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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

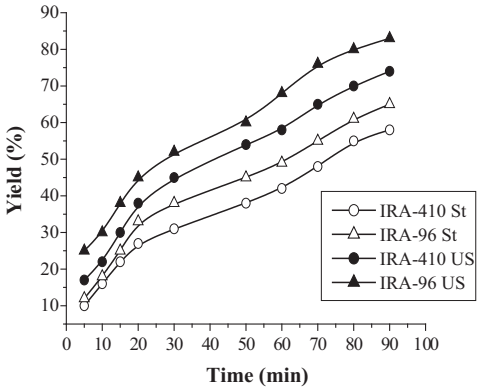

Fig. 1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate through the conventional stirring and ultrasound irradiation.

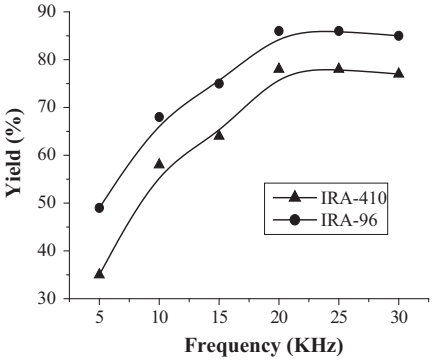

Fig. 2. Effect of ultrasonic frequency on Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.