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Water extract of onion catalyzed Knoevenagel condensation reaction: an efficient green procedure for synthesis of α -cyanoacrylonitriles and α -cyanoacrylates

Prabakaran Kaliyan, Sivakumar Matam, Seenivasa Perumal Muthu* 

Department of Chemistry, The Gandhigram Rural Institute-Deemed to be University, Gandhigram, Dindigul district, Tamilnadu-624 302, India

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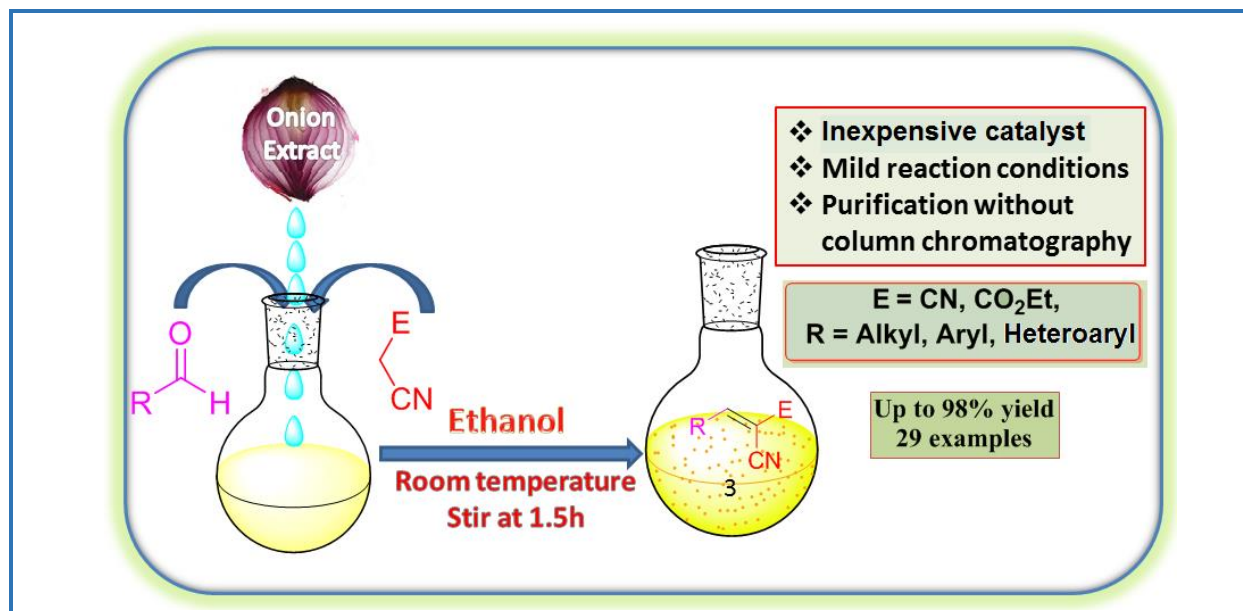
KEYWORDS

Knoevenagel product
Malononitrile
Aldehydes
Water extract of onion

ABSTRACT

A useful method for Knoevenagel condensation has been developed from the reaction between active methylene compound **1** and aldehyde **2** using the water extract of onion as a green catalyst. This method is suitable for variety of aldehydes including, substituted aromatic, aliphatic, α , β -unsaturated, and heterocyclic with malononitrile or ethyl cyanoacetate, and affords the α -cyanoacrylonitriles and α -cyanoacrylates in excellent yields (Up to 98%). The products are isolated without column chromatography. The use of water extract of onion has several advantages such as low price, easy handling, simple work up procedure and environmentally benign.

