

Long Chain Dicationic Phase Transfer Catalysts in the Condensation Reactions of Aromatic Aldehydes in Water Under Ultrasonic Effect

Ilker Esen, Cigdem Yolacan, and Feray Aydogan*

Department of Chemistry, Yildiz Technical University, Davutpasa Campus, 34010, Esenler, Istanbul, Turkey

*E-mail: feray_aydogan@yahoo.com

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Long chain dicationic ammonium salts were used successfully as phase transfer catalyst in the condensation reactions of aromatic aldehydes in water under ultrasonic irradiation for the first time. The quaternary salt having longer distance between the cation centers was more effective than the mono- and dicationic ones having short chain.

Key Words: Phase transfer catalyst, Ultrasound-assisted synthesis, Aromatic aldehyde, Arylacrylonitrile, α,β -Unsaturated ketone

Introduction

The development of new synthetic methods that are more environmentally benign has been propelled by the growing importance of green chemistry.¹ In this fact, scientists have been aimed to produce safer and environmentally friendly chemicals and processes in recent years. Among these processes, using catalytic reactions is essential for chemists.² Phase transfer catalysis (PTC) is an alternative solution to heterogeneity problem with the reactions in which the interaction between two substances located in different phases of a mixture is inhibited because of the inability of reagents to come together. The most important advantages of PTC are simplicity, mild conditions, high-reaction rates, high selectivities, and the use of inexpensive reagents.³ A number of catalysts are being developed and recently multi-site phase transfer catalysts have become more attractive among chemists because of their superior features such as facile preparation, low energy requirement and high reactivity in a particular synthetic transformation under mild reaction conditions, when compared with single-site ones.⁴

Dicationic ammonium salts, which have long aliphatic chain, have excellent surfactant properties, because they are more efficient in lowering surface tension than single chain ones and they are very attractive for adsorption applications, analytical separations, solubilization processes.⁵ Although these compounds are widely used as effective emulsifiers, dispersing and anti-foaming agents, they have not been investigated widely for their phase transfer properties. Here we wish to report the use of dicationic ammonium salts having long aliphatic chain as phase transfer catalysts in the condensation reactions of various aromatic aldehydes with benzyl cyanide and 3,3-dimethylbutan-2-one in water under ultrasonic effect.

Experimental

General. All reagents were of commercial quality and reagent quality solvents were used without further purification. IR spectra were determined on a Perkin Elmer, 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 (^1H : $\delta = 7.27$), CDCl_3 (^{13}C : $\delta = 77.0$) and TMS as internal standard. Column chromatography was conducted on silica gel 60 (70 - 230 mesh). TLC was carried out on aluminum sheets precoated with silica gel 60F₂₅₄ (Merck). Elemental analysis were carried out on Thermo Flash EA 1112 series apparatus. Ultrasound irradiation was performed in Bandelin Sonorex ultrasonic cleaner, whose frequency was 35 kHz and output power was 350 W. The reaction flasks were located in the maximum energy area in 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 1 a-c. 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 evaporation of the solvent, the crude product was washed with acetone and recrystallized from ethanol/diethyl ether (1:2).

1,3-Bis(dodecyldimethylamino)propane dibromide (1a): White powder. Yield: 597 mg, 95%, mp 118 - 119 °C. IR (atr) ν 2948, 2916, 2870, 2849, 1486, 1471, 1463, 1433, 1382 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, $J = 5.4$ Hz, 6H, CH_3), 1.23 (brs, 22H, CH_2), 1.32 (brs, 8H, CH_2), 1.72 (brs, 4H, CH_2), 2.07 (brs, 4H, CH_2), 2.85 (brs, 4H, CH_2), 3.27 (s, 12H, N- CH_3), 3.40 (m, 4H, CH_2), 3.81 (brs, 4H, CH_2); Anal. Calcd for $\text{C}_{31}\text{H}_{68}\text{Br}_2\text{N}_2$ (628.69): C, 59.22; H, 10.90; N, 4.46. Found: C, 59.15; H, 10.87; N, 4.55.

1,6-Bis(dodecyldimethylamino)hexane dibromide (1b): White powder. Yield: 657 mg, 98%, mp 225 - 226 °C. IR (atr) ν 2949, 2916, 2850, 1484, 1464, 1401, 1376 cm^{-1} ; ^1H 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); Anal. Calcd for $\text{C}_{34}\text{H}_{74}\text{Br}_2\text{N}_2$ (670.77): C, 60.88; H, 11.12; N, 4.18. Found: C, 60.79; H, 11.08; N, 4.23.

