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Green condensation reaction of aromatic aldehydes with active methylene compounds catalyzed by anion-exchange resin under ultrasound irradiation

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ABSTRACT

To realize a practical and green chemistry, two important challenges need to be addressed, namely the effective process for the activation of reaction and efficient, eco-friendly and robust chemical methods for the reaction conversion to target products via highly selective catalytic and reactions. Ultrasonic energy promotes the conversion process through its special cavitational effects. Combined with anion-exchange resin as a heterogeneous, reusable and efficient catalyst, Ultrasonic energy enhances the Knoevenagel condensation and leads to reduced reaction time at lower reaction temperature with less amounts of solvent and catalyst.

1. Introduction

The application of ultrasound irradiation in organic synthesis has been largely extended in recent years [1–9]. Compared with traditional methods, ultrasound has been shown to have desirable effects on both homogeneous and heterogeneous reactions, such as good yields, short reaction times, easier work-up procedure, formation of pure products in milder conditions and waste minimization [6]. Ultrasound irradiation method is now recognized as a viable and environmentally-benign alternative. Therefore, it is more convenient for green chemistry [10]. Ultrasound enhancements may be attributed either to its chemical or mechanical effects or to both of them simultaneously. The chemical effect of ultrasonic comes from local hotspots produced by cavitation. Moreover, ultrasound is a mechanical acoustic wave with the frequency [11]. It imparts high energy to reaction medium by cavitation and secondary effects [12]. As regards cavitation, it is a phenomenon characterized by the formation of vapor bubbles in a liquid. This bubble formation occurs when a pressure drop produces a new thermodynamic state corresponding to a point on the saturation curve. It is worthy to note that cavitation is the major mechanism for ultrasound intensification [13]. The key to the efficient application of ultrasound is the control and selection of the energy intensity and population of active cavitation. While the energy intensity depends on the mean behavior of bubbles, the population of active cavitation determines the cavitational efficiency [14]. One of the most important aspects of applying Ultrasonic energy to systems is how its energy is transferred to reactant solutions. This has three steps: 1) the transformation of electrical input into mechanical energy through a piezoelectric or piezomagnetic transducer; 2) the delivery of vibrational energy (acoustic energy) from the emission tip of the transducer to the liquid medium; 3) the conversion of the energy of ultrasonic streaming to the energy that activates reactants by acoustic cavitation [15]. Conventionally, convective heating devices such as heat baths or electric heating mantles are used for these reactions, which have major adverse effects on the environment as well as consumption of energy for heating and cooling [16].

Knoevenagel condensation reaction is one of the most primitive route for the synthesis of α,β-unsaturated carbonyl compounds by the condensation of aldehydes or ketones with active methylene compounds [12]. Since it was introduced by Knoevenagel in 1896 [17], it has drawn so much attention, especially in the preparation of a range of substituted alkenes and bioactive molecules. It is also regarded as a key step in the synthesis of natural products, therapeutic drugs and pharmacological products [18]. Overall, the Knoevenagel condensation is carried out homogenously using nitrogenous molecules such as aliphatic amines, urea and piperidine or their corresponding ammonium salts and amino acids [19,20]. Several Lewis bases and acids have also been reported as catalysts in the Knoevenagel condensation, including phosphates

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such as [(NP)/KF, NP/$NaNO_3$] [21], Na_2CaP_2O7 [22], $Ca_2P_2O_7$ [22] and $K_2NiP_2O_7$ [23]. There are also reports on the use of ZrO_2 [24], $ZnCl_2$ [25], CdI_2 [26], $TiCl_4$ [27], Al_2O_3 [28], Ni–SiO_2 [29], MgO and ZnO [30], $AlPO_4$–Al_2O_3 [31], KF–Al_2O_3 [32], SiO_2–NH_4OAc [33], ionic liquid [34], fly ash supported CaO [35], poly(vinyl chloride) supported tetraethylenepentamine [36], enzyme [37] and a proline-functionalized polyacrylonitrile fiber [38] as catalysts in the Knoevenagel condensation.