Graphical Abstract



Introduction

The Knoevenagel reaction has been widely used to construct a carbon-carbon double bond from an activated methylene compounds and substituted aldehydes [1–4]. The formed alkene products are highly useful intermediates for the synthesis of the organic molecules such as heterocyclic compounds [5–7], natural products, anti-hypertensive drug, coumarin derivatives, perfumes, and cosmetics [8–13]. It is typically performed in organic solvents in the presence of bases such as primary or secondary amines and their salts. Recently, a wide range of catalysts, including Lewis acids [14–19], heterogeneous catalysts [20–34], ionic liquids [35–41], metal oxides [42–48], zeolites [49–51], polymer-supported amines [52–53], amino acids [54–56] and ionic exchange resins [57–58] have been used to catalyze this reaction. However, many of these methods have some limitations. Occasionally, the reaction needs expensive or toxic reagents, drastic condition, extensive reaction time or it requires to alter the reaction conditions, like microwave radiation [2–3, 12] or ultrasonication [21, 36, 54, 57]. In several cases [59–62], the variety of aldehydes were limited to only aromatic aldehydes and a very few examples used aliphatic aldehydes at room temperature with good yields.

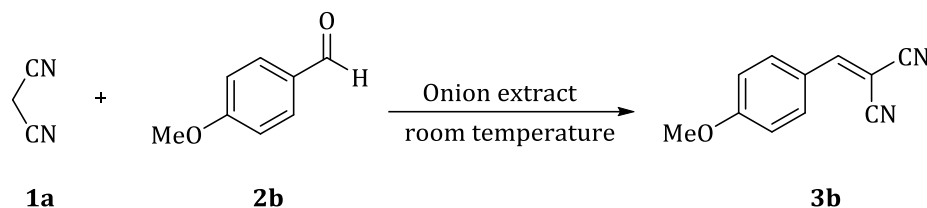
α -Cyanoacrylates and acrylonitriles are an important class of compounds, and have a tendency to stick wide range of substrates, therefore that are highly useful by industry and homeowners in various applications [63–66]. They were polymerize quickly without any additional agents and form a strong bond between two adherends. Due to its biocompatibility, low toxicity and biodegradability

gained many biomedical applications such as tissue adhesives [63–66], antibacterial [67], hemostatic [68], drug delivery [69], fingerprint development in forensic sciences [70]. The co-polymer of 1,3-butadiene and acrylonitrile is called Buna-*N* rubber. Acrylonitriles were polymerize readily to form linear polymers having fibrous characteristics. A small portion of acrylate added to the acrylonitrile, improves the dyeing characteristic [71].

Presently, in organic synthesis the development of environmentally benign and economical processes are highly demandable. Keeping in mind, a simple, high yielding method for the preparation of α -cyano acrylate and α -cyanoacrylonitrile is being reported by Knoevenagel condensation between active methylene compounds with aliphatic, aromatic and heteroaromatic aldehydes in good to excellent yields using readily available, inexpensive water extract of onion as a catalyst. The reaction was carried out using equimolar amounts of active methylene compounds with aldehydes in the presence of 2 mL of water extract of onion at room temperature to give Knoevenagel condensation product **3b** in excellent yield (Scheme 1). Under identical conditions without water extract of onion, gave traces of product, thus the role of onion extract is highlighted. Number of organic reactions using various fruit juices are reported in the literature [72]. Due to their acidic nature, aqueous fruit juices such as lemon [73], pineapple [74], coconut [75], and tamarind [76] have been found to be useful in homogeneous acid catalysis.

The onion (*Allium Cepa* L.) is one of the most popular and commonly consumed vegetable. It is also a very good source of phytochemicals such as organo sulfur and flavonoid quercetin. The composition of the phytochemical may varies geographical, seasonal harvesting and processesing. Due to the presence of these phytochemicals, it has many applications in material chemistry [77–78] (Nanoparticle preparation) and medicinal field, including anticancer, anti-inflammatory, antiproliferative, reducing serum cholestereol, and blood pressure, immune stimulation, surgical scars, ability to modulate the detoxification system and free radical scavenging activity [79–87]. The main constituent of onion is 1-propenylcysteine sulfoxide (Isoalliin, an alkylated cysteine sulfoxide). When the onion is cut, the isoalliin undergoes a series of rapid reactions. The enzyme Alliinase catalyzes the conversion of 1-propenylcysteine sulfoxide to (E)-1-propenesulfenic acid, which is then rearranged to the volatile and highly reactive lachrymatory factor (LF) (Z)-propanethial S-oxide, [88–89] which on treatment with water to produce acetaldehyde, sulphuric acid and hydrogen sulfide [90–91]. The prepared onion extract is an acidic in nature, having the pH of 3.6 with the strength of 0.0034 N. So, it may work as acid catalyst for condensation reactions (Scheme 1). Therefore, this water extract of onion has been employed as a catalyst for Knoevenagel condensation reaction. We report herein, onion extract catalyzed Knoevenagel condensation reaction of active methylene

