N-donor Ligand as Catalyst: A Simple Aza-Michael Addition Reaction in Aqueous Media

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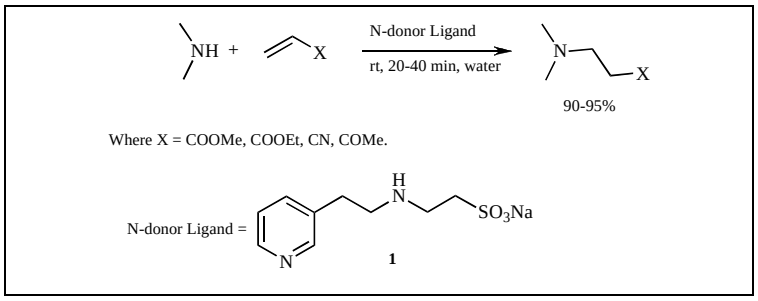

A novel approach for the Aza-Michael addition reactions between various amines and α,β-unsaturated esters, nitriles and ketones using N-donor Ligand catalyst (3 mol %) is described. The reactions are carried out in aqueous media at an ambient temperature to afford the products in excellent yields.

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INTRODUCTION

Conjugate addition (Michael addition) of nucleophiles to α,β-unsaturated carbonyl compounds is one of the most important bond forming strategies in synthetic organic chemistry [1]. The versatility of the conjugate addition is due to the large variety of nucleophiles (organometallic reagents, other carbanions, heteroatoms, Michael donors) and acceptors (α,β-unsaturated carbonyl compounds, esters, nitriles and notroalkenes) that can be used [2]. Among the variety of synthetic transformations, the development of new methods for new and efficient conjugate addition reactions with a wide range of heteroatom nucleophiles has attracted special attention [3]. In particular, the conjugate addition of nitrogen nucleophiles to α,β-enones (aza-Michael reaction) is noteworthy as a widely used method for carbon-nitrogen bond formation. The products of aza-Michael additions, β-amino carbonyl compounds and derivatives, can be used in peptide analogues or as precursors to optically active amino acids, amino alcohols, diamines and lactams, many of which serve as powerful antibiotics or other drugs [4]. Among the methods for generating β-amino carbonyl compounds, Lewis acid and base catalyzed conjugate addition of nitrogen containing nucleophiles to α, β-unsaturated carbonyl compounds is one of the most simple and effective methods [5]. To avoid typical disadvantages resulting from the presence of such protic catalysts, a good number of alternative procedures have been developed over the past few years. In particular, various metal catalysts, such as $Yb(OTf)_3$, $InCl_3$, $CeCl_3.7H_2O/NaI$, $Bi(NO)_3$, $Bi(OTf)_3$, $Cu(OTf)_2$, $FeCl_3.7H_2O/Co(OAc)_2$, $LiClO_4$, heterogeneous solid acids, ionic liquids, quaternary ammonium salts, $Cu(acac)_2$ immobilized in ionic liquids have efficiently catalyzed the aza-Michael reaction [6]. Unfortunately many of these procedures requires a large excess of reagents, long reaction times and drastic reaction conditions in acetonitrile or 1,2-dichloroethane which are very high on the list of damaging chemicals. In some cases stoichiometric amounts of Lewis acids such as $AlCl_3$, $TiCl_3$ or $SnCl_4$ are required. These conditions are not in agreement with clean chemistry, and hence the challenge for a sustainable environment calls for the use of alternative procedures avoiding the use of harmful solvents and reagents. Thus, the need for an environmentally benign and facile protocol for the aza-Michael reaction still exists.

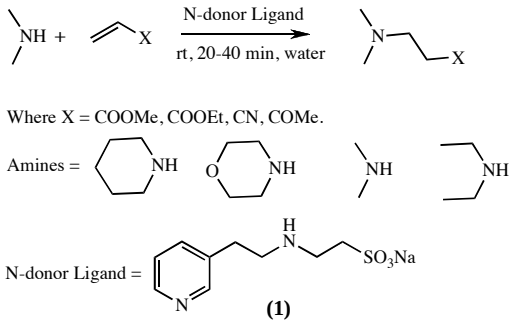
Organic reactions in water or aqueous media have attracted great interest [7]. With tightened regulatory pressure focusing on organic solvents, the search for alternatives is of increasing importance. In this respect, the development of water-tolerant catalysts has rapidly become an area of intense research. Surprisingly, however, there are few reports on the conjugate addition of nitrogen nucleophiles to α,β-unsaturated carbonyl compounds in water [6b,6g,6h,6l]. These findings promoted us to investigate the aza-Michael reaction in aqueous media, in continuation of our interest in

developing novel synthetic methodologies, particularly carbon-carbon and carbon-heteroatom bond formations [6f,6n,8].