1,12-Bis(dodecyldimethylamino)dodecane dibromide (1c): White powder. Yield: 732 mg, 97%, mp 135 - 136 °C (Lit.^{5c} 129 - 134 °C). IR (atr) ν 2955, 2916, 2851, 1488, 1469, 1421, 1400, 1378 cm^{-1} ; ^1H 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, CH₂), 3.50 (m, 4H, CH₂); Anal. Calcd for C₄₀H₈₆Br₂N₂ (754.93): C, 63.64; H, 11.48; N, 3.71. Found: C, 63.57; H, 11.41; N, 3.79.

General procedure for the condensation reactions. Sodium hydroxide (1.0 mmol) and catalyst **1c** were dissolved in water (20 mL), then aldehyde (1.0 mmol) and benzyl cyanide or 3,3-dimethylbutan-2-one (1.0 mmol) were added. The reaction mixture was sonicated at 25 °C for a period of time long enough to complete the reaction (TLC), then the solid formed in the reaction mixture was filtrated, and the crude products were purified by recrystallisation (ethanol) or column chromatography over silica gel (EtOAc:Hexane 1:3 or 1:6).

(Z)-2,3-Diphenylacrylonitrile (4a): White crystals. Yield: 203 mg, 99%, mp 87 - 88 °C (Lit.⁶ 86 - 87 °C). IR (atr) v 3098, 3053, 3032, 2946, 2218, 1608, 1595 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (m, 6H, ArH), 7.54 (brs, 1H, =CH), 7.68 (m, 2H, ArH), 7.88 (m, 2H, ArH); Anal. Calcd for C₁₅H₁₁N (205.25): C, 87.77; H, 5.40; N, 6.82. Found: C, 87.69; H, 5.36; N, 6.90.

(Z)-3-(4-Fluorophenyl)-2-phenylacrylonitrile (4b): White crystals. Yield: 221 mg, 99%, mp 115 - 116 °C. IR (atr) v 3059, 2962, 2212, 1601, 1593, 1584 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.07 (m, 2H, ArH), 7.33 (m, 3H, ArH), 7.40 (brs, 1H, =CH), 7.57 (m, 2H, ArH), 7.81 (m, 2H, ArH); Anal. Calcd for C₁₅H₁₀FN (223.25): C, 80.70; H, 4.51; N, 6.27. Found: C, 80.66; H, 4.47; N, 6.34.

(Z)-2-Phenyl-3-*p*-tolylacrylonitrile (4c): White crystals. Yield: 120 mg, 55%, mp 61 - 62 °C. IR (atr) v 3030, 2213, 1604, 1590 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H, CH₃), 7.27 (m, 2H, ArH), 7.41 (m, 3H, ArH), 7.50 (brs, 1H, =CH), 7.67 (m, 2H, ArH), 7.80 (m, 2H, ArH); Anal. Calcd for C₁₆H₁₃N (219.28): C, 87.64; H, 5.98; N, 6.39. Found: C, 87.53; H, 5.86; N, 6.42.

(Z)-3-(4-Methoxyphenyl)-2-phenylacrylonitrile (4d): Yellow crystals. Yield: 158 mg, 67%, mp 93 - 94 °C (Lit.⁷ 95 °C). IR (atr) v 3014, 2965, 2843, 2208, 1602, 1592 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.87 (s, 3H, OCH₃), 6.98 (m, 2H, ArH), 7.39 (m, 3H, ArH), 7.46 (brs, 1H, =CH), 7.65 (m, 2H, ArH), 7.88 (m, 2H, ArH); Anal. Calcd for C₁₆H₁₃NO (235.28): C, 81.68; H, 5.57; N, 5.95. Found: C, 81.57; H, 5.52; N, 6.02.

(Z)-2-Phenyl-3-(thiophen-2-yl)acrylonitrile (4e): Yellow crystals. Yield: 190 mg, 90%, mp 96 - 97 °C. IR (atr) v 3094, 3070, 3027, 2206, 1587 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (m, 1H, thiophen), 7.37 (brd, *J* = 7.0 Hz, 1H, thiophen), 7.43 (m, 2H, ArH), 7.54 (brd, *J* = 4.6 Hz, 1H, thiophen), 7.63 (brs, 1H, =CH), 7.65 (m, 3H, ArH); Anal. Calcd for C₁₃H₉NS (211.28): C, 73.90; H, 4.29; N, 6.63; S, 15.18. Found: C, 73.87; H, 4.26; N, 6.68; S, 15.21.