compounds with various aldehydes such as aromatic, aliphatic, heterocyclic and α , β -unsaturated (Scheme 1).



Scheme 1. General scheme for the synthesis of α -cyanoacrylonitriles and α -cyanoacrylates

Experimental

Materials and methods

¹H NMR (300 MHz or 400 MHz) and ¹³C NMR (75 MHz or 100 MHz) were recorded BRUKER-FT NMR spectrometer using DMSO-d₆ or CDCl₃ as a solvent and TMS as an internal standard (Chemical shift in δ ppm). The chemical shifts are expressed in downfield from the signal of internal Tetramethylsilane (TMS). The infrared spectra were recorded on JASCO FT-IR spectrophotometer model 400 plus using dry KBr pellets. Melting points were determined using a Guna Enterprises, India capillary on melting point apparatus and are uncorrected. Analytical thin layer chromatographic tests were carried out on glass plates (3 \times 10 cm) coated with 250 μ m Merck GF₂₅₄ silica gel. The spots were visualized by short exposure to iodine vapour or UV light. Ethyl-2-cyanoacetate and Malononitrile were purchased from CDH, India, and Spectrochem, PVT. LTD, India. Anisaldehyde, o-nitrobenzaldehyde, benzaldehyde, 4-chlorobenzaldehyde, cinnamaldehyde, crotonaldehyde were purchased from SRL, India. 4-cyanobenzaldehyde, 4-hydroxybenzaldehyde, 4-nitrobenzaldehyde, thiophene-2-carboxaldehyde, furfural, anthraldehyde, and 4-fluorobenzaldehyde were supplied by Sigma Aldrich, USA. The solvent ethanols purchased from Changshu Yangquan chemicals, china and are further purified by dry distillation method.

General procedure

To a stirred solution of active methylene compound **1** (2 mmol), aldehyde **2** (2 mmol) in ethanol (5 mL) was added onion extract (2 mL) at room temperature. After 15 min pale yellow precipitate observed. Further, the reaction mixture was stirred at this temperature for respective time given in the Table 3. The progress of the reaction was monitored by TLC. After complete conversion of the starting material, the pale yellow solid was filtered, washed with chilled ethanol (5 mL) to afford the Knoevenagel condensation product **3** in good yield. The products are re-crystallized in ethanol.

2-(4-hydroxybenzylidene)malononitrile 3a

Pale yellow solid, yield 0.285 g (84%), mp 186-188 °C (Lit [29], 187-189 °C), IR (KBr) (ν_{\max} / cm^{-1}): 3353, 3029, 2924, 2230, 1610, 1564, and 837 cm^{-1} . $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 11.15 (s, 1H), 8.37 (s, 1H), 7.96 (d, J 8.8 Hz, 2H), 7.04 (d, J 8.4 Hz, 2H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6): δ 164.3, 160.9, 134.3, 123.2, 117.0, 115.5, 114.6, 75.5.

2-(4-methoxybenzylidene)malononitrile 3b

Yellow solid, yield 0.361 g (98%), mp 108-110 °C (lit [18], 119 °C), IR (KBr) (ν_{\max} / cm^{-1}): 3435, 3028, 2919, 2851, 2223, 1605, 1571, 1512, 1278, 1185, 1022, 834, and 571 cm^{-1} . $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.37 (s, 1H), 7.96 (d, J 8.8 Hz, 2H), 7.17 (d, J 8.8 Hz, 2H), 3.86 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6): δ 164.8, 160.9, 133.8, 124.6, 115.6, 115.2, 114.3, 77.3, 56.3.

