

Visible light induced Knoevenagel condensation: A clean and efficient protocol using aqueous fruit extract of *tamarindus indica* as catalyst

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Abstract

Visible light induced a highly efficient and environmentally-friendly Knoevenagel condensation of various aliphatic and aromatic aldehydes with malononitrile has been achieved in excellent yield in presence of aqueous tamarind juice. The tamarind juice could be simply prepared from unripe fruit of *Tamarindus indica* in water and the reactions go to completion within 2-7 min. A plausible mechanism of light induced Knoevenagel condensation reaction catalyzed by tamarind juice was discussed.

Keywords: Knoevenagel condensation, visible light, aqueous tamarind juice, aldehydes, malononitrile.

1. Introduction

Knoevenagel condensation [1] is one of the most important and widely employed methods for the formation of carbon-carbon bonds [2-4]. It has been used for the preparation of a wide range of substituted alkenes, and for the synthesis of intermediate such as coumarin derivatives which are useful in perfumes, cosmetics and bioactive compounds [5-8]. In addition, Knoevenagel condensation products exhibit inhibition of antiphosphorylation of EGF-receptor and antiproliferative activity [9]. Due to their importance from a pharmacological, industrial and synthetic point of view a large number of methods for the Knoevenagel condensation have been reported using various Lewis acids/bases [10-14], microwave assisted reaction [15-17], ultrasound irradiation [18,19], biotechnology-based approach [20,21], solid phase [22,23], ionic liquid [24-26] or using green solvent like water [27-29], and grindstone method under solvent-free condition [30-32]. It is noteworthy to observe that all these protocols have some drawbacks, such as use of expensive catalyst, high thermal conditions, disposal of toxic solvents and catalyst, long reaction time often pose a problem.

In the past two decades, classical organic chemistry had been rewritten around new approaches that search for products and processes in the chemical industry that are environmentally acceptable [33]. Therefore, to address depletion of natural resources and preservation of ecosystem is just urgent to develop so called "greener technologies" to make chemical agents for wellbeing of human health [34].

An attractive area in organic synthesis involves photochemical reactions particularly using visible light in environment-friendly solvent like water or aqueous ethanol and is generally considered as a clean and green procedure. This type of photo-activation of substrate very often minimizing the for-

mation of byproducts and requires much lesser time corresponds to thermal methods and for this reason, photochemical reactions occupy an interesting position and excellent reviews/paper have been published [35-40]. The use of water as a reaction medium is not only inexpensive and environmentally benign but also provides completely different reactivity [41]. It has been suggested that the effect of water on organic reaction may be due to the high internal pressure exerted by a water solution which results from the high cohesive energy of water [42].

In literature, a number of organic reactions using natural catalysts such as clay [43-46], natural phosphates [47-49], animal bone [50], and various fruit juices are reported. Due to acidic nature aqueous fruit juice like lemon [51-57], pineapple [58], [59], coconut [60], *Acacia concinna* [61], *Sapindus trifolustus* [62] and *Tamarindus indica* [63] fruit has been found to be a suitable replacement for various homogeneous acid catalysts.

Tamarind (*Tamarindus indica*) is grown extensively in Africa, South Asia, Northern Australia, South East Asia, Taiwan and China. Tamarind has long been one of the most popular of the non-citrus tropical and subtropical fruits, largely because of its attractive flavor and refreshing sugar-acid balance. The main ingredients [64] of 100 gm of pulp of tamarind fruit contain water (15-30%), protein (2-9%), fat (0.5-3%), total carbohydrate (56-82%), edible fiber (2.2-18.3%), ash (2.1-3.3%), calcium (81-466 mg), phosphorous (86-190mg), iron (1.3-10.9 mg), sodium (23-28 mg), potassium (62-570 mg). It also contains 41-58% sugars of which 25-45% is in the form of reducing sugars and 16% is in the form of non-reducing sugars and tartaric acid is (8-18%) and ascorbic acid is (3-9 mg). The composition of the tamarind fruit juice varies with geographical, cultural and seasonal harvesting and processing. An aqueous extract of tamarind fruit juice is acidic due to presence of tartaric acid and ascorbic acid and acidity percentage is 50.3% and hence it will be

