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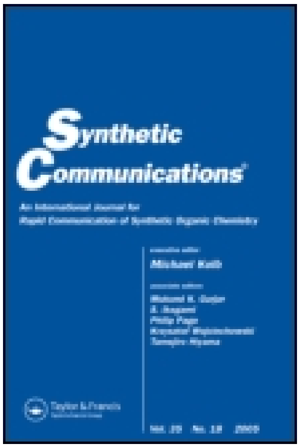

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Tetra-n-butylammonium Hydroxide (TBAH)-Catalyzed Knoevenagel Condensation: A Facile Synthesis of α-Cyanoacrylates, α-Cyanoacrylonitriles, and α-Cyanoacrylamides

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Tetra-*n*-butylammonium Hydroxide (TBAH)–Catalyzed Knoevenagel Condensation: A Facile Synthesis of α-Cyanoacrylates, α-Cyanoacrylonitriles, and α-Cyanoacrylamides

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Abstract: Tetra-*n*-butylammonium hydroxide (TBAH) has been utilized as a novel and efficient catalyst for the Knoevenagel condensation of aldehydes with acidic methylene compounds such as methyl- and ethylcyanoacetate, malononitrile, and cyanoacetamide to afford substituted olefins.

Keywords: Active methylene compounds, aldehydes, alkenes, Knoevenagel condensation, microwave irradiation, tetra-*n*-butylammonium hydroxide

INTRODUCTION

The Knoevenagel condensation is an important carbon–carbon bond-forming reaction in organic synthesis.[1] The Knoevenagel reaction has been widely used in organic synthesis to prepare coumarins and their derivatives, which are important intermediates in the synthesis of cosmetics, perfumes, and pharmaceuticals.[2] The Knoevenagel reaction is generally carried out in the presence of weak bases such as primary and secondary amines and their corresponding ammonium salts, potassium fluoride, or amino acids such as glycine, *β*-alanine, and L-proline under homogeneous conditions.[3] But

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there are only a few acidic catalysts that are known to promote this reaction.[4] Recently, using inorganic solid supports such as alumina,[5] Al_2O_3-$AlPO_4$,[6] xonotlite/tert-butoxide,[7] cation-exchanged zeolites,[8] calcite or fluorite, NP/KF, and also some basic solid catalysts under heterogeneous conditions have been reported as suitable methods for the Knoevenagel condensation.[9]

During the past decade, microwave-assisted reactions have received much attention because of their simplicity in operation, enhanced reaction rates, and greater selectivity. Meanwhile, solvent-free conditions under microwave irradiation were used for the Knoevenagel condensation.[10]

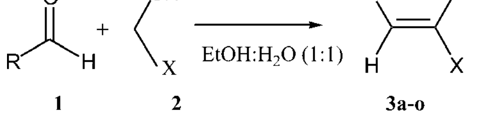
It was found that Knoevenagel condensation could be catalyzed in water.[11] It was recently reported that triphenylphosphate (TPP) can catalyze Knoevenagel condensation.[12]

All these improved procedures can overcome the drawback of the classical methods. Some reported methods normally require prolonged reaction time, high temperatures, and harmful organic solvents.

In this report, we highlight our findings on the tetra-*n*-butylammonium hydroxide (TBAH)–catalyzed condensation of active methylene compounds such as malononitrile, alkyl cyanoacetates, and cyanoacetamide with aromatic and heteroaromatic aldehydes in water and in room temperature.

RESULTS AND DISCUSSION

TBAH has been used as a basic catalyst for a variety of organic transformations such as arylation,[13] Robinson annulation,[14] intramolecular Horner–Emmons closure,[15] dehydration,[16] and formation of carbenes.[17] This reagent is a 12.5 mol% solution in H_2O, which is an advantage for this reaction because the reaction could be carried out in aqueous phase, and it could also be used as a charge transfer catalyst. The reaction of benzaldehyde with ethyl cyanoacetate in the presence of 12.5 mol% TBAH in water resulted in the formation of ethyl 2-cyano-3-phenyl-(E)-2-propenoate in 84% pure yield under microwave irradiation. In all cases, the reaction proceeds smoothly with 12.5 mol% of TBAH in a mixture of EtOH–H_2O (1:1) at room temperature or under microwave irradiation. TBAH acts as a strong base capable of deprotonating the active methylene compounds with the consequent formation of a carbanion. The reaction is highly stereoselective and affords α,β-ethylenic compounds in excellent yields with an E-geometry (Scheme 1).



Scheme 1.