Results and discussion

In continuation of our previous work [92] towards developing of new methods using onion extract as catalyst, we have studied the reaction between the active methylene group **1** and aldehyde **2**. The reactions were proceeded smoothly in the presence of onion extract (2 mL) to afford the Knoevenagel product **3** in good to excellent yields (Up to 98%). The preparation process required water extract of onion reported earlier from our research group [92]. Since, the prepared water extract of onion is pH 3.6, we have carried out the control experiments using HCl (pH 3.6), H_2SO_4 (pH 3.6) in ethanol for 2 h. These acids also catalysed the reaction and gave lesser yield than onion extract catalyst. The optimization of the catalyst loadings are summarised in Table 1.

Further efforts were undertaken to optimize solvent. The results are summarized in Table 2. We have chosen polar solvent such as H_2O , methanol, ethanol, 2-PrOH, CH_2Cl_2 , MeCN, DMF, DMSO, hexane, and AcOH solvent for our study.

After optimizing the reaction condition, we have examined the scopes and limitations of the onion extract catalyst, various active methylene compounds such as malononitrile (pKa=8) [93] **1a**, ethyl cyanoacetate (pKa=9) [93] **1b**, diethyl malonate (pKa=13.3) [93] **1c**, ethyl acetoacetate (pKa=10.7) [93] **1d**, acetonyl acetone (pKa=14.15) [94] **1e**, benzoyl acetone (pKa=14.25) [94] **1f** and benzoyl methane (pKa=15.2) [94] **1g** were treated with a range of aliphatic, aromatic, heterocyclic and α , β -unsaturated aldehydes in the presence of catalytic amount of onion extract in ethanol. The results are summarised in Table 3. The reaction was clean and proceeded smoothly to give corresponding Knoevenagel product in good to excellent yields.

The appearance of olefinic proton at δ 7.48 to 8.34 indicated the products **3o-3ac** is only *E* geometry [**1c-d**, **6b**, **6g**] [95-98]. The nucleophilic addition of active methylene groups to aldehydes,

Table 1. Optimization of study for catalyst quantity^a

Reaction scheme showing malononitrile (**1a**) reacting with anisaldehyde (**2b**) in the presence of onion extract at room temperature to yield the Knoevenagel condensation product (**3b**).

Entry	Onion extract (mL)	Time (h)	Yield (%) ^b
1	0.1	2	57
2	0.4	4	67
3	0.5	4	80
4	1.0	3	88
5	1.5	3	93
6	2.0	2.5	98
7	0	3	Trace

^a Model reaction: malononitrile **1a** (1 eq) and anisaldehyde **2b** (1 eq) in the presence of onion extract with different concentrations and time in 5 mL of EtOH

^b The yields are all isolated

Table 2. Optimization of reaction condition with various solvents^a

Reaction scheme showing malononitrile (**1a**) reacting with anisaldehyde (**2b**) in the presence of 2 mL of onion extract for 2.5 h at room temperature to yield the Knoevenagel condensation product (**3b**).

Entry	Solvents	Yield (%) ^b
1	H ₂ O	70
2	MeOH	89
3	EtOH	98
4	2-PrOH	76
5	CH ₂ Cl ₂	59
6	MeCN	77
7	DMF	74
8	DMSO	78
9	Hexane	74

10^c

AcOH

71

^a Model reaction: malononitrile **1a** (1 eq) and anisaldehyde **2b** (1 eq) with various solvents (5 mL) in the presence of onion extract (2 mL) at room temperature for 2.5 h

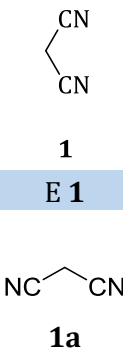
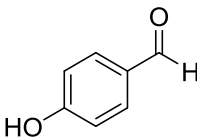
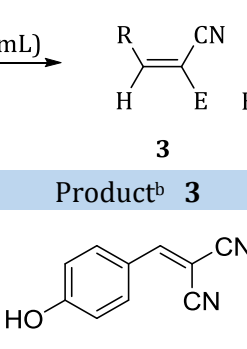
^b The yields are all isolated