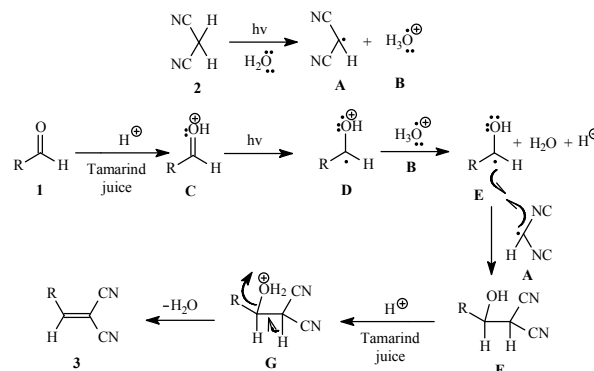
Table 1: Optimization of experimental condition for synthesis of **3a**

Entry	Aq. tamarind juice (mL)	Water (mL)	pH of the solution	Mode of reaction	Reaction time (min)	Yield (%)
1.	5	-	3.0	visible light	2	94
2.	5	-	3.0	rt with stirring	10	60
3.	5	-	3.0	reflux	10	75
4.	-	5	7.0	visible light	10	40
5.	-	5	7.0	rt with stirring	60	-
6.	-	5	7.0	reflux	60	30
7.	5	-	4.5	visible light	2	70
8.	5	-	2.0	Visible light	2	85
9.	10	-	3.0	visible light	2	94

Under the optimized condition, the generality of the process investigated with different aromatic and aliphatic aldehydes, and the results are summarized in Table 2. The light induced reactions were found to be very clean and the products were obtained in extremely pure crystalline states with an average yield of 80-98% and the reaction time varied on an average 2-7 min. The products are isolated from the reaction mixture in pure crystalline form by cooling in an ice-bath and need no further crystallization for aromatic aldehydes. However, in case of aliphatic aldehydes for entries 21, 22 (Table 2) the products are oily liquid and obtained by chromatographic separation over silica gel and the results are given in Table 2. The possibility of application of the presented method is demonstrated by using various substituted aromatic and aliphatic aldehydes to reacts with malononitrile. The procedure was successfully applied for heteroaromatic (entries 18-20) and long-chain aliphatic aldehyde (entry 22). The ether (entries 3, 9, 15, 16) and esters (entries 14, 15) linkages in the aromatic aldehydes were unaffected under photochemical conditions. The reaction was further explored for the synthesis of p-bis-2-(phenylidene) malononitrile in 98% yield by the condensation of terephthalaldehyde (entry 23) with two moles of malononitrile under similar reaction conditions.

In the present instance, we speculate that the reaction may plausibly be initiated by homolytic C-H bond cleavage of malononitrile (**2**) in the presence of visible light to produce a radical **A** and hydrogen radical which is trapped immediately by water molecule to form radical **B**. Aldehyde (**1**) becomes

activated by protonation from tamarind juice to produce a protonated species **C**. One electron transfer from **B** to **D** produced a radical **E**, which couples with radical **A** to form **F**. Protonation of **F** followed by dehydration from **G** to form the title compound **3** as depicted in Scheme 2.

**Scheme 2.** Plausible mechanistic pathway for the photochemical Knoevenagel condensation of malononitrile and aldehydes catalyzed by aqueous tamarind juice.

4. Conclusion

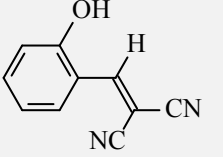
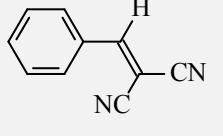
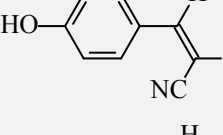
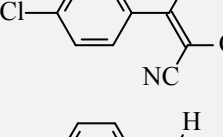
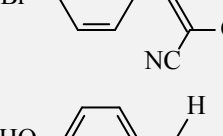
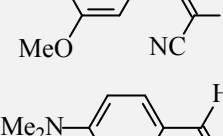
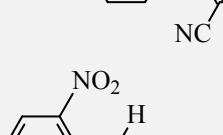
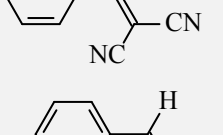
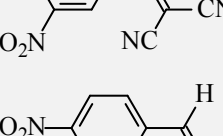
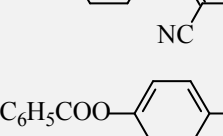
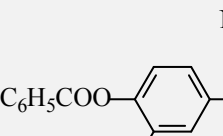
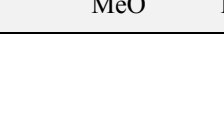
We have established a potentially efficient, absolutely clean and high yielding eco-friendly methodology, for the light induced Knoevenagel condensation of various aromatic and aliphatic aldehydes with malononitrile using aqueous tamarind juice devoid of any toxic catalyst/solvents, solid support and surfactant and may be considered as an excellent improvement over the existing methods. All the products may act as a good dienophiles in Diels-Alder reactions and the products **3a**, **3n-p**, **3r**, **3t**, **3w** are new compounds which may have potential biological activities.

