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## Catalyzed Preparation of Ylidenemalononitriles and 3-Cyanocoumarin in Water

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#### ABSTRACT

As sodium hydroxide is used as catalyst, Knoevenagel condensation of malononitrile with aromatic aldehydes can take place at room temperature in water. 3-Cyanocoumarin was obtained by one-pot synthesis.

Key Words: Water phase; Catalyze; Knoevenagel condensation.

#### 4531

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#### INTRODUCTION

Knoevenagel condensation is an important method for formation of alkenes from carbonyl compounds. Malononitrile is a typical compound with active methylene, often used to undergo Knoevenagel reaction with aldehydes. These reactions are usually carried out in organic solvents by treating with basic catalysts, such as ammonium salt, primary and secondary amine.<sup>[1]</sup> or solid basic catalyst.<sup>[2]</sup> Later, Lewis acid ZnCl<sub>2</sub> was reported effective for this kind of reaction.<sup>[3]</sup> In recent years, with application of microwave techniques, Knoevenagel reactions can be carried out under catalysis of piperidine,<sup>[4]</sup> LiCl,<sup>[5]</sup> silica gel,<sup>[6]</sup> P<sub>2</sub>O<sub>5</sub>-piperidine,<sup>[7]</sup> ammonium acetate,<sup>[8]</sup> ammonium acetate-basic alumina,<sup>[9]</sup> NaCl or NH<sub>4</sub>OAc/HOAc,<sup>[10]</sup> and urotropine.<sup>[11]</sup> Over the last decade, water has drawn considerable attention as a solvent in organic reactions, due to its cost-effective and nontoxic qualities. It is generally considered that the 1,2-elimination of  $\beta$ -hydroxyl intermediate is inhibited by protic solvent and the retro-Knoevenagel reaction can take place in aqueous solution.<sup>[12]</sup> But it was reported that Knoevenagel reactions can occur in water in the presence of CTMAB. This prompted us to reseach this reaction in water further. We found that knoevenagel reaction of malononitrile with aldehydes can be carried out in water at room terperature under catalysis of basic reagent (NaOH, Et<sub>3</sub>N, CH<sub>3</sub>NH<sub>2</sub>) (Sch. 1).

#### **RESULTS AND DISCUSSION**

Condensation of malononitrile with benzaldehyde in water without catalyst requires 16 hr. Basic catalysts can speed up the reaction greatly requiring only 0.5 hour (Table 1).

We further investigated condensation of malononitrile with other aromatic aldehydes with choice of catalyst NaOH. Reactions of liquid aldehydes (1a, 2a, 3a, 4a) require 0.5 h, but solid aldehydes (5a, 6a) need much longer time, perhaps because the spreading speed of liquid is faster than that of solid. Reaction rate of *p*-hydroxybenzaldehyde with malononitrile is related closely to the amount of sodium hydroxide used. The rate is 20 hours when the molar ratio of sodium hydroxide to malononitrile is 0.1, but can be shortened to 0.5 h

ArCHO + 
$$CH_2$$
  $H_2O/Base$   
CN  $R.T.$  ArCH  $CN$  +  $H_2O$ 

Scheme 1.

	Г <sup>СНО</sup> + < <sup>СN</sup> СN	$\longrightarrow$	-CH=CN +	H <sub>2</sub> O
Entry	Catalyst	Amount of catalyst (mmol)	Time (h)	Yield (%)
1		0	16	91
2	NaOH	1	0.5	91
3	Et <sub>3</sub> N	1	0.5	91
4	CH <sub>3</sub> NH <sub>2</sub>	1	0.5	90

Table 1. Catalyst effect on the reaction.

Note: Used amounts of malononitrile and benzaldehyde are both 10 mmol.

by increasing the molar ratio to 1.1, because solid-liquid, two-phase reactions become liquid homogeneous reactions with increasing the amount of sodium hydroxide (Table 2).

Condensation of o-hydroxybenzaldehyde with malononitrile in water produce two substances: ylidenemalononitrile (8c) and sodium salt of 3cyanocoumarin (8d). (8c) is susceptible to heat and decomposes, and is not convenient for isolation. After condensation, concentrated hydrochloric acid

Table 2. Condensation of malononitrile with aromatic aldehydes.

	ArCHO -	CN + CH <sub>2</sub> - CN	H₂O/Base R.T. ► ArCł	H CN + H	l <sub>2</sub> O			
	а	b		c				
Entry		Ar	NaOH (mmol)	Time (h)	Yield (%)			
1	C <sub>6</sub> H <sub>5</sub> -		1	0.5	91			
2	o-Cl C <sub>6</sub> H <sub>4</sub> -		1	0.5	92			
3	p-CH <sub>3</sub> O C <sub>6</sub> H <sub>4</sub> -		1	0.5	92			
4	Furyl –		1	0.5	91			
5	$p-(CH_3)_2NC_6H_{4^-}$		1	21	95			
6	p-HO C <sub>6</sub> H <sub>4</sub> -		1	20	91			
7	<i>p</i> -HO C <sub>6</sub> H <sub>4</sub> -		11	0.5	91			

Note: Used amounts of malononitrile and aldehyde are both 10 mmol.

Zhang and Zhang



was added to the reaction mixture, then (8c) and (8d) were all converted to 3-cyanocoumarin (Sch. 2).

So 3-cyanocoumarin can be prepared by one-pot synthesis.

#### EXPERIMENTAL SECTION

Condensation of malononitrile with aldehydes: 25 mL distilled water, 10 mmol malononitrile, and specified amount of catalyst were stirred to be a clear solution, then 10 mmol aromatic aldehyde was added and stirred at room temperature for a specified period of time. The product (1c, 2c, 3c, 4c, 5c) was isolated by filtration. The product (6c, 7c) was isolated by filtration after acidification of the reaction mixtures.

Synthesis of 3-cyanocoumarin: 25 mL distilled water, 10 mmol malononitrile, 1 mmol NaOH, was stirred to be a clear solution, then 10 mmol o-hydroxybenzaldehyde was added. After stirring at room temperature for 18 hours, 12.5 mL concentrated hydrochloric acid was added, then heated at 60°C for 0.5 h. After cooling, 3-cyanocoumarin was obtained by filtration.

All the products gave m.p.s. and spectral data consistent with the reported ones.<sup>[13–15]</sup>

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Preparation of Ylidenemalononitriles and 3-Cyanocoumarin in Water 4535

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