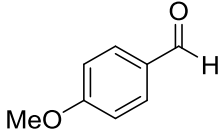
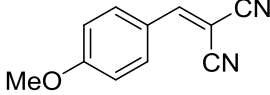
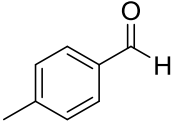
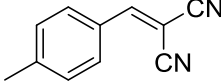
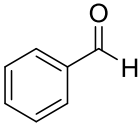
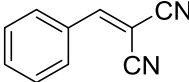
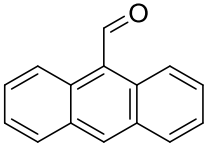
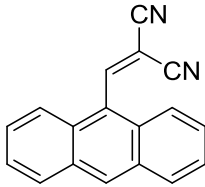
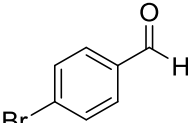
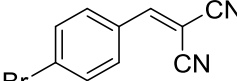
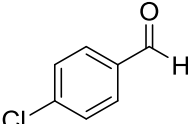
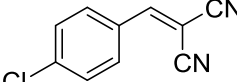
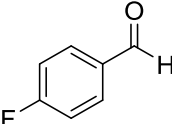
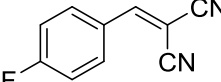
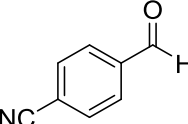
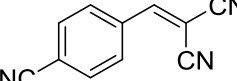
^c The reaction was carried out using anisaldehyde **2b** (1 eq), malononitrile **1a** (1 eq) in AcOH (5 mL) at room temperature for 6 h

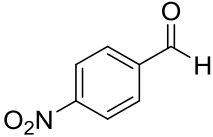
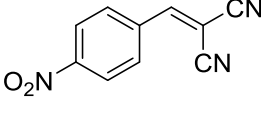
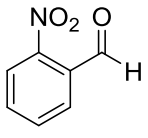
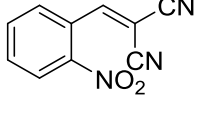
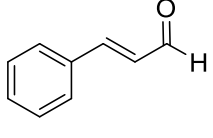
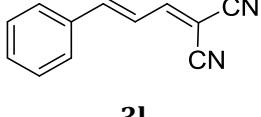
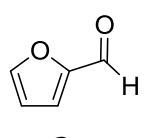
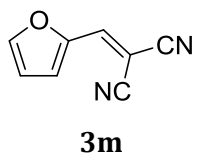
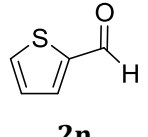
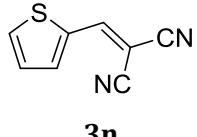
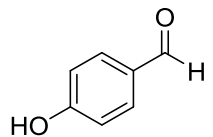
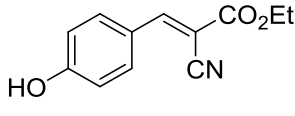
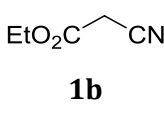
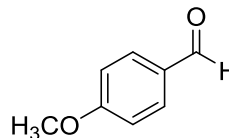
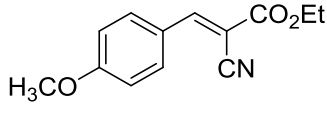
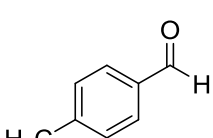
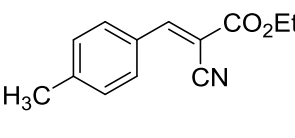
catalysed by onion extract was found to be dependent on electronic factors of the active methylene compounds and the aldehydes. The different reactivities of the active methylene compounds were found to be depend on the different pKa values. The malononitrile (pKa=8) [93] **1a**, requires lesser period than ethyl cyanoacetate **1b**, (pKa=9) [93] to complete the reaction. This may due to the acidity of the active methylene compounds. In the case of active methylene compounds **1c-1g** (pKa=10.7-15.2), no reaction was observed even after extended heating (24 h) at reflux temperature. It was concluded that, as the pKa value increased, the reactivity of the active methylene compounds reduced. The pKa of active methylene compound >9 the reaction does not proceeded.

