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Ultrasound-assisted aza-Michael reaction in water: A green procedure

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ABSTRACT

The conjugate addition of amines to conjugated alkenes (commonly known as aza-Michael reaction) constitutes a key step for the synthesis of various complex natural products, antibiotics, α-amino alcohols and chiral auxiliaries. Ultrasound-induced addition of several amines to α, β-unsaturated ketones, esters and nitriles has been carried out very efficiently in water as well as under solvent-free conditions. No catalysts or solid supports have been used in this method. Remarkable enhancement of reaction rate has been observed in water under ultrasound-induced method. This environmentally benign procedure has provided clean formation of the products with better selectivity.

1. Introduction

Nitrogenous heterocycles and their derivatives have broad application in synthetic, natural product, materials, and biological chemistry. Consequently, syntheses of these types of molecules are subjects of considerable interest [1]. Conjugate addition reactions of nitrogen-centered heterocyclic nucleophiles to electron-deficient olefins serve as a powerful preparative method in the area of heterocyclic chemistry. The aza-Michael addition of nucleophiles to α, β-unsaturated ketones, esters and nitriles is established as a powerful tool for carbon–nitrogen bond formation. This reaction is widely reported as a key step for the synthesis of kinase inhibitor [2], alkaloids [3], lactams [4], amino acid [5], aziridine [6], and β-aminophosphonates [7]. Therefore, a number of new catalysts, supports, methods and solvents are reported for this reaction. Some of which includes $ZrCl_4$ [5], cinchona alkaloid [8], hexafluoroisopropyl (HFIP) alcohol [9], silica gel supported over perchloric acid ($HClO_4$–SiO_2) [10], $LaCl_3$ [11], triethylammonium acetate (TEAA) [12], alkaline Al_2O_3 [13], polystyrenesulfonic acid [14], amberlyst-15 [15], silica gel [16], *p*-toluenesulfonic acid under high pressure [17], ionic liquid [18], organocatalyst [19], enzyme [20] and tetrabutylammonium bromide [21]. These methods have extended the scope of this reaction. However they have limitations in some of the following areas: costly catalysts, low yield, long reaction time, difficult product isolation procedure and use of toxic metal catalysts as well as hazardous solvents.

Ultrasound-induced synthesis of organic molecules is a powerful green synthetic approach [22,23]. Over the past decade, protection of the environment and waste prevention has been increasingly emphasized by researchers from both academia and industry [24]. For this reason the elimination or reduction of volatile solvents in organic synthesis is an important goal. These types of processes can contribute significantly in green chemistry [25,26]. A recent trend of synthetic organic chemistry indicates that ultrasound can be used as an important tool to achieve a number of chemical reactions in high yield and within a shorter reaction time [27]. In this context development of solvent-free synthetic methods or the replacement of hazardous solvents with environmentally benign solvents has become an important and popular research topic in recent years. We have developed ultrasound-assisted aza-Michael reaction without using any catalysts or solid supports. We have tested this new method with different solvents as well as under solvent-free conditions. High yields are obtained in water and also under solvent-free conditions. However, the reaction in water proceeds much faster than organic solvents or solvent-free conditions (Scheme 1).

2. Experimental

2.1. General: apparatus and analysis

Melting points were determined in a Fisher Scientific electrochemical Mel-Temp* manual melting point apparatus (Model 1001) equipped with a 300 °C thermometer. Elemental analyses (C, H, N) were conducted using the Perkin–Elmer 2400 series II ele-

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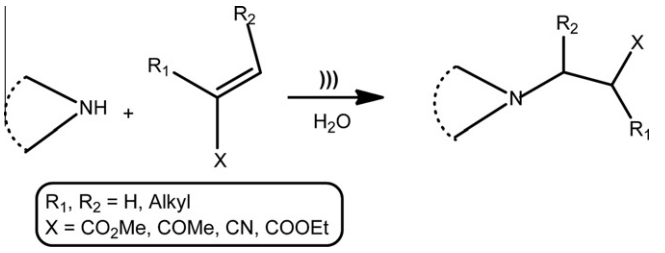


