September 2006 Volume 2 Issues 1-3

Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Note

OCAIJ, 2(1-3), 2006 [46-47]

Ultrasound-Assisted Synthesis Of Arylmethylenemalononitriles In Aqueous Media

Corresponding Author

Jian-Long Du
College of Chemistry & Environmental Science, Hebei University, Baoding 071002 (P.R.CHINA)
Tel. & Fax: +86-312-5079628
E-mail: dujl@mail.hbu.edu.cn

Co-Authors

Li-Jun Li, Ya-Hui Yin
College of Chemistry & Environmental Science, Hebei University, Baoding 071002 (P.R.CHINA)

Received: 23rd February, 2006
Accepted: 11th March, 2006

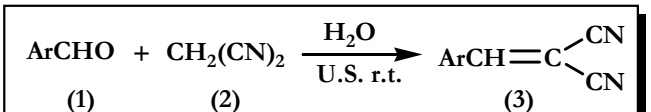
Web Publication Date : 23rd September, 2006

ABSTRACT

Knoevenagel condensation of malononitrile with aromatic aldehydes under ultrasound irradiation in water results in the formation of the arylmethylenemalononitriles in high yields within 80 min, without addition any catalyst.

INTRODUCTION

Arylmethylenemalononitriles have attracted strong interest because of their increasing applications in industry, agriculture, medicine and biologicalscience[1]. Also they are important intermediates for cyclization reactions[2]. Preparation of arylmethylenemalononitriles is generally catalyst by bases[3-5], or Lewis acids[6] in organic solvents. These methods suffer from drawbacks such as longer reaction time, high temperature, or necessary catalyst. Ultrasound irradiation has increasingly been used in organic synthesis recent years. A lot of organic reactions can be carried out in higher yield, shorter reaction time and milder conditions under ultrasound irradiation in organic solvents[7]. Recently, there is



SCHEME 1: Synthesis of arylmethylenemalononitriles

TABLE 1: Solvents effect on the yield of (3a).

Entry	Solvent	Time (min)	Yield (%)
1	H_2O	60	85
2	EtOH	60	84
3	DMF	60	87
4	THF	60	48

Note

TABLE 2: Synthesis of arylmethylenemalononitriles under ultrasound

Entry	Ar	Time (min)	Yield (%)	m.p. (°C)	
				Found	Reported[10]
a	C_6H_5	60	85	82-83	82-83
b	3-ClC_6H_4	40	82	120-121	121-122
c	4-ClC_6H_4	40	86	161-162	162-163
d	2,4-$Cl_2C_6H_3$	50	85	153-154	155-156
e	3,4-$(OCH_2O)C_6H_3$	80	93	201-202	201-202
f	4-$NO_2C_6H_4$	40	90	162-163	161.5-162
g	2-OHC_6H_4	80	85	161-162	163-164
h	4-OHC_6H_4	80	89	185-186	187-188
i	4-$OCH_3C_6H_4$	80	91	113-114	113.5-114
j	4-$(CH_3)_2NC_6H_4$	80	82	180-181	180-181
k	4-OH-3-$OCH_3C_6H_3$	80	87	136-137	137-138

growing interest in synthetic organic reactions in water that are environment-friendly[8-9]. Herein, we would like to report a green procedure for synthesis of arylmethylenemalononitriles under ultrasound irradiation in aqueous media (SCHEME 1).

The results are summarized in TABLE 1 and 2. It can easily be seen that the condensation of a series of aldehydes with malononitrile leading to arylmethylenemalononitriles give good yields under ultrasound irradiation. To better understand the solvent effect on the reaction, solvents with difficult properties were employed in the model reaction between benzaldehyde and malononitrile. The data reported in TABLE 1 showed that the reaction is favored in polar ones. We selected water as the medium of choice because it displays some advantages due to its low cost, no inflammability and easy product isolation by filtration. The ultrasound technique represented a better procedure in terms of the high yield, milder reaction and easier workup. As shown in TABLE 2, the condensation of aldehydes **(1)** and malononitrile **(2)** affords product **(3)** in good yield in water. More importantly, aromatic aldehydes carrying either election-donating or electron-withdrawing subsituents all reacted very well, giving excellent yields.

In conclusion, we have described a clean and efficient procedure for the preparation of arylidenemalononitriles in water with no catalyst under ultrasound irradiation.

ACKNOWLEDGEMENT

We acknowledge Natural Science Foundation of Hebei University (Q200404).

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