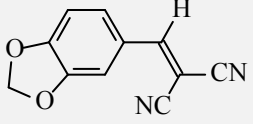
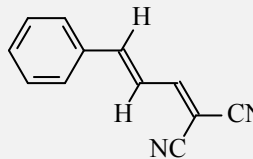
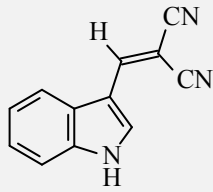
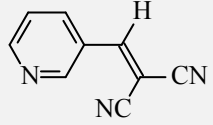
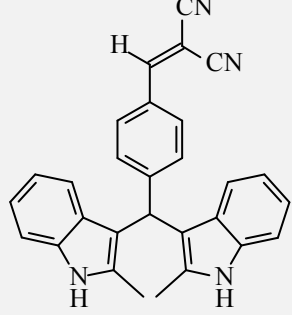
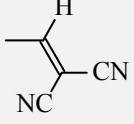
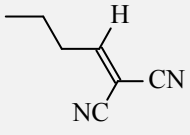
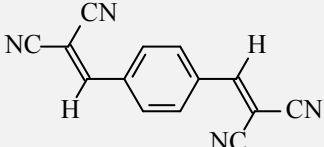
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Table 2: Results of photochemical Knoevenagel condensation of malononitrile with aldehydes catalyzed by aqueous tamarind juice

Entry	Substrate	Product ^a	Color and nature of product	Yield ^b (%)	Time (min)	Mp [lit. mp °C] ^c
1	3-Hydroxybenzaldehyde (1a)		Yellow crystal	94	2	164
2	4-Methylbenzaldehyde (1b)		White crystal	95	4	132-134 [134-135] ²⁴
3	4-Methoxybenzaldehyde (1c)		Yellow crystal	88	5	112-114 [116] ⁵⁹

4	2-Hydroxybenzaldehyde (1d)		Yellow crystal	82	4	158 [159] ⁵⁹
		3d				
5	Benzaldehyde (1e)		Light brown crystal	90	2	80-82 [80-83] ³⁰
		3e				
6	4-Hydroxybenzaldehyde (1f)		Yellowish crystal	85	4	184 [185- 186] ¹⁷
		3f				
7	4-Chlorobenzaldehyde (1g)		Colorless crystals	96	4	160-162 [162- 164] ¹⁶
		3g				
8	4-Bromobenzaldehyde (1h)		Colorless crystals	85	7	156-158 [156] ⁵⁹
		3h				
9	Vaniline (1i)		Lemon yellow solid	96	6	134-136 [135- 136] ¹⁷
		3i				
10	4- <i>N,N</i> -Dimethyl- aminobenzaldehyde (1j)		Yellow orange crystals	88	5	180 [180] ⁵⁹
		3j				
11	2-Nitrobenzaldehyde (1k)		Yellow crys- tals	95	3	135-137 [136- 138] ²⁴
		3k				
12	3-Nitrobenzaldehyde (1l)		Off-white crystals	90	4	105-107 [107- 108] ¹⁷
		3l				
13	4-Nitrobenzaldehyde (1m)		Pale-yellow crystals	96	5	162-164 [160- 162] ¹⁶
		3m				
14	4-Benzoyloxybenzaldehyde (1n)		Colorless crystal	96	7	152
		3n				
15	4-Benzoyloxy-3- methoxybenzaldehyde (1o)		Colorless solid	98	7	140-141
		3o				

16	Piperanal (1p)		Yellowish crystals	96	4	198
		3p				
17	Cinnamaldehyde (1q)		Yellow crystals	80	5	126-128 [127-129] ³⁰
		3q				
18	Indole-3-aldehyde (1r)		Yellow crystals	82	5	170-172
		3r				
19	Pyridine-3-aldehyde (1s)		White crystal	92	3	82-84 [84-85] ²⁴
		3s				
20	<i>p</i> -[3,3'-Bis(2-methylindolyl)]methylbenzaldehyde (1t)		Pale-yellow crystal	80	7	320-322
		3t				
21	Acetaldehyde (1u)		Oily liquid	82	5	Liquid ¹⁶
		3u				
22	Butanal (1v)		Oily liquid	85	7	Liquid ¹⁶
		3v				
23	Terephthalaldehyde (1w)		White crystal	98	3	298-300
		3w				

a) All products were identified by their physical and spectral data.

b) Yield refers to combined amounts of first and second crops of crystallized products obtained either directly or after chromatography.

c) Literature references of melting point.

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