Scheme 1.

mental analyzer, their results were found to be in good agreement (±0.2%) with the calculated values for C, H, N. Sonication was performed in B5510-DTH, Branson ultrasonic cleaner (Model-5510, frequency of 42 kHz and an output power of 135 W) with digital timer, heater, temperature monitor & degas. Inside tank dimensions were 11.5 in. × 9.5 in. × 6 in. (length × width × height) with a fluid capacity of 2.5 gallons. FT-IR spectra were measured on a Bruker IFS 55 Equinox FT-IR spectrophotometer as KBr discs. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were obtained at room temperature with JEOL Eclipse-300 equipment using TMS as internal standard and $CDCl_3$ as solvent. Analytical grade chemicals (Sigma–Aldrich Corporation) were used throughout the project. Deionized water was used for the preparation of all aqueous solutions.

2.2. General procedure for the aza-Michael reaction

Michael acceptor (1 mmol) and amine (1 mmol) in water (1 mL) was irradiated at room temperature in a B5510-DTH (Branson ultrasonic cleaner; Model-5510, frequency 42 kHz with an output power of 135 W), as specified in Table 2. After completion of the reaction, it was extracted with diethyl ether (2 × 5 mL), washed with brine solution (10 mL) and dried over Na_2SO_4. The extract was then concentrated and the crude product was purified using flash chromatography (silica gel, 30% EtOAc/70% hexane) to afford pure compound. Products obtained from entries (1–15) are already reported (Table 2) and are easily identified by comparison of their spectroscopic data.

2.3. Spectral data for the new compounds (entries 16 and 17, Table 2)

2.3.1. 3,3′-(Piperazine-1,4-diyl)bis(1,3-diphenylpropan-1-one) (entry 16, Table 2)

Yellowish-brown amorphous solid. Mp. 126–128 °C; IR (KBr disc. ν cm^{-1}): 3124, 1652 1594, 1476, 1260, 1072, 971, 861, 735, 718, 673; ^{1}H NMR δ (ppm): 2.73 (m, 8H, piperizine methylene), 2.98 (m, 4H, methylene), 4.38 (m, 2H, methine), 7.27–7.40 (m, 10H, Ar–H), 7.59–8.01 (m, 10H, Ar–H); ^{13}C NMR δ (ppm): 50.91 (4C), 69.12 (2C), 71.32 (2C), 126.91 (2C), 127.81 (4C), 127.92 (4C), 128.74 (4C), 128.11 (4C), 135.12 (2C), 137.10 (2C), 139.43 (2C), 201.11 (2C). Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57. Experimental: C, 81.03; H, 6.71; N, 5.51.

2.3.2. 3,3′-(4,4′-(Propane-1,3-diyl)bis(piperidine-4,1-diyl))bis(1,3-diphenylpropan-1-one) (entry 17, Table 2)

Brownish-white amorphous solid. Mp. 141–144 °C; IR (KBr disc. ν cm^{-1}): 3138, 1659, 1588, 1461, 1265, 1071, 975, 863, 723, 675; ^{1}H NMR δ (ppm): 1.21–1.35 (m, 10H, aliphatic H), 1.49–1.61 (m, 6H, aliphatic H), 2.39–2.56 (m, 8H, aliphatic H), 2.83 (m, 2H, methylene), 3.06 (m, 2H, methylene), 4.49 (m, 2H, methine), 7.27–7.31 (m, 6H, Ar–H), 7.42 (m, 4H, Ar–H), 7.54–7.65 (m, 6H, Ar–H), 7.98–8.01 (m, 4H, Ar–H); ^{13}C NMR δ (ppm): 19.21 (2C), 24.27 (1C), 26.01 (4C), 36.71 (2C), 48.79 (4C), 71.89 (2C), 73.05 (2C), 126.29 (4C), 127.81 (4C), 127.98 (2C), 129.39 (4C), 129.97 (4C), 135.10 (2C), 136.22 (2C), 138.52 (2C), 197.91 (2C). Anal. Calcd for $C_{43}H_{50}N_2O_2$: C, 82.39; H, 8.04; N, 4.47. Experimental: C, 82.27; H, 7.89; N, 4.52.