RESULTS AND DISCUSSION

As a part of our ongoing project [9], we have developed methodology for the aza-Michael addition reaction, which makes use of milder conditions over the reported procedure as depicted in Scheme 1.

Scheme-1



The methodology developed is simple with good to excellent yields. *N*-Donor ligand was synthesized by reacting 3-(2-aminoethyl)pyridine with sodium vinyl-sulfonate in water using a literature procedure [10]. We first compared the catalyst effect on different solvents for the aza-Michael addition reactions, and the results are summarized in Table 1.

Table 1

Aza-Michael addition reaction between piperidine and methyl acrylate using different solvents.[a]

Entry	Reagent	Solvent	Reaction time (min)	Yield (%)[b]
1	1	DCM	180	35
2	1	CH_3CN	150	45
3	1	THF	120	40
4	1	$CHCl_3$	150	50
5	1	DMSO	120	45
6	1	DMF	130	50
7	1	CH_3CN/H_2O (1:1)	90	67
8	1	THF/H_2O (1:1)	60	60
9	1	DCM/H_2O (1:1)	90	70
10	1	H_2O	20	95

[a] Standard conditions: 1 mmol methyl acrylate, 1.1 mmol piperidine, 3 mol % catalyst (**1**), water, rt; [b] Isolated yields.

In a typical experiment, the conjugate addition of piperidine to methyl acrylate in water was carried in the presence of N-donor ligand (**1**) to afford the corresponding (1- piperidinyl)-propionic acid methyl ester in 95% yield. The reaction proceeds rapidly at ambient temperature with 3 mol % of catalyst (**1**) and completes within 20 min (Table 1, entry 10). The use of different solvents like CH_3CN, THF, $CHCl_3$, DMSO and DCM afforded very low yields (Table 1, entry 1-6). However, the addition of water to the above solvents gave slightly higher yields (Table 1, entry 7-9). These results suggest

Table 2.

N- Donor ligand (1)-catalyzed aza-Michael addition reaction between amines and α, β-unsaturated carbonyl compounds or nitriles

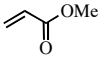
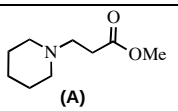
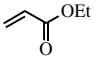
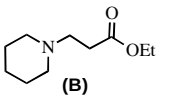
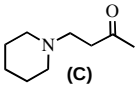
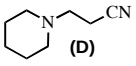
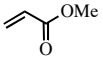
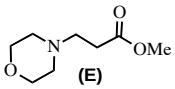
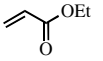
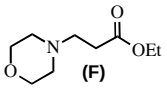
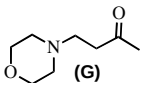
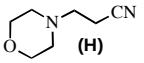
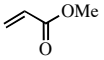
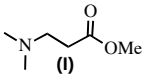
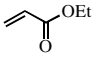
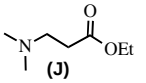
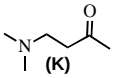
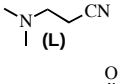
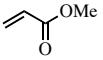
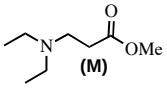
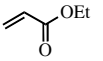
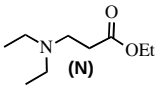
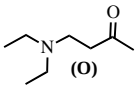
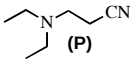
Entry	Amines	α,β-unsaturated carbonyl compounds or nitriles	Product	Time [a]	Yield [b]
1			 (A)	20	95
2			 (B)	25	93
3			 (C)	25	94
4			 (D)	30	90
5			 (E)	25	91
6			 (F)	35	91
7			 (G)	30	92

Table 2 (continued)

Entry	Amines	α,β-unsaturated carbonyl compounds or nitriles	Product	Time [a]	Yield [b]
8			 **(H)**	25	94
9			 **(I)**	20	94
10			 **(J)**	35	93
11			 **(K)**	25	92
12			 **(L)**	30	93
13			 **(M)**	25	95
14			 **(N)**	25	94
15			 **(O)**	25	95
16			 **(P)**	40	90

[a]All the reactions were performed in H_2O as solvent at room temperature; [b]Isolated yields

that water is the best solvent for aza-Michael addition reaction. It may be due to the fact that N-donor ligands have greater solubility and greater basicity in water than in organic solvents.