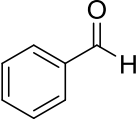
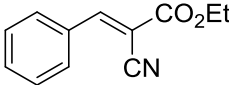
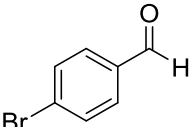
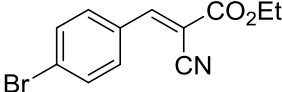
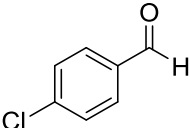
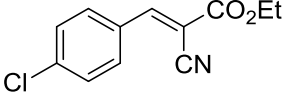
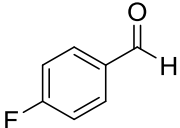
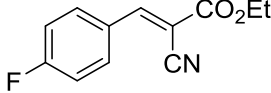
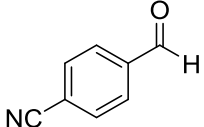
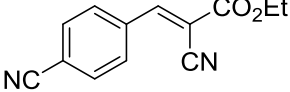
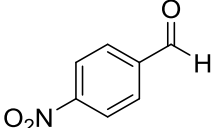
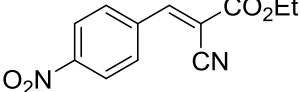
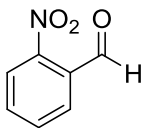
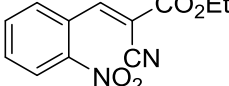
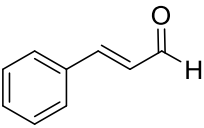
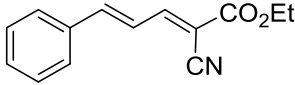
The different reactivities of the aldehydes were dependent on the substituents on the benzene ring. The presence of electron withdrawing group on the benzene ring increased the reactivity of the substance (Table 3, entry 6-11 and 19-24). An electron releasing substituents present on the benzene ring, it was observed that relatively lesser yield than the electron withdrawing substituents (Table 3, entry 1-3 and 15-17). No significant effect was observed on o-substituted aldehydes (Table 3, entry 11 and 24). Further, we have examined the reaction between malononitrile **1a** and ketones such as cyclohexanone, acetone. Unfortunately, could not gave the corresponding Knoevenagel products under these conditions. Since water extract of onion available plenty, cheap and natural. Hence, we could not tried anything regarding recyclability of the catalyst.

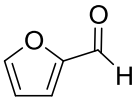
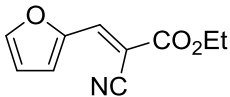
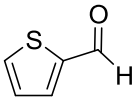
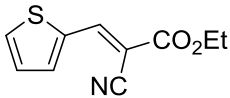
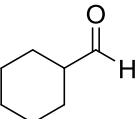
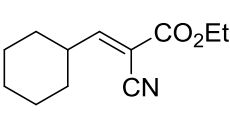
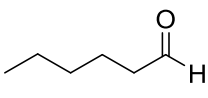
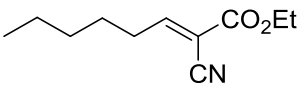
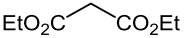
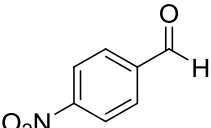
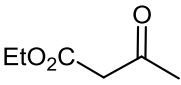
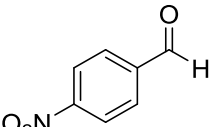
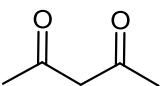
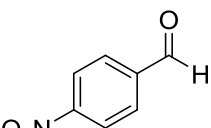
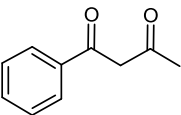
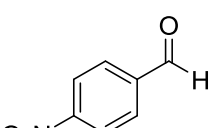
Table 3. Synthesis of Knoevenagel product^a **3**