In most cases, organic synthesis catalyzed with homogeneous basic or acid medium has various disadvantages, such as the catalyst recovery and generation of secondary products. Besides, most organic syntheses catalyzed under homogeneous conditions involve not only the use of hazardous solvents, but also expensive and toxic reagents, as well as special efforts needed to prepare catalysts and starting materials.

Anion-exchange resin may be considered as an insoluble base, and might consequently be expected to advance reactions catalyzed by conventional bases. Only a few examples of reactions catalyzed by anion-exchange resin are reported in the literature [39–42]. The advantages of insoluble catalysts lies in the fact that the separation problems are manifestly simpler, these catalysts are regenerated and can be recycled several times, and sensitive molecules can, in some cases, react without polymerization or other reactions. Moreover, ultrasound reactions using green catalysts such as anion-exchange resin are attractive in the growing field of green and more sustainable chemistry.

This research work is interested in developing cleaner reaction profiles and operational simplicity for the Knoevenagel condensation of aromatic aldehydes with active methylene groups catalyzed by anion-exchange resins under ultrasound irradiation. This method allows for a high yield in a short time under mild reaction conditions. A reusable, easily separable, eco-friendly and highly effective resin-catalyst is also reported.

2. Experimental

2.1. Chemicals and apparatus

All reagents were purchased and used without further purification. Two commercial anion-exchange resins (IRA-410 and IRA-96) were used as catalysts for the preliminary reactions between benzaldehyde and ethyl cyanoacetete. The two basic resins (IRA-96 and IRA-410) are marketed as Cl^-, so they are activated by a sodium hydroxide solution to be used as catalysts for the preliminary reactions between benzaldehyde and ethyl cyanoacetete.

The ultrasonication was performed in a Bioblock –750 W ultrasound cleaner with a low frequency of 20 kHz (amplitude of 30%).

The melting points were determined by using Perkin Elmer Spectrum apparatus version 10. The yields of the reactions were determined using an analysis by gas chromatography (GC). The device type is “Shimadzu GC-2014”, equipped with an FID detector and a capillary column DB-5.

The NMR of the isolated products was recorded in solution in $CDCl_3$ on a spectrometer type AC Bruker (^1H at 350 MHz and ^{13}C at 75 MHz). The internal reference was $CDCl_3$.

2.2. General procedure for Knoevenagel condensation

Aldehyde (10 mmol), the active methylene compound (10 mmol), 0.20 g/0.01 mol is the ratio of resin and 2 mL of ethanol were charged in a 10 mL glass reactor. The glass was located at the maximum energy area in the ultrasonic cleaner and the addition or removal of water was used to control the temperature of the water bath at room temperature (25–30 °C). After each test, the reaction mixture was filtered to recover the catalyst. It was then washed with hot ethanol (10 mL). Afterwards, the sample was taken and analyzed by GC to determine the yield of the reaction.

2.3. Spectroscopic analysis

In general, no further purification method was required. All the products were previously reported and characterized by the melting point, IR, ^1H NMR, ^{13}C NMR.

The spectral data of some isolated compounds, taken as representative examples, are listed below.

Ethyl (E) 2-cyano-3-(2-methoxyphenyl)-2-propenoate (c): IR [ν, cm^{-1}] 1590 (C=C), 3073 (C=C—H), 2224 (CN); 1726 (O—C=O); ^1H NMR [δ, ppm] 1.36 (3H, t, $J = 7.2$ Hz); 3.87 (3H, s), 4.34 (2H, q, $J = 7.2$ Hz), 7.02 (1H, t), 7.47 (1H, m), 8.25 (1H, dd, $J = 1,5$ Hz and $J = 7.8$ Hz), 8.72(1H, s); ^{13}C NMR [δ, ppm] 13.6, 55.2, 61.9, 101.9, 110.7, 115.4, 120.2, 120.4, 128.8, 134.5, 149.2, 158.7 162.3.