(Z)-3-(5-Methylfuran-2-yl)-2-phenylacrylonitrile (4f): Light yellow crystals. Yield: 199 mg, 95%, mp 83 - 84 °C. IR (atr) v 3056, 3022, 2213, 1615, 1567 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H, CH₃), 6.19 (d, *J* = 3.5 Hz, 1H, furan), 7.09 (d, *J* = 3.5 Hz, 1H, furan), 7.30 (brs, 1H, =CH), 7.38 (m, 3H, ArH), 7.61 (m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 14, 106, 110, 117, 119, 126, 128, 129, 130, 135, 149, 156; Anal. Calcd for C₁₄H₁₁NO (209.24): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.31; H, 5.23; N, 6.72.

(E)-4,4-Dimethyl-1-phenylpent-1-en-3-one (5a): White crystals. Yield: 186 mg, 99%, mp 41 - 42 °C (Lit.⁸ 38 - 40 °C). IR

(atr) v 3061, 3026, 2967, 2868, 1682, 1608, 1576, 1476 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 9H, CH₃), 7.12 (d, *J* = 15.6 Hz, 1H, =CH), 7.37 (m, 3H, ArH), 7.56 (m, 2H, ArH), 7.68 (d, *J* = 15.6 Hz, 1H, =CH); Anal. Calcd for C₁₃H₁₆O (188.27): C, 82.94; H, 8.57. Found: C, 82.89; H, 8.52.

(E)-1-(4-Fluorophenyl)-4,4-dimethylpent-1-en-3-one (5b): White crystals. Yield: 196 mg, 95%, mp 50 - 51 °C. IR (atr) v 3043, 2968, 2934, 2868, 1675, 1611, 1596, 1475 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.15 (s, 9H, CH₃), 6.98 (m, 3H, ArH and =CH), 7.48 (m, 2H, ArH), 7.56 (d, *J* = 15.6 Hz, 1H, =CH); Anal. Calcd for C₁₃H₁₅FO (206.26): C, 75.70; H, 7.33. Found: C, 75.67; H, 7.28.

(E)-4,4-Dimethyl-1-*p*-tolylpent-1-en-3-one (5c): Yellow crystals. Yield: 81 mg, 40%, mp 79 - 80 °C. IR (atr) v 3028, 2959, 2926, 2867, 1673, 1600, 1567, 1473 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.15 (s, 9H, CH₃), 2.30 (s, 3H, CH₃), 7.01 (d, *J* = 15.6 Hz, 1H, =CH), 7.12 (d, *J* = 8.2 Hz, 2H, ArH), 7.40 (d, *J* = 8.2 Hz, 2H, ArH), 7.59 (d, *J* = 15.6 Hz, 1H, =CH); Anal. Calcd for C₁₄H₁₈O (202.29): C, 83.12; H, 8.97. Found: C, 83.06; H, 8.92.

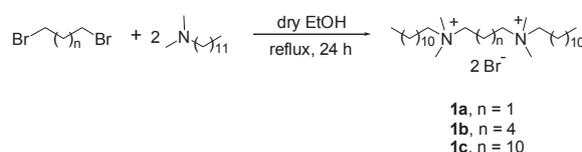
(E)-4,4-Dimethyl-1-(thiophen-2-yl)pent-1-en-3-one (5e): Yellow oil. Yield: 180 mg, 93%. IR (atr) v 3106, 3078, 2965, 2930, 2867, 1676, 1587, 1475 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.14 (s, 9H, CH₃), 6.83 (d, *J* = 15.6 Hz, 1H, =CH), 6.98 (dd, *J* = 5.0, 3.9 Hz, 1H, thiophen), 7.21 (brd, *J* = 3.9 Hz, 1H, thiophen), 7.29 (brd, *J* = 4.3 Hz, 1H, thiophen), 7.71 (d, *J* = 15.2 Hz, 1H, =CH); Anal. Calcd for C₁₁H₁₄OS (194.29): C, 68.00; H, 7.26; S, 16.50. Found: C, 67.94; H, 7.23; S, 16.54.

(