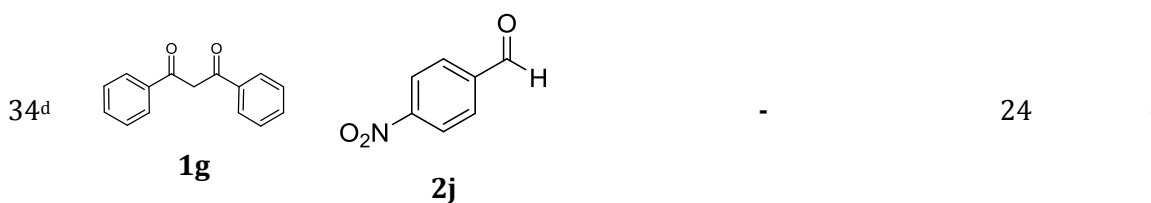
Entry	E 1	R 2	Product ^b 3	Time (h)	Yield ^c
1	 <p>1a</p>	 <p>2a</p>	 <p>3a</p>	2.5	84

2	 2b	 3b	2.5	98
3	 2c	 3c	2.5	81
4	 2d	 3d	3.5	80
5	 2e	 3e	2.5	93
6	 2f	 3f	2	94
7	 2g	 3g	2	90
8	 2h	 3h	1.5	96
9	 2i	 3i	1.5	93

10	 2j	 3j	1.5	96	
11	 2k	 3k	1.5	95	
12	 2l	 3l	3.5	69	
13	 2m	 3m	1.5	98	
14	 2n	 3n	2	87	
15	 2a	 3o	8	85	
16	 1b	 2b	 3p	4	76
17	 2c	 3q	4	61	

18	 2d	 3r	7.5	85
19	 2f	 3s	7	83
20	 2g	 3t	7	79
21	 2h	 3u	2.5	91
22	 2i	 3v	2.5	94
23	 2j	 3w	2.5	97
24	 2k	 3x	3	89
25	 2l	 3y	6	81

26			4	89
	2m	3z		
27			4	84
	2n	3aa		
28			6	90
	2o	3ab		
29			4	93
	2p	3ac		
30 ^d			24	-
	1c	2j		
31 ^d			24	-
	1d	2j		
32 ^d			24	-
	1e	2j		
33 ^d			24	-
	1f	2j		



^aAll the reactions were carried out by using aldehyde **2** (2 mmol) and active methylene **1** (2 mmol) in ethanol (5 mL) at room temperature in the presence of onion extract (2 mL) for specific period mentioned in the [Table 3](#)

^bAll the products were characterized by using IR, ¹H NMR, ¹³C NMR and Mass spectroscopic technique

^cThe yields are all isolated

^dAll the reaction was carried out by using 4-NO₂-benzaldehyde **2j** (2 mmol) and malononitrile **1a** (2 mmol) in ethanol (5 mL) at reflux in the presence of onion extract (2 mL) for 24 h

To evaluate the possibility of applying this methodology in a large scale synthesis, we have carried out the reaction of equimolar amounts of (50 mmol) malononitrile **1a** with 4-nitrobenzaldehyde **2j**. The Knoevenagel product **3j** was obtained in 97% yield. Previously, it was reported in the literature that the pineapple juice [74] (pH 3.7) and onion extract (pH 3.6 reported by us) have been employed as catalyst for Knoevenagel condensation and enaminone synthesis [92] respectively. Based on that the plausible mechanism has been proposed ([Figure 1](#)).

[Table 4](#) compares the catalytic activity of onion extract catalyst with the recently reported catalytic system in the Knoevenagel condensation reaction. Although, less quantity of the catalyst used ([Table 4](#), entries 1-4), required more time or high temperature and even gave less yield than present study. When fruit juices used as catalyst ([Table 4](#), entries 5 and 6) for Knoevenagel condensation with a lesser amount of the catalyst and reduced time the yields are slightly lesser than present study. Hence, onion extract catalysed Knoevenagel condensation is superior over other reported methods.