2-(2-methoxbenzylidene) malononitrile (i): IR [ν, cm^{-1}] 1599 (C=C), 3047 (C=C—H) 2221.44 (CN); ^1H NMR [δ, ppm] 3.90 (3H, s), 7.03(2H, m), 7.56 (1H, m), 8.15 (1H, dd, $J = 1.2$ Hz; $J = 7.1$ Hz), 8.27(1H, s); ^{13}C NMR [δ, ppm] 55.5, 80.9, 111.0, 112.5, 113.8, 119.7, 120.7, 128.4, 136.0, 154.0, 158.5.

3. Results and discussion

3.1. Ultrasonic induced reaction

A series of preliminary tests between the stoichiometric amount of benzaldehyde and ethyl cyanoacetete in small volumes of ethanol (2 mL) over anion-exchange resin through conventional

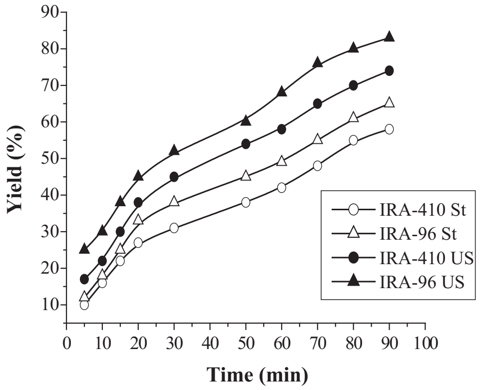


Fig. 1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate through the conventional stirring and ultrasound irradiation.

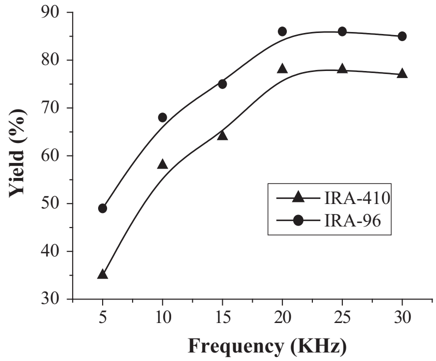


Fig. 2. Effect of ultrasonic frequency on Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

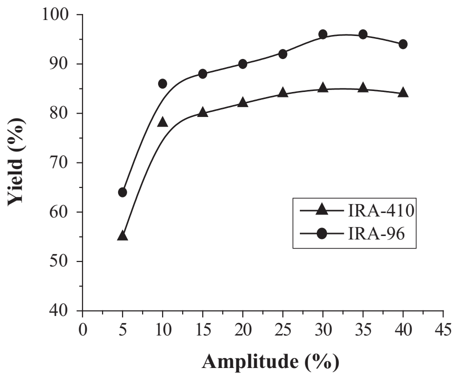


Fig. 3. Effect of ultrasonic amplitude on Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

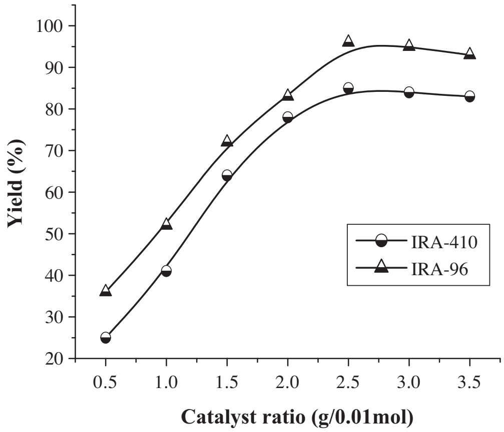
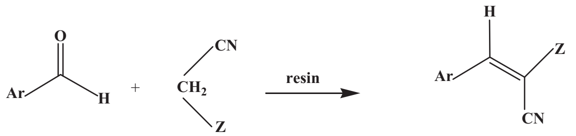


Fig. 4. Effect of catalyst ratio on Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate under ultrasound irradiation.



Scheme 1. Schematic representation of Knoevenagel condensation.

stirring (St) or under ultrasound irradiation (US) at the frequency of 10 kHz and 10% Amplitude were performed in order to optimize the main experimental parameters involved in the conduct of the Knoevenagel condensation reaction.