Furthermore, the amount of TBAH was 0.1 equivalents in all of the room-temperature reactions and 0.3 equivalents under microwave (MW) irradiation. These ratios were optimized for all of the reactions. We had the Cannizzaro by-products in higher ratios of TBAH. At room temperature and also under MW condition, all of the reactions were carried out in a 1:1 mixture of ethanol–H_2O. In addition, the use of TBAH as a catalyst helps to avoid the environmentally unfavorable solvents as the reaction medium, because the reactions proceeds smoothly in the mixture of environmentally friendly solvents (ethanol and water). Microwave irradiation has been used as an attractive synthetic tool to achieve enhanced rates and improved yields. Potassium or natrium hydroxide cannot be used as the base for this reaction, because the Cannizzaro products will be formed as by-products. Only by using TBAH was no other by-product formed and alkene was the unique product. Electron-deficient aldehydes gave relatively higher yields than electron-rich counterparts. The absence of a carbonyl group of aldehydes in the IR spectra and appearance of olefinic hydrogens in ^{1}H NMR spectra at the 7.3–8.3 ppm region are indicative of the reaction products. The temperature in the microwave was controlled by pulsed irradiation (1 min with 20-s intervals).

In conclusion, TBAH was employed for the first time as a novel and efficient catalyst for the preparation of olefin compounds through the Knoevenagel condensation at room temperature and also under microwave irradiation in a mixture of EtOH–H_2O (1:1). Mild reaction conditions, high yields, high conversions, cleaner reaction profiles, operational simplicity and readily available catalyst will make this method an efficient environmentally friendly and attractive strategy for the preparations of olefins.

EXPERIMENTAL SECTION

Melting points were recorded on a BÜCHI B-545 melting-point apparatus and are uncorrected. IR spectra were recorded on a FT-IR Perkin-Elmer spectrum 1 spectrophotometer using KBr disks. ^{1}H NMR data were recorded on JEOL-90 spectrometer in $CDCl_3$ using TMS as the internal standard. A domestic microwave oven (Moulinex 2735 A) at 2450 MHz (100% power corresponding to 850 W) was used in all experiments.

General Procedure for the Preparation of α,β-Unsaturated Compound at Room Temperature

A mixture of aldehyde (5 mmol), alkylcyanoacetate (6 mmol), and TBAH (0.5 mmol) 12.5 mol% in a 60-mL mixture of solvents (EtOH–H_2O 1:1) was stirred at room temperature for the required time to complete the reaction (Table 1). Progress of the reaction was monitored by TLC. After

Table 1. Synthesis of alkenes via Knoevenagel codensation at room temperature with microwave irradation

No.	R	X	Condition	Time (min)	Yield (%)[a]
a	C_6H_5	CN	MW	4	89
b	C_6H_5	COOEt	MW	4	84
c	C_6H_5	COOMe	MW	4	79
d	p-(Me_2N)-C_6H_4	CN	r.t	10	91
e	p-(Me_2N)-C_6H_4	$CONH_2$	r.t	10	94
f	p-(Me_2N)-C_6H_4	COOEt	r.t	10	93
g	p-(Me_2N)-C_6H_4	COOMe	r.t	10	94
h	p-OH-C_6H_4	CN	r.t	10	96
i	p-OH-C_6H_4	COOEt	r.t	4	85
j	m-NO_2-C_6H_4	COOEt	r.t	30	71
k	m-NO_2-C_6H_4	COOMe	r.t	30	77
l	p-NO_2-C_6H_4	CN	r.t	10	96
m	p-NO_2-C_6H_4	COOEt	r.t	10	90
n	p-NO_2-C_6H_4	COOMe	r.t	10	91
o	2-Thienyl	COOEt	r.t	30	84

[a] In all cases, the yields are pure forms after purification.

completion of the reaction, the mixture was neutralized by the addition of hydrochloric acid (2 M). The precipitate was filtered off and washed with water. Further purification was done by recrystalization with EtOH.

General Procedure for the Preparation of α,β-Unsaturated Compounds under Microwave Irradiation

A tall beaker containing a mixture of aldehyde (5 mmol), alkylcyanoacetate (6 mmol), and TBAH (1.5 mmol) 12.5 mol% in a 5-mL mixture of solvents ($EtOH-H_2O$ 1:1) was placed in the microwave oven. The beaker was covered with a watch glass and irradiated under microwave irradiation at 100% power (850 W) for 4 min in 1-min intervals (Table 1). The workup procedure was the same as the previous procedure. Most of compounds are known, and products were identified by spectral and melting-point comparison with the authentic samples.

Selected Data for Compounds 3a–p

3a: 1,1-dicyano-2-phenylethylene: mp 83°C (lit:82°C[6]); IR (KBr, cm^{-1}) 3436, 2917, 2223, 1731; ^{1}H-NMR (δ, CDC13) 7.90 (s, 1H, H–C=C), 7.50–8.15 (m, 5J, Ar)

3b: Ethyl (E)-2-cyano-3-phenyl-2-propenoate: mp 47°C (lit: 49°C[6]); IR (KBr, cm^{-1}) 3033, 2953, 2225, 1729.

3c: Methyl (E)-2-cyano-3-phenyl-2-propenoate: mp 87°C (lit: 89°C[10a]); IR (KBr, cm^{-1}) 3031, 2983, 2224, 1728; ^{1}H-NMR (δ CDCI$_3$) 3.90 (s, 3H, OMe), 7.70–8.15 (m, 5H, Ar), 8.25 (s, 1H, H–C=C).