Conclusion

We have achieved a simple and convenient procedure to synthesize the α -cyanoacrylonitriles and α -cyanoacrylates through Knoevenagel condensation from easily available aldehydes and active methylene compounds. In this process, water extract of onion is used as green catalyst. The products are precipitated as yellow solid and do not require any further purification and obtained only the *E*-isomers. Also, we have demonstrated this methodology for large scale synthesis where we used equimolar quantities of substrates. Though these reactions are catalyzed by HCl and H₂SO₄, the water

extract of onion catalyzed reactions has some advantages including, environmentally friendly, easy availability, low cost, easy handling, and simple workup procedure.

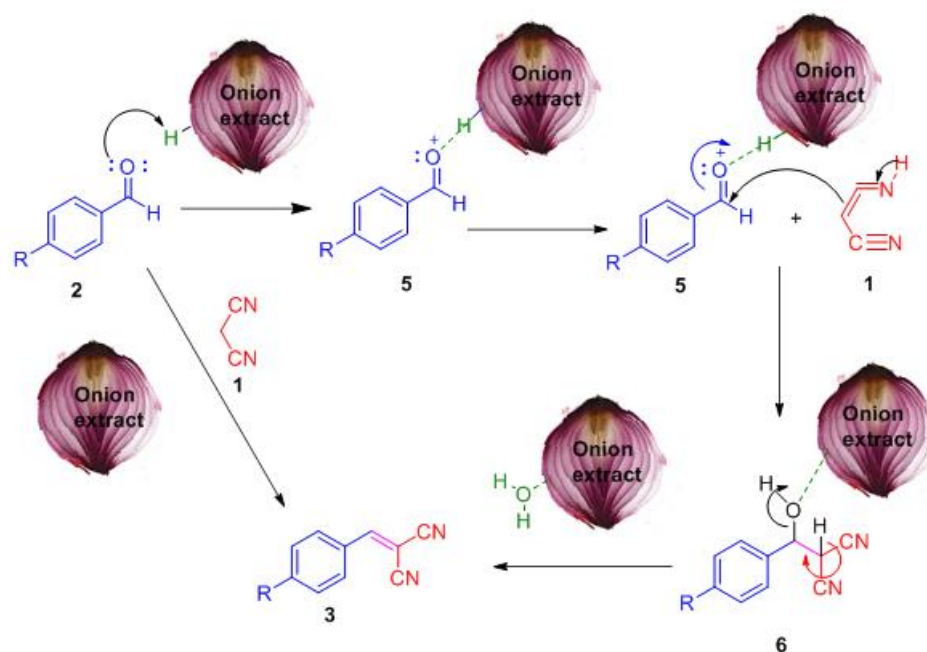


Figure 1. Proposed mechanism

Table 4. Recently reported green catalytic system

Entry	Catalyst	Reaction time	Yield (%)	Ref
1	Graphene oxide	0.5 mL of catalyst (1.5 mg/mL), RT, 4 h,	83	22
2	Silica Supported Ammonium Acetate	0.2 g of catalyst in CH_2Cl_2 , reflux, 7 h.	87	29
3	TPP	20 mol % of catalyst, 75-80 °C, 4 h	83	97
4	Lipase	200 mg of catalyst in DMSO, 35 °C, 24 h	98	11
5	Lemon juice	1 mL of catalyst, RT, 2 h	90	73
6	Pineapple juice	1 mL of catalyst, RT, 2 h	95	74
7	Water onion extract	2 mL of catalyst, RT, 2.5 h	98	-

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Disclosure statement

No potential conflict of interest was reported by the authors.

Orcid

Muthu Seenivasa Perumal  0000-0002-2234-1346

Supporting Information

Additional supporting information related to this article can be found, in the online version, at DOI:[10.22034/ajgc.2018.137885.1079](https://doi.org/10.22034/ajgc.2018.137885.1079)

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