The comparison of the results shown in Fig. 1 reveals the remarkable influence of ultrasonic activation on the kinetics of the reaction. Compared to the magnetic stirring, ultrasonic activation has achieved the reactions in a very short time. For example, using IRA-410, the yield passes from 42% through the conventional stirring to 58% after 60 min under ultrasound irradiation, and using IRA-96, it passes from 49 to 68% after 60 min.

3.2. Ultrasonic frequency

As shown in Fig. 2, the experimental data indicate that the activation energy increases with the increase in ultrasound frequency at 10% of amplitude. The optimal yields of 78% for IRA-410 and 86% or IRA-96 were obtained at the frequency of 20 kHz after 60 min, from which the reaction performance did not have any significant change.

However, ultrasonic frequency influences the behavior of bubble cavitation through the change in the duration time of acoustic cycle. On the other hand, high frequency does not favor the occurrence of active cavitations as the time for the growth, radial motion and collapse of bubbles may be insufficient [43].

3.3. Ultrasonic amplitude

As can be seen from the Amplitude effect study in Fig. 3, the reaction conversation reaches its maximum at 30% of ultrasonic amplitude at the frequency of 20 kHz where the yields are using IRA-410 and IRA-96 after 60 min.

Generally, the increase of ultrasonic power means that the higher intensity of ultrasound was introduced into the reaction vessel, which would accelerate the reactions. It can be seen that such increase led to relatively higher yield and shorter reaction time before the ultrasound power intensity reached 30%, and then the yield decreased slightly with the increase in ultrasound power intensity. Ultrasound which is used in heterogeneous chemistry has been shown to increase the reaction rate of processes by emulsifying liquid–liquid systems or by producing the erosion, disruption and dispersion of solid particles. The parameters affecting the solid catalyst such as the weight percentage of the catalyst and reusability in the reaction were studied.

3.4. Catalyst ratio

Solid catalysts provide a green and promising way for chemical synthesis with less corrosion than homogeneous acid/base catalysts and simplified recovery of the catalysts. The effect of catalyst ratio was then studied. The same reaction model (0.01 mol each reagent) was carried out using different amounts of resins at 25–30 °C for 60 min under ultrasound irradiation. As shown in Fig. 4, the maximum yield was obtained when the catalyst/reagent

Table 1
Knoevenagel condensation catalyzed by anion-exchange resins under ultrasound irradiation.

Entry	Ar	Z	Time (min)	Yield (%)		mp (°C)	
				IRA-96	IRA-410	Found	Reported
a	C_6H_5	CO_2Et	60	96	85	49–50	50–51 [46]
b	2-Furyl	CO_2Et	15	98	90	87–88	86–87 [46]
c	$2\text{-}CH_3OC_6H_4$	CO_2Et	60	93	84	72–74	_
d	$4\text{-}CH_3OC_6H_4$	CO_2Et	60	89	79	85–86	86–87 [46]
e	$2\text{-}ClC_6H_4$	CO_2Et	60	100	92	53–54	52–53 [47]
f	$4\text{-}ClC_6H_4$	CO_2Et	60	100	93	91–92	89–90 [46]
g	C_6H_5	CN	15	98	89	81–82	80–82 [46]
h	2-Furyl	CN	15	98	90	67–68	65–66 [46]
i	$2\text{-}CH_3OC_6H_4$	CN	15	97	87	85–86	_
j	$4\text{-}CH_3OC_6H_4$	CN	15	95	85	114–115	114–116 [46]
k	$2\text{-}ClC_6H_4$	CN	15	93	87	94–95	94–96 [47]
l	$4\text{-}ClC_6H_4$	CN	15	95	88	159–160	161–162 [46]

Table 2
Comparison of our results with those of some reports.