Table 1
Effect of solvents on aza-Michael reaction of piperidine (1 mL) and methyl acrylate (1 mL) in 1 mL solvent under ultrasound.

Entry	Solvent	Time (min)	Yield (%)[a]
1	Tetrahydrofuran	60	45
2	Ethanol	60	62
3	Methanol	60	57
4	Dichloromethane	60	55
5	Acetone	60	48
6	Acetonitrile	60	71
7	Water	5	98
8	Water (without ultrasound, stirring at room temperature)	30	96
9	No solvent	15	93

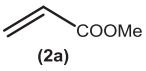
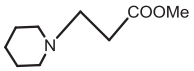
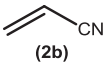
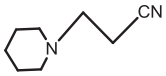
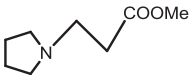
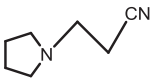
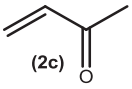
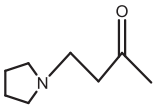
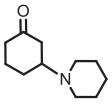
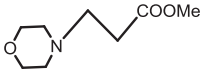
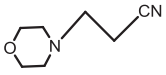
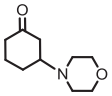
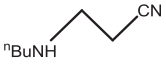
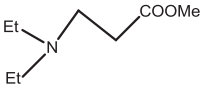
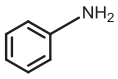
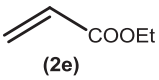
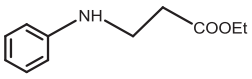
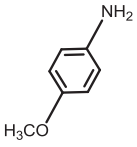
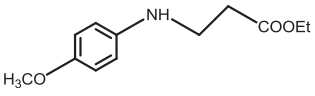
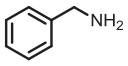
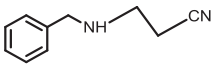
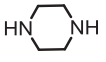
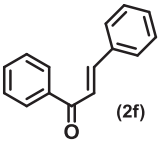
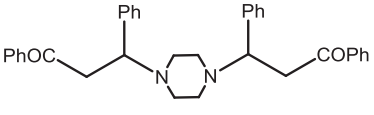
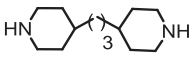
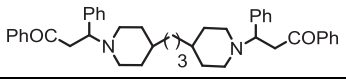
[a] Isolated yield.

3. Results and discussion

Development of an efficient and simple aza-Michael procedure in water without any catalyst or support is timely and highly challenging. To evaluate the effect of solvents piperidine (1 mmol) and methyl acrylate (1 mmol) in 1 mL of solvent were used as a probe (Table 1). Moderate yields of the products were obtained when tetrahydrofuran, ethanol, methanol, dichloromethane, acetone or acetonitrile were used as solvents under ultrasound irradiation for 60 min (entries 1–6, Table 1). The desired product was isolated in 98% yield within 5 min in presence of water (entry 7, Table 1). The same reaction in water produced 96% yield of the Michael adduct in 30 min when it was performed at room temperature (entry 8, Table 1). Solvent-free condition gave 93% yield of the Michael adduct in 15 min (entry 9, Table 1). Six- and three-fold rate accelerations were observed under ultrasound and solvent-free conditions in comparison with reactions that were conducted in water at room temperature.