3d: 2(4-N,N-dimethylaminophenylmethylene) malononitrile: mp 183°C (lit: 200°C[18]; IR (KBr, cm^{-1}) 2915, 2210, 1614, 1567.

3e: 2-cyano-3-(N,N-dimethylaminophenyl)-2-propenamide: mp 199°C (lit:200°C[18]); IR (KBr, cm^{-1}) 3405, 3156, 2200, 1683, 1610, 1561.

3f: Ethyl-(E)-2-cyano-3-(4-N,N-dimethylaminophenyl)-2-propenoate: mp 125°C; IR (KBr, cm^{-1}) 2944, 2212, 1713, 1611, 1575; ^{1}H-NMR (δ, CDCl$_3$) 1.40 (t, 3H, J = 8 Hz, CH$_2$), 3.10 (s, 6H, 2Nme), 4.30 (q, 2H, J = 8 Hz, OCH$_2$), 6.70 (d, 2H, J = 9 Hz, Ar), 7.90 (d, 2H, J = 9 Hz, Ar), 8.10 (s, 1H, =CH).

3g: Methyl (E)-2-cyano-3-(4-N, N-dimethylaminnophenly)-2-propenoate: mp 146°C; IR (KBr, cm^{-1}) 2907, 2215, 1715, 1610, 1575; ^{1}H-NMR (δ, CDCl$_3$) 3.10 (s, 6H, –Nme$_2$), 3.90 (s, 3H, OMe), 6.70 (d, 2H, J = 9 Hz, Ar). 7.90 (d, 2H, J = 9 Hz, Ar), 8.20 (s, 1H, –CH).

3h: 2-(4-Hydroxphenylmethylene)malononitrile: mp 190°C (lit: 188°C[19]); IR (KBr, cm^{-1}) 3346, 2923, 2230, 1615, 1563; ^{1}H-NMR (δ CDCl3) 7.0 (d, 2H, J = 9 Hz, Ar), 7.90 (d, 2H, J = 9 Hz), 8.30 (s, 1H, –CH), 11.0 (brs, 1H, OH).

3i: Ethyl (E)-2-cyano-3(4-hydroxyphenyl)-2-propenoate: mp 174°C (lit: 172°C[20]); IR (KBr, cm^{-1} 3293, 2981, 2229, 1715, 1519.

3j: Ethyl (E)-2-cyano-4-(3-nitrophenly)-2-propenoate: mp 139°C; IR (KBr, cm^{-1}) 3036, 2226, 1727, 1609, 1537, 1359; ^{1}H-NMR (δ CDCl3) 1.50 (t, 3H, J = 7.2 Hz, CH$_3$), 4.40 (q, 2H, J = 7.2 Hz, OCH$_2$), 7.6–8.5 (m, 4H, Ar), 8.7 (s, 1H, =CH).

3k: Methyl (E)-2-cyano-4-(3-nitrophenyl)-2-propenoate: mp 135°C (lit:135°C[10c]); IR (KBr, cm^{-1}) 3080, 2226, 1720, 1609, 1536, 1359.

3l: 2-(4-nitrophenylmethylene)malononitrile: m.p. 160°C (lit: 159°C[16]); IR (KBr, cm^{-1}) 3110, 2231, 1604, 1521, 1344; ^{1}H-NMR (δ CDCl3) 7.88 (s, 1H, H—C=C), 8.10 (d, 2H, J = 7.2 Hz, Ar), 8.39 (d, 2H, J = 7.2 Hz, Ar).

3m: Ethyl (E)-2-cyano-3(4-nitrophenyl)-2-propenoate: mp 169°C (lit: 168°C[6]); IR (KBr, cm^{-1}) 3096, 2211, 1721, 1593, 1514, 1347.

3n: Methyl-(E)-2-Cyano-3(4-nitrophenyl)-2-propenoate: mp 178°C; IR (KBr, cm^{-1}) 3119, 2847, 2225, 1731, 1613; ^{1}H-NMR (δ CDCl3) 4.0 (s, 3H, OMe), 8.15 (d, 2H, J = 9 Hz, Ar), 8.34 (s, 1H, H–C=C), 8.38 (d, 2H, J = 9 Hz, Ar).

3o: Ethyl (E)-2-Cyano-3(2-thienyl)-2-propenoate: mp 105–108°C, IR (KBr, cm^{-1}): 3085, 2215, 1715, 1600, 1460, ^{1}H-NMR (δ, CDCl3) 1.38 (t, 3H, J = 6.9 Hz, CH_3) 4.38(q, 2H J = 6.9 Hz, OCH_2) 7.22–7.30 (dd, 1H, J = 8.8, 3.9 Hz, 1H), 7.78(d, 1H, J = 4.4 Hz), 7.83(d, 1H, J = 3.6 Hz), 8.3(s,1H, =CH).

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