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Solvent-free Michael addition of 2-cyclohexenone under ultrasonic irradiation in the presence of long chain dicationic ammonium salts

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Long chain dicationic ammonium salts (**1a-1c**), easily prepared from tert-amines and dihaloalkanes, were successfully used as efficient phase-transfer catalysts in the Michael addition reaction of various active methylene compounds to 2-cyclohexenone without solvent under ultrasonic irradiation. The investigated dicationic salts were more effective than monocationic tetrabutylammonium bromide, with short reaction times and high yields. This methodology was established under phase-transfer catalytic conditions and ultrasonic effects with many advantages, including the easy and cost-effective synthesis of the catalyst, mild reaction conditions, short reaction times, good yields, simple work-up procedures, and environmental friendliness.

Key Words: Michael addition, phase-transfer catalyst, ultrasound-assisted synthesis, solvent-free reaction, 2-cyclohexenone

Introduction

Phase-transfer catalysis (PTC) is one of the most important and useful methods in synthetic organic reactions because of its simple reaction procedure, mild conditions, high reaction rates, high selectivities, inexpensive and environmentally friendly reagents, and ease in the scaling-up of reactions.[1] A number of catalysts are being developed, and multisite phase-transfer catalysts have recently become more attractive among chemists because of their superior features, such as facile preparation, low energy requirements, and high reactivity in a particular synthetic transformation under mild reaction conditions, when compared with single-site catalysts.[2]

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Dicationic ammonium salts, which have long aliphatic chains, have excellent surfactant properties because they are more efficient in lowering surface tension than single chains, and they are very attractive for adsorption applications, analytical separations, and solubilization processes.[3] Although these compounds are widely used as effective emulsifiers and dispersing and antifoaming agents, they have not been investigated widely for their phase-transfer properties. Synthetic chemists have also focused on the use of PTC under solvent-free conditions for environmental reasons.[4]

Solvent-free organic reactions have drawn great interest, particularly from the viewpoint of green chemistry, and environmentally friendly solvent-free reactions have been investigated widely. Solvent-free reactions have some unique advantages, such as the elimination of harmful organic solvents, which account for a great proportion of the waste material generated in syntheses and impose health and environmental risks. Solvent-free reactions also reduce pollution, reduce handling costs due to the simplification of the experimental procedure and work-up technique, and have high selectivity in some cases.[5]

The Michael addition reaction is among the most important organic reactions leading to the formation of carbon-carbon bonds. It is widely used in organic synthesis because it is catalyzed by a large number of catalysts, it is completely atom economical, most of the functionalities of the starting materials are preserved in the products, and the starting materials are readily available or are easily prepared.[6] Effective and high-yielding processes are still being developed.[7]

In general, conjugated addition reactions require basic conditions or acidic catalysts. In order to overcome some of these limitations, a number of alternative procedures have been reported over the past few years, using a variety of reagents such as Pd compounds, $InCl_3$, $CeCl_3.7H_2O$-NaI, $Yb(OTf)_3$, $Bi(NO_3)_3$, $Bi(OTf)_3$, Cu salts, $LiClO_4$, clay, silica gel, boric acid, and SmI_2.[8]

Ultrasound irradiation has been considered as a useful protocol in organic synthesis in recent years. A large number of organic reactions can be carried out in higher yields, with shorter reaction times or milder conditions, under ultrasonic irradiation. Combined ultrasonic techniques and various catalysts for organic reactions have been reported.[9] Some catalysts such as KF/basic alumina, $KHSO_4$, PTSA, and metal salts have been reported as effective for Michael reactions under ultrasonic irradiation, and good results were obtained.[10] However, there were some disadvantages, such as long reaction times or the use of anhydrous solvents or toxic and corrosive catalysts. Besides classic acid and base catalysts, several phase-transfer catalysts have also been successfully used to catalyze the Michael reaction.[11] However, most of these reactions were carried out in 2-phase systems including water and toxic toluene or dichloromethane. As far as we know, solvent-free PTC has not been widely investigated under ultrasonic effects for the Michael reaction.[12]

Recently, we successfully used long chain aliphatic dicationic ammonium salts as phase-transfer catalysts in the condensation reactions of aromatic aldehydes in water under ultrasonic effects.[13] In this paper, we investigate the effect of dicationic ammonium salts **1a-1c** in combination with ultrasonic effects and solvent-free conditions on the Michael addition of 2-cyclohexenone. This type of dicationic ammonium salt was used for PTC under these conditions for the first time for this reaction.