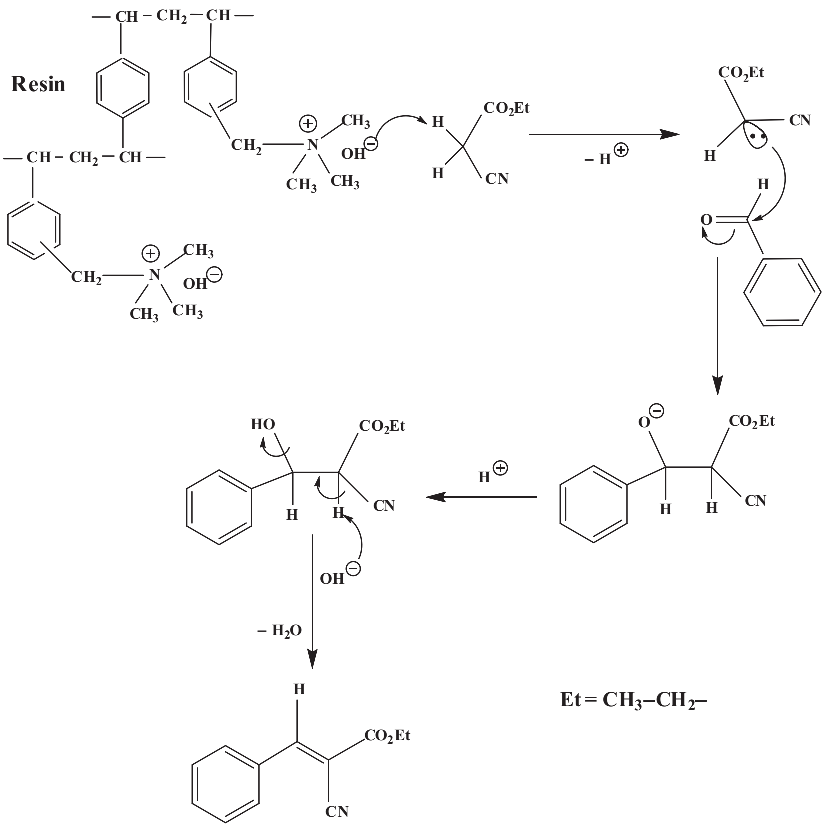
Entry	Report			Our work	
	Yield (%)	Time (min)		Yield (%)	Time (min)
a	85	480	[33]	96	60
	87	180	[35]		
	99	240	[38]		
c	75	900	[29]	93	60
d	93	150	[36]	89	60
e	90	240	[38]	100	60
f	92	150	[36]	100	60
	85	570	[33]		
g	89	180	[24]	98	15
	87	420	[33]		
	98	240	[38]		
h	87	30	[24]	98	15
i	91	60	[36]	97	15
	70	900	[29]		
j	80	150	[24]	97	15
	68	20	[46]		
k	90	60	[36]	93	15
l	88	120	[24]	95	15
	65	20	[46]		
	90	390	[33]		

ratio is equal to 0.25 g/0.01 mol of each reagent. From this ratio the yield remains constant. The results have demonstrated that the maximum yield is obtained when the catalyst/reagents ratio is equal to 0.25 g/0.01 mol of each reagent. A higher ratio (0.3 g/0.01 mol) seems to decrease the yield, because the reaction mixture became very viscous, under a small volume of solvent, thus reducing the diffusion of reagents molecules. This might be explained by a higher adsorption of reagents on active sites of resins. A lower catalyst ratio (0.2 g/0.01 mol) was shown to afford reduced yield. It seems that this ratio is insufficient to catalyze the reaction and that a resin ratio equal to 0.25 g/0.01 mol is optimal in these reaction conditions.

However, other variables can have ultrasound effects, such as the concentration of solids (in our case the clay-catalyst) and mainly the viscosity. Raso et al. [44] have confirmed that at higher viscosities, cavitation is more difficult to induce and the number of cavitating bubbles per unit volume is reduced. Besides, Duran-Valle et al. [45] have reported that when one of the phases is a solid the ultrasonic irradiation has several additional enhancement effects, which are particularly convenient when the solid acts as catalyst. The cavitation effects form microjects of liquid, which bombard the solid surface, which causes the exposition of unreacted surfaces of solid, increasing the interphase surface able to react. In general, the sonication presents beneficial effects on the chemical reactivity. In fact, it can accelerate the reaction, reduce the induction period and enhance the catalyst efficiency.

