiments (A*, Tabble 1, Entries 1,4) in acetonitrile gave, after 3 min. of MWI just 12 % and 9 % yields of the products. It is obvious that the yields obtained in the same time are much higher when the solvent free technique is used. The reason is probably in the reaction temperature. While the final temperature of reaction mixtures with acetonitrile was 75°C, solvent-free reaction mixtures reached temperatures above 200 °C.

Bandgar et al[10] found that Envirocat EPZG^{R} is an efficient heterogeneous catalyst for the conversion of aromatic aldoximes into nitriles. The reaction time was 16 to24 hours, applying the classical heating. We decided to examine the possibility to use this catalyst in one pot conversion of aldehydes to nitriles under microwave irradiation. (Method B). Very good yields were reached just after 2 - 3 min of microwave irradiation. The final temperature reached by the reaction mixture was, in the most cases, 250 °C. To see if there is a special microwave effect we performed the experiments at classical heating. The reaction mixture

Table Conversion of aldehydes into nitriles

Entry	R (Scheme)	Method	T$_{fin}$ (°C)	Yield (%)	m.p. (obs.) (°C)
1.		A	220	84	oil
		A*	75	12	
		B	242	80	
2.		A	231	73	oil
		B	250	79	
3.		A	230	78	58-59
		B	250	68	
		B*	250	83	
4.		A	202	72	43
		A*	75	9	
		B	250	88	
5.		A	206	79	89-90
		B	225	78	
		B*	225	71	
6.		A	204	88	61
		B	250	94	
7.		A	204	90	71-72
		B	250	86	
8.		A	231	86	73-74
		B	250	87	
9.		A	151	57	116-117
		B	250	87	
10.		A	237	91	224
		B	250	95	
11.		A	203	70	48-49
		B	248	74	
12		A	221	69	oil
		B	250	85	
13		A	203	84	oil
		B	130	78	

A* with 50 ml acetonitrile, B* classical heating was immersed for 3 min. into a bath heated to the final temperature (Method B*, Entries 3,5). From the results is possible to see that the yields are comparable, that means that there is no special microwave effect at this reaction. Microwave irradiation probably has not any accelerated effect in this reaction and the results are depended on the reaction temperature.

The versatility of both methodologies has been demonstrated by the wide range of different aromatic aldehydes. The reaction proceeds well for aromatic (Entries 1–10) and heteroaromatic (Entry 11) aldehydes. This method can be applied to aldehydes containing other reactive group such as double bond (Entry 12). Even 2-furaldehyde (Entry 13) gives good yield of product in spite the literature[8] which claim that such reaction was not successful.

The advantages of both methods are: high yields, easy work–up as well purification of the products and short reaction time.

Experimental:

All reagents were commercially available and used without further purification. The experiments were carried out in the SYNTHEWAVE 402, PROLABO microwave reactor at 120 watts for 3 minutes.The products were characterized by their physical properties and ^{1}H NMR spectral characteristics. Melting points were determined on a Kofler-hot stage and uncorrected. The ^{1}H NMR spectra were measured at 300 MHz on a Varian Gemini spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard.

General procedure:

Method A

A mixture of aldehyde (0.01 mol), hydroxylamine hydrochloride (0.76g, 0.011 mol), trietylamine (1.54 ml, 0.011 mol) and phtalic anhydride (1.5 g, 0.01 mol) was irradiated in the microwave reactor for 3 min. Dichlormethane (50 ml) was added, after cooling the reaction mixture stirred for a while. Dichlormethane solution was filtered and washed with 5 % ammonia (to remove phthalic acid). The separed organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was recrystalized from izohexane – ethyl acetate or purified by column chromatografy using $CHCl_3$ as the eluent to give pure nitrile.

Method B

A mixture of aldehyde (0,01 mol), hydroxylamine hydrochloride (0.76g, 0.011 mol), triethylamine (1,54 ml, 0,011 mol) and Envirocat EPZG^R (100 mg) was irradiated in the microwave reactor for 3 min. The reaction mixture was, after cooling to room temperature, treated with dichlormethane (20 ml) and stirred for a while. The catalyst was removed by filtration. The filtrate was washed with wather and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue left was almost pure product, which was sometimes crystallized as described above.

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