Experimental

All reagents were of commercial quality, and reagent-quality solvents were used without further purification. Melting points were determined on a Gallenkamp digital melting point apparatus and are uncorrected. IR spectra were determined on a PerkinElmer Spectrum One FT-IR spectrometer. NMR spectra were recorded on Mercury VX-400 MHz and Varian Unity Inova 500 MHz spectrometers. Chemical shifts, δ, are reported in ppm relative to $CHCl_3$ (^{1}H: $\delta = 7.27$) and TMS as the internal standard. Column chromatography was conducted on silica gel 60 (70-230 mesh). Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F254 (Merck). Mass spectra were recorded on an Agilent 6890N GC System-5973 IMSD (EI, 70 eV) spectrometer. Ultrasound irradiation was performed in a BANDELIN SONOREX ultrasonic cleaner, with a frequency of 35 kHz and output power of 350 W. The reaction flasks were located in the maximum energy area of the cleaner, and the temperature of the water bath was controlled by the circulation of cold water by a pump.

General procedure for the synthesis of catalysts 1a-1c

A mixture of *N*,*N*-dimethyldodecylamine (2.0 mmol) and dihaloalkane (1.0 mmol) in absolute ethanol (10 mL) was refluxed for 24 h. After the evaporation of the solvent, the crude product was washed with acetone and recrystallized from ethanol and diethyl ether (1:2).

1,4-Bis(dodecyldimethylamino)butane dibromide (1a): White powder (mp 220-223 °C). IR (atr): ν 2915, 2849, 1470 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.82 (t, $J = 6.8$ Hz, 6H, CH_3), 1.21 (m, 28H, CH_2), 1.30 (brs, 8H, CH_2), 1.71 (brs, 4H, CH_2), 2.05 (brs, 4H, CH_2), 3.28 (s, 12H, N-CH_3), 3.41 (m, 4H, N-CH_2), 3.87 (brs, 4H, N-CH_2).

1,6-Bis(dodecyldimethylamino)hexane dibromide (1b): White powder (mp 225-226 °C). IR (atr): ν 2949, 2916, 2850, 1484, 1464, 1401, 1376 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.82 (t, $J = 6.8$ Hz, 6H, CH_3), 1.22 (m, 28H, CH_2), 1.29 (brs, 8H, CH_2), 1.51 (brs, 4H, CH_2), 1.66 (brs, 4H, CH_2), 1.93 (brs, 4H, CH_2), 3.33 (s, 12H, N-CH_3), 3.44 (m, 4H, CH_2), 3.64 (m, 4H, CH_2).

1,12-Bis(dodecyldimethylamino)dodecane dibromide (1c): White powder (mp 135-136 °C). IR (atr): ν 2955, 2916, 2851, 1488, 1469, 1421, 1400, 1378 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.82 (t, $J = 6.8$ Hz, 6H, CH_3), 1.21 (m, 40H, CH_2), 1.32 (brs, 8H, CH_2), 1.66 (brs, 8H, CH_2), 2.43 (brs, 4H, CH_2), 3.29 (s, 12H, N-CH_3), 3.42 (m, 4H, CH_2), 3.50 (m, 4H, CH_2).

General procedure for the condensation reactions

To a mixture of 2-cyclohexenone (1 mmol) and Michael donor (2 mmol), sodium hydroxide (0.05 mmol) and a phase-transfer catalyst (0.05 mmol) were added. The reaction mixture was sonicated at 25 °C for a period of time long enough to complete the reaction (TLC), and then underwent extraction with $CHCl_3$ (2 × 25 mL). The combined organic extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc and *n*-hexane).