With optimum conditions in hand, we reacted various amines such as piperidine, morpholine, diethyl amine and dimethyamine with a variety of α, β- unsaturated carbonyl compounds such as methyl acrylate, ethyl acrylate, acrylonitrile and methyl vinyl ketone. The corresponding 1,4 addition aza-Michael products were formed in good to excellent yields (90-95%). All the reactions were completed within 20-40 minutes, and all the products were confirmed by ^{1}H NMR, IR and mass spectroscopy and results are summarized in Table 2.

In conclusion, the N-donor ligand provides an efficient methodology for the synthesis of β-amino carbonyl compounds *via* aza-Michael reaction. The remarkable advantages offered by this method are a simple procedure, mild conditions, fast reactions and excellent yields of products.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a 400 MHz Varian-Mercury Plus spectrometer and are reported as parts per million (ppm) downfield from a tetramethylsilane internal standard. The following abbreviations are used; singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (b). Mass spectra were Micromass-QUATTRO-II of WATER mass spectrometer. IR spectra were measured with a Bruker Vector 22 FTIR spectrophotometer. All chemicals were obtained from commercial suppliers and were used without purification.

Typical Procedure for aza-Michael addition reaction in aqueous media. The appropriate amine (1 mmol) and α,β-unsaturated carbonyl compound (1.1 mmol) were added to a 25 mL conical flask containing 10 mL water and to this 3 mol % of N-donor ligand (**1**) was added. The reaction mixture was stirred at room temperature for 20 min. The progress of the reaction was monitored using TLC. Upon completion, the reaction mixture was extracted with diethyl ether (10 mL x 2) and the organic layer was dried over anhydrous sodium sulphate. Filtration and evaporation under reduced pressure afforded a residue that was purified by column chromatography (60-120 mesh silica gel, 5% ethyl acetate in hexane).

3-(1-Piperidinyl)-propionic acid methyl ester (A) [6p]. Colorless oil; IR (KBr): 2935, 1737, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.66 (s, 3H, -OCH_3), 2.69 (t, 2H, J=7.40 Hz, N-CH_2), 2.55 (t, 2H, J=7.40 Hz, -CH_2-C=O), 2.42 (m, 4H, N-CH_2), 1.59 (m, 4H, CH_2), 1.42 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 173.3 (-O-C=O), 54.4 (N-CH_2), 51.7 (-OCH_3, N-CH_2), 32.1 (CH_2-C=O), 26.0 (-CH_2), 24.4 (-CH_2); MS (EI, 70 eV): m/z = 172 $[M+H]^+$; Anal. Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.10; H, 9.92; N, 8.24.

3-(1-Piperidinyl)-propionic acid ethyl ester (B) [6l]. Colorless oil; IR (KBr): 2937, 2848, 1737, 1173 cm^{-1}; ^{1}H NMR

($CDCl_3$, 400 MHz, δ, ppm): 4.07 (q, 2H, J=7.10 Hz, -OCH_2), 2.62 (t, 2H, J=7.72 Hz, N-CH_2), 2.43 (t, 2H, J=7.72 Hz, -CH_2-C=O), 2.36 (m, 4H, N-CH_2), 1.51 (m, 4H, CH_2), 1.39 (m, 2H, CH_2), 1.24 (t, 3H, J=7.10 Hz, -CH_3); MS (EI, 70 eV): m/z = 186 $[M+H]^+$; Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.68; H, 10.12; N, 7.28.