After optimizing the reaction conditions and in order to generalize this model reaction, the reactivity of different aromatic aldehydes and various active methylene compounds such as ethyl cyanoacetate and malononitrile (Scheme 1) was tested in the same conditions: $T = 25–30\,°C$, catalyst ratio = 0.25 g/0.01 mol under ultrasound irradiation (frequency of 20 KHz, 30% amplitude). The results of the obtained yields and selectivities are listed in Table 1.

The obtained results have revealed that, in general, the reactions were clean and the isolated compounds were obtained after crystallization in pure form (IR, NMR and GC) without further purification. The yields are less than 100% due to the remaining starting reagents. Compared to the Knoevenagel reactions of malononitrile with aromatic aldehydes, the reactions of ethyl cyanoacetate with the same aromatic aldehydes need longer time. Because the electron withdrawing ability of the CN group is stronger than that of carbonyl or carboxylic group, the methylene group of malononitrile is more activated than ethyl cyanoacetate.



Scheme 2. The proposed mechanism of synthesis of Ethyl α-cyanocinnamate.

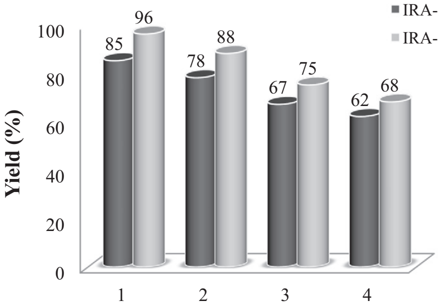


Fig. 5. The yield of ethyl α-cyanocinnamates after four cycles of use of resins.

It is important to note that all reactions selectively produced the dehydrated products without any side reactions, self condensation, Michael addition, Cannizaro products or hydrated products of Knoevenagel adducts, etc. were observed (GC). When ethyl cyanoacetate was used as active methylene compound, the reaction occurred with the stereoselective formation of *E* configured olefins and with 100% selectivity. For example, in the case of the product obtained from the condensation of 2-methoxy benzaldehyde and ethyl cyanoacetate (entry c), a small Nuclear Overhauser Effect (NOE) was detected between the olefinic proton and the methylene of the carboethoxy group. The selective choice of catalyst and the activation process is one of the factors that lead to increase the selectivity of the reaction. In our case the combination of the Ultrasonic energy and anion-exchange resin can be the primary factor promoting condensation reaction with 100% selectivity. Moreover, previous research work has shown that organic reactions activated by ultrasonic irradiation offer products with high selectivity [1].

Compared with some reports (Table 2), our method is more efficient, showing the significant role played by ultrasound for the acceleration of chemical reaction at lower reaction temperature.

3.5. Proposed mechanism

The basic sites of resin produce a carbanion from ethyl cyanoacetete as shown in Scheme 2, the conjugated base generated here is stable due to conjugation with the cyano-group. Now, this anion makes a nucleophilic attack on the carbonyl-carbon atom of the benzaldehyde to form Ethyl (*E*) α-cyanocinnamate by simple dehydration.

3.6. Catalyst reusability

The reusability of the two resins was also studied for four consecutive cycles of use. Actually, the reaction was carried out using the same procedure for the synthesis of Ethyl α-cyanocinnamates. The results in Fig. 5 demonstrate the good catalytic activity of the anion-exchange resins even after four cycles since good yields were obtained over IRA-96 and IRA-410 (62% and 54% respectively).

4. Conclusion

The present research work offers a simple method of the Knoevenagel condensation of aromatic aldehydes with active methylene groups under ultrasound irradiation in the presence of anion-exchange resins. Not only does the proposed method work under milder and cleaner reaction profiles, but also provides products with higher purity and yields. It also needs shorter reaction time, easier work-up procedure, and generates less waste. It is worthy to mention that no column purification is required and the products can be purified by simple crystallization. The catalyst can be easily recovered and reused several times without the significant loss of its catalytic activity.

Acknowledgment

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