Diethyl (3-oxocyclohexyl)propandioate (2): Colorless oil. R_f: 0.50 (EtOAc and *n*-hexane, 1:3). IR (atr): ν 2977, 2941, 1744, 1726, 1713, 1447, 1423, 1368, 1254, 1227, 1151 cm^{-1}; ^{1}H-NMR (400 MHz,

$CDCl_3$): δ 1.23 (t, J = 7.2 Hz, 3H, CH_3), 1.24 (t, J = 7.2 Hz, 3H, CH_3), 1.42-1.52 (m, 1H, CH_2), 1.59-1.71 (m, 1H, CH_2), 1.89-1.95 (m, 1H, CH_2), 2.00-2.08 (m, 1H, CH_2), 2.18-2.27 (m, 2H, CH_2), 2.34-2.44 (m, 2H, CH_2), 2.45-2.55 (m, 1H, CH and CH_2), 3.26 (d, J = 8.0 Hz, 1H, $CH(CO_2C_2H_5)_2$), 4.14-4.19 (q, J = 7.2 Hz, 2H, CH_2CH_3), 4.15-4.20 (q, J = 7.2 Hz, 2H, CH_2CH_3); GC-MS: t_R 23.33 min, MS (m/z) (rel. abund.): 256 [M^+] (3), 228 (2), 211 (49), 183 (25), 160 (100), 136 (66), 110 (23), 97 (87).

3-Oxocyclohexylphenylacetonitrile (3): Yellow oil. R_f: 0.28 (EtOAc and n-hexane, 1:3). Diastereomeric ratio = 50:50. IR (atr): ν 3032, 2944, 2240, 1708, 1494, 1453, 1422, 1368, 760, 699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.48-1.63 (m, 4H, CH_2), 1.90-1.93 (m, 2H, CH_2), 1.96-2.14 (m, 2H, CH_2), 2.15-2.24 (m, 7H, CH_2), 2.30-2.35 (m, 3H, CH and CH_2), 3.69 (d, J = 4.4 Hz, 1H, CH-CN), 3.83 (d, J = 4.4 Hz, 1H, CH-CN), 7.19-7.25 (m, 4H, ArH), 7.28-7.34 (m, 6H, ArH); GC-MS: t_R 25.73/26.20 min, MS (m/z) (rel. abund.): 213 [M^+] (24), 117 (33), 97 (100), 69 (100).

Ethyl 3-oxo-2-(3-oxocyclohexyl)butanoate (4): Colorless oil. R_f: 0.40 (EtOAc and n-hexane, 1:3). Diastereomeric ratio = 50:50. IR (atr): ν 2941, 2865, 1737, 1707, 1447, 1422, 1359, 1250, 1225, 1152 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.26 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.33-1.40 (m, 1H, CH_2), 1.42-1.49 (m, 1H, CH_2), 1.60-1.70 (m, 2H, CH_2), 1.80-1.91 (m, 2H, CH_2), 1.99-2.06 (m, 2H, CH_2), 2.11-2.14 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.22-2.27 (m, 2H, CH_2), 2.30-2.40 (m, 4H, CH_2), 2.51-2.60 (m, 2H, CH-CH_2), 3.35 (d, J = 8.4 Hz, 1H, CH-CO), 3.37 (d, J = 8.4 Hz, 1H, CH-CO), 4.14-4.21 (2q, J = 7.2 Hz, 4H, CH_2CH_3); GC-MS: t_R 20.96/21.04 min, MS (m/z) (rel. abund.): 226 (M^+) (2), 183 (25), 153 (23), 137 (44), 97 (62), 43 (100).

3-(3-Oxocyclohexyl)pentan-2,4-dione (5): Yellow solid (mp 53-55 °C). R_f: 0.44 (EtOAc and n-hexane, 1:1). IR (atr): ν 2939, 2865, 1711, 1695, 1448, 1421, 1358, 1152 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.30-1.40 (m, 1H, CH_2), 1.62-1.74 (m, 1H, CH_2), 1.75-1.82 (m, 1H, CH_2), 1.98-2.06 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.20-2.31 (m, 2H, CH_2), 2.35-2.41 (m, 1H, CH_2), 2.61-2.71 (m, 1H, $CHCH_2$), 3.61 (d, J = 10.4 Hz, 1H, $CH(COCH_3)_2$); GC-MS: t_R 18.08 min, MS (m/z) (rel. abund.): 196 (M^+) (1), 153 (43), 111 (23), 97 (57), 43 (100).