4-Piperidin-1-yl-butan-2-one (C) [6l]. Colorless oil; IR (KBr): 2936, 1715, 1168 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.66 (t, 2H, N-CH_2), 2.45 (t, 2H, -CH_2-C=O), 2.37 (m, 4H, N-CH_2), 2.14 (s, 3H, O=CCH_3), 1.64 (m, 4H, CH_2), 1.45 (m, 2H, -CH_2); MS (EI, 70 eV): m/z = 156 $[M+H]^+$; Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.81; H, 11.18; N, 9.28.

3-(1-Piperidinyl)-propionitrile (D) [6l]. Colorless oil; IR (KBr): 2939, 2247, 1673, 1116 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.69 (t, 2H, J=7.18 Hz, N-CH_2), 2.49 (t, 2H, J=7.18 Hz, CH_2-CN), 2.39 (m, 4H, N-CH_2), 1.58 (m, 4H, CH_2), 1.43 (m, 4H, CH_2); MS (EI, 70 eV): m/z = 139 $[M+H]^+$; Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.71; H, 10.18; N, 20.48.

3-(1-Morpholinyl)-propionic acid methyl ester (E). Colorless oil; IR (KBr): 2951, 1741, 1111 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.67-3.69 (m, 7H, -OCH_3, CH_2-O), 2.61 (t, 2H, J=7.20 Hz, N-CH_2), 2.42 (t, 2H, J=7.20 Hz, -CH_2-C=O), 2.39 (m, 4H, N-CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 173.0 (-O-C=O), 68.8 (CH_2-O), 53.8 (-OCH_3), 53.2 (N-CH_2), 51.5 (N-CH_2), 33.1 (CH_2-C=O); MS (EI, 70 eV): m/z = 174 $[M+H]^+$; Anal. Calcd for $C_8H_{15}NO_3$: C, 55.14; H, 8.73; N, 8.09. Found: C, 55.37; H, 8.71; N, 8.20.

3-(1-Morpholinyl)-propionic acid ethyl ester (F) [6p] Colorless oil; IR (KBr): 2953, 1739, 1117 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 4.07 (q, 2H, J= 7.10 Hz, -OCH_2), 3.69 (m, 4H, CH_2-O), 2.64 (t, 2H, J=7.20 Hz, N-CH_2), 2.47 (t, 2H, J=7.20 Hz, -CH_2-C=O), 2.42 (m, 4H, N-CH_2), 1.18 (t, 3H, J= 7.10 Hz, -CH_3); MS (EI, 70 eV): m/z = 188 $[M+H]^+$; Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.55; H, 9.05; N, 7.59.

4-Morpholin-4-yl-butan-2-one (G) [6o]. Colorless oil; IR (KBr): 2951, 1172, 1111 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.67 (t, 4H, CH_2-O), 2.64 (t, 2H, J=6.28 Hz, N-CH_2), 2.53 (t, 2H, J=6.28 Hz, -CH_2-C=O), 2.39 (m, 4H, N-CH_2), 2.12 (s, 3H, O=CCH_3); MS (EI, 70 eV): m/z = 158 $[M+H]^+$.

3-(1-morpholinyl)-propionitrile (H) [6p]. Colorless oil; IR (KBr): 2954, 2238, 1671, 1106 cm^{-1};^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.69 (t, 4H, CH_2-O), 2.65 (t, 2H, N-CH_2), 2.54 (t, 2H, CH_2-CN), 2.48-2.52 (m, 4H, N-CH_2); MS (EI, 70 eV): m/z = 141 $[M+H]^+$; Anal. Calcd for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98. Found: C, 59.65; H, 8.45; N, 19.79.

3-Dimethylamino-propionic acid methyl ester (I). Faint yellow oil; IR (KBr): 2968, 1741, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.68 (s, 3H, -OCH_3), 2.80 (t, 2H, J=7.22 Hz, N-CH_2), 2.46 (t, 2H, J=7.22 Hz, -CH_2-C=O), 2.52 (s, 6H, N-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 173.0 (-O-C=O), 55.1 (N-CH_2), 50.9 (-OCH_3), 45.6 (N-CH_2), 33.2 (CH_2-C=O). MS (EI, 70 eV): m/z = 132 $[M+H]^+$;*Anal*. Calcd for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 54.81; H, 9.90; N, 10.62.