Our ultrasound-induced reaction (Scheme 1) in water has been tested with several amines and unsaturated ketones, unsaturated nitrile an unsaturated ester. The results are spectacular (Table 2). All the products were identified by their NMR, IR and elemental analysis data. All the ultrasound-assisted reactions in water were very rapid compared to reactions in organic solvents under identical conditions. No catalysts were necessary to complete the reaction. In a typical experiment, piperidine (1 mmol) and methyl acrylate (1 mmol) in 1 mL water were irradiated using ultrasound to obtain the corresponding methyl 3-(piperidine-1-yl)propanoate in 98% yield (entry 1) and the reaction was completed within 5 min. Encouraged by this result, diverse amines were tested with various Michael acceptors. All the reactions were completed within 10 min to give the desired products in excellent yields (86–99%), with high regio and chemo selectivity. No side products were formed. In general, the nucleophilic addition of amines to carbonyl compounds depends on steric effects of the partners used in the reactions. In contrast, primary, secondary (cyclic, heterocyclic and acyclic), benzylic as well as aromatic amines produce products in excellent yield in the present study. This method suggests that it is not necessary to use large excess of corrosive acid, catalytic amounts of Lewis acids or solid acidic surfaces in Michael reaction of amines with unsaturated ketones, esters and nitriles. Primary amines produced mono addition products (entries 10, 11, 13, 14, and 15) selectively and no *bis* addition products were formed. The reaction between piperidine with methyl acrylate (entry 1) in solvent-free condition gave 93%

Table 2
Ultrasound-assisted aza-Michael reaction following Scheme 1.

Entry	Amine	Enone	Product	Time (min)	Yield (%)[a]	Refs.
1	 (**1a**)	 (**2a**)		5	98	[28a]
2	(**1a**)	 (**2b**)		5	96	[28a]
3	 (**1b**)	(**2a**)		5	95	[28b]
4	(**1b**)	(**2b**)		5	91	[28b]
5	(**1b**)	 (**2c**)		5	95	[28c]
6	(**1a**)	 (**2d**)		10	92	[28d]
7	 (**1c**)	(**2a**)		5	93	[28d]
8	(**1c**)	(**2b**)		5	90	[28d]
9	(**1c**)	(**2d**)		10	93	[28c]
10	$^{n}BuNH_2$ (**1e**)	(**2a**)		5	99	[28a]
11	(**1e**)	(**2b**)		5	95	[28a]
12		(**2a**)		5	97	[28a]
13		 (**2e**)		5	92	[28b]
14		(**2e**)		5	95	[28b]
15		(**2b**)		5	93	[28b]
16		 (**2f**)		10	87	–
17		(**2f**)		10	86	–

[a] Isolated yield.

yield of the Michael adduct in 15 min whereas 98% yield of the same Michael adduct was obtained in 5 min. It is interesting to note that this reaction produced products with primary aromatic amines and electron-deficient alkenes (entries 13 and 14).

The presence of water accelerated the reaction probably through hydrogen bond formation with the carbonyl group and this increased the electrophilic character at the β-carbon of the unsaturated compounds [29]. As a result, nucleophilic attack by the amine increased significantly. On the other hand, hydrogen bond formation between the oxygen atom of water and the hydrogen-atom of the amine increased the nucleophilic power of the N-atom of the amine. The introduction of ultrasound (i.e., sound energy with frequencies in the range 15 kHz–1 MHz) into liquid reaction mixtures is known to cause a variety of chemical transformations. Ultrasonic irradiation of liquid reaction mixtures induces electro hydraulic cavitations by which the radii of preexisting gas cavities in the liquid oscillate in a periodically changing pressure. These oscillations eventually become unstable, forcing violent implosion of the gas bubbles. The rapid implosion of a gaseous cavity is accompanied by adiabatic heating of the vapor phase of the bubble, yielding localized and transient high temperatures and pressures. Thus, the apparent chemical effects in liquid reaction media are either direct or indirect consequences of these extreme conditions [30]. Water has a high dielectric constant with a permanent dipole moment, which allows the coupling between the oscillating electric field and the molecular tumbling to occur with high efficient heating. Therefore, water acts as a pseudo-organic solvent at elevated temperature. Isolation of products is also facilitated due to the decreased solubility of organic materials upon post reaction cooling. On the other hand, organic reactions in water without using harmful organic solvents is also one of the current focuses because water is abundant, nontoxic and environment-friendly compared with any organic solvents.

4. Conclusion

In conclusion, ultrasound-induced ecofriendly aza-Michael reaction is reported. In this method no metallic, enzymatic or corrosive catalysts or solid supports are used. The present procedure has notable advantages that include simple operation procedure, environmentally benign reaction conditions, faster reactions and high yields of products. The method as reported herein will find applications in other areas of research.

Acknowledgement

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