2-(3-Oxocyclohexyl)-1,3-diphenylpropan-1,3-dione (6): Colorless oil. R_f: 0.24 (EtOAc and n-hexane, 1:3). IR (atr): ν 3063, 2940, 1711, 1693, 1666, 1595, 1579, 1447, 1372, 758, 686 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.44-1.54 (m, 1H, CH_2), 1.56-1.67 (m, 1H, CH_2), 1.83-1.89 (m, 1H, CH_2), 1.93-2.00 (m, 1H, CH_2), 2.16-2.23 (m, 2H, CH_2), 2.30-2.39 (m, 2H, CH_2), 2.91-3.01 (m, 1H, $CHCH_2$), 5.16 (d, J = 8.8 Hz, 1H, $CH(COPh)_2$), 7.34-7.42 (m, 4H, ArH), 7.46-7.51 (m, 2H, ArH), 7.87-7.93 (m, 4H, ArH); GC-MS: t_R 27.91 min, MS (m/z) (rel. abund.): 320 (M^+) (2), 224 (22), 105 (100), 77 (36).

2-(3-Oxocyclohexyl)-2*H*-indene-1,3-dione (7): Brown solid (mp 87-89 °C). R_f: 0.80 (EtOAc and n-hexane, 1:1). IR (atr): ν 3073, 3032, 2933, 2868, 1741, 1703, 1682, 1593, 1450, 1425, 1387 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.18-2.90 (m, 10H, CH and CH_2), 7.80 (brs, 2H, ArH), 7.92 (brs, 2H, ArH); GC-MS: t_R 31.31 min, MS (m/z) (rel. abund.): 242 (M^+) (68), 199 (51), 186 (19), 172 (18), 148 (95), 115 (100), 97 (61), 76 (51), 42 (33).

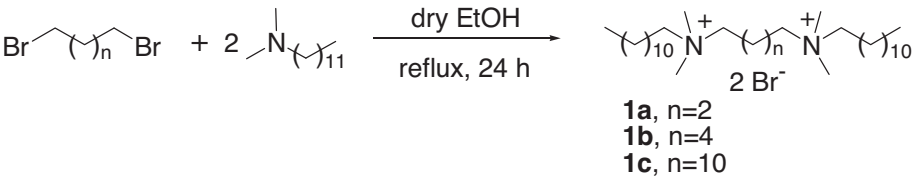
3-(1-Nitromethyl)cyclohexanone (8): Colorless oil. R_f: 0.30 (EtOAc and n-hexane, 1:2). IR (atr): ν 2942, 2865, 1708, 1541, 1448, 1431, 1381, 1347 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.43-1.56 (m, 1H, CH_2), 1.67-1.87 (m, 1H, CH_2), 1.94-2.03 (m, 1H, CH_2), 2.07-2.17 (m, 2H, CH_2), 2.24-2.33 (m, 1H, CH_2), 2.40-2.53 (m, 2H, CH_2), 2.58-2.71 (m, 1H, CH), 4.26 (d, J = 7.0 Hz, 1H, CH_2NO_2), 4.35 (d, J = 6.2 Hz,

1H, CH_2NO_2); GC-MS: t_R 14.40 min, MS (m/z) (rel. abund.): 157 (M^+) (4), 110 (27), 82 (30), 55 (100), 41 (73).

3-(1-Nitroethyl)cyclohexanone (9): Colorless oil. R_f: 0.46 (EtOAc and n-hexane, 1:2). Diastereomeric ratio = 50:50. IR (atr): ν 2947, 2870, 1710, 1542, 1450, 1421, 1391, 1357 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.40-1.48 (m, 2H, CH_2), 1.57 (d, J = 9.6 Hz, 6H, CH_3), 1.85-1.90 (m, 2H, CH_2), 1.91-1.97 (m, 2H, CH_2), 2.08-2.20 (m, 4H, CH_2), 2.25-2.32 (m, 2H, CH_2), 2.39-2.44 (m, 4H, CH_2), 2.46-2.48 (m, 2H, CH), 4.44-4.53 (m, 2H, $CHNO_2$); GC-MS: t_R 15.30/16.10 min, MS (m/z) (rel. abund.): 171 (M^+) (2), 156 (2), 124 (50), 97 (20), 56 (100).