3-Dimethylamino-propionic acid ethyl ester (J). Colorless oil; IR (KBr): 2967, 1741, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.97 (q, 2H, -OCH_2), 2.80 (t, 2H, J=7.26 Hz, N-CH_2), 2.46 (t, 2H, J=7.26 Hz, -CH_2-C=O), 2.32 (s, 6H, N-CH_3), 1.30 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 173.0 (-O-C=O), 55.1 (N-CH_2), 50.9 (-OCH_3), 45.6 (N-CH_3), 33.2 (CH_2-C=O), 13.9 (-CH_3); MS (EI, 70 eV): m/z = 146 $[M+H]^+$; Anal. Calcd for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; N, 9.65. Found: C, 58.04; H, 10.69; N, 9.71.

4-Dimethylamino-butan-2-one (K) [8a]. Colorless oil; IR (KBr): 2955, 1741, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.72 (t, 2H, J=7.30 Hz, N-CH_2), 2.64 (t, 2H, J=7.30 Hz, -CH_2-C=O), 2.52 (s, 6H, N-CH_3), 2.06 (s, 3H, O-CCH_3); MS (EI, 70 eV): m/z = 116 $[M+H]^+$.

3-Dimethylamino-propionitrile (L). Colorless oil; IR (KBr): 2968, 2246, 1741, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.68 (t, 2H, J=7.32 Hz, N-CH_2), 2.62 (t, 2H, J=7.32 Hz, -CH_2-C=O), 2.52 (s, 6H, N-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 114.2 (-CN), 57.1 (N-CH_2), 44.2 (N-CH_3), 1682 (CH_2); MS (EI, 70 eV): m/z = 99 $[M+H]^+$; Anal. Calcd for $C_5H_{10}N_2$: C, 61.19; H, 10.27; N, 28.54. Found: C, 61.04; H, 10.39; N, 28.71.

3-Diethylamino-propionic acid methyl ester (M) [6l]. Colorless oil; IR (KBr): 2961, 1739, 1212 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 3.75 (s, 3H, -OCH_3), 2.90 (t, 2H, J=7.35 Hz, N-CH_2), 2.59 (q, 4H, J=7.22 Hz, N-CH_2), 2.51 (t, 2H, J=7.35 Hz, CH_2C=O), 1.03 (t, 6H, J=7.22 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 173.0 (-O-C=O), 54.1 (N-CH_2), 51.2 (-OCH_3), 47.6 (-CH_2-N), 33.9 (CH_2-C=O), 13.1 (-CH_3); MS (EI, 70 eV): m/z = 160 $[M+H]^+$; Anal. Calcd for $C_8H_{17}NO_2$: C, 60.35; H, 10.76; N, 8.80. Found: C, 60.40; H, 10.89; N, 8.71.

3-Diethylamino-propionic acid ethyl ester (N) [6n]. Colorless oil; IR (KBr): 2961, 1740, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 4.99 (q, 2H, -OCH_2), 2.82 (t, 2H, J=7.35 Hz, N-CH_2), 2.52 (q, 4H, J=7.22 Hz, N-CH_2), 2.49 (t, 2H, J=7.35 Hz, CH_2C=O), 1.03-1.12 (t, 9H, J=7.22 Hz, CH_3); MS (EI, 70 eV): m/z = 174 $[M+H]^+$.

4-Diethylamino-butan-2-one (O) [6l]. Colorless oil; IR (KBr): 2968, 1741, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.72 (t, 2H, J=7.32 Hz, N-CH_2), 2.64 (t, 2H, J=7.32 Hz, -CH_2-C=O), 2.52 (q, 4H, J=7.22 Hz, N-CH_2), 2.06 (s, 3H, O=CCH_3), 1.06 (t, 6H, J= 7.22 Hz, CH_3); MS (EI, 70 eV): m/z = 144 $[M+H]^+$.

3-Diethylamino-propionitrile (P) [6l]. Colorless oil; IR (KBr): 2971, 2256, 1741, 1209 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 2.76 (t, 2H, J=7.32 Hz, N-CH_2), 2.59 (t, 2H, J=7.32 Hz, -CH_2-C=O), 2.54 (q, 4H, J=7.18 Hz, N-CH_2), 1.06 (t, 6H, J=7.18 Hz, CH_3); MS (EI, 70 ev): m/z = 127 $[M+H]^+$.

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