Results and discussion

Ammonium salts **1a-1c**, having different spacer lengths, were synthesized by the reaction of dibromoalkanes with N, N-dimethyldodecylamine according to the previously reported procedure (Scheme 1). The structures of the compounds were determined by their spectroscopic data and were in accordance with the literature.[13]



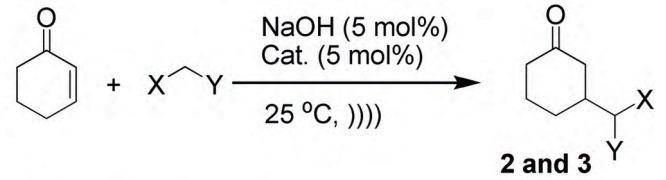
Scheme 1.

We first carried out a set of reactions between 2-cyclohexenone and diethyl malonate or benzyl cyanide under solvent-free conditions and ultrasonic effects in the presence of tetrabutylammonium bromide (TBAB). Several bases, such as sodium hydroxide, triethylamine, and potassium carbonate, were used, and different catalyst amounts, such as 2.5, 5, and 10 mol%, were used to determine the optimum conditions. It was decided that sodium hydroxide was a good base at 5 mol%, and the best catalyst amount was 5 mol%, according to the yields. These reactions were also done without ultrasonic effects, and it was then found that the reactions took place at lower yields and with longer reaction times. All experiments were done with tetrabutylammonium bromide (TBAB) and dicationic salts **1a-1c** to make comparisons. As seen in Table 1, the dicationic ammonium salts were more effective than TBAB under the conditions investigated.

It is obvious that the reaction takes place at the solid-liquid interphase (Scheme 2). Thus, the dicationic salts with long alkyl groups are more easily dispersed into the organic phase than monocationic short chain salt TBAB, and they also have dual cationic effects.

There was a slight difference among the yields from catalysts **1a-1c**. However, catalyst **1b** was effective with a shorter reaction time than **1a** and a higher yield than **1c**. This salt was therefore chosen as the catalyst for the Michael additions of other active methylene compounds (Table 2). All of the compounds were known in the literature and all spectroscopic data were in full agreement with their structures.[7d,14]

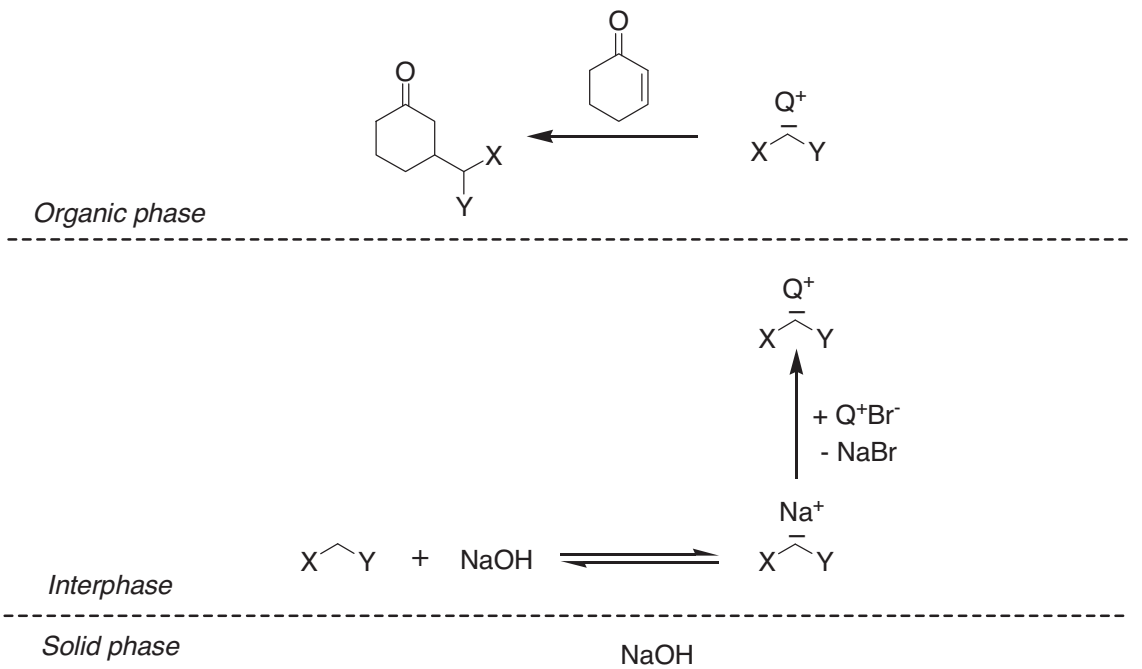
Table 1. Comparison of the activity of catalysts.



Compound 2: X = Y = COOEt
Compound 3: X = Ph; Y = CN

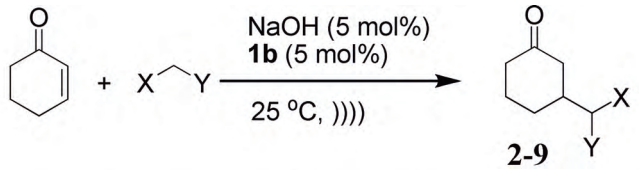
	Compound 2				**Compound 3**			
Catalyst	Reaction time (min)		Yield[a] (%)		Reaction time (min)		Yield[a] (%)	
	))))	Stirring	))))	Stirring	))))	Stirring	))))	Stirring
TBAB	10	15	85	80	10	15	83	76
1a	5	10	98	87	4	8	94	86
1b	2	8	98	90	1	7	97	90
1c	2	9	87	80	1	8	92	85

[a]Isolated yields



Scheme 2.

Table 2. Synthesis of Michael adducts.



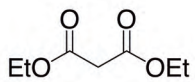
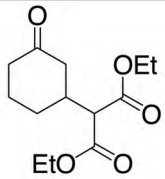
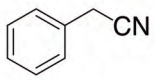
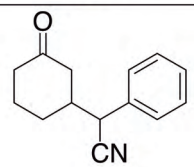
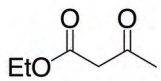
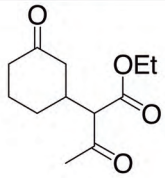
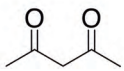
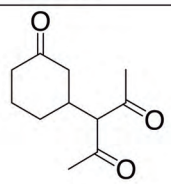
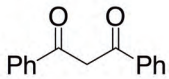
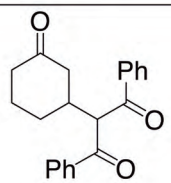
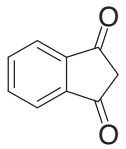
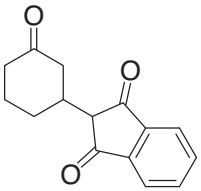
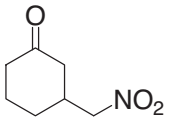
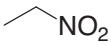
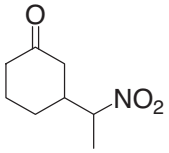
X Y	Product	Reaction time (min)	Yield[a] (%)
	 **2**[14a]	2	98
	 **3**[14b]	1	97
	 **4**[14c]	5	87
	 **5**[14c]	8	80
	 **6**[14d]	8	45

Table 2. Continued.

X Y	Product	Reaction time (min)	Yield[a] (%)
	 **7**[7d]	25	75
	 **8**[14e]	2	55
	 **9**[14e]	5	75

[a] Isolated yields

Conclusion

We used long chain dicationic ammonium salts as phase-transfer catalysts in combination with ultrasound irradiation for the Michael addition of active methylene compounds to 2-cyclohexenone under solvent-free conditions at room temperature. It was found that these salts were more effective than the monocationic one in these reactions. In contrast to the existing methods, this solvent-free technique is a very efficient, general, simple, high-yielding, air- and moisture-stable, environmentally benign, and less expensive process, which will contribute to the progress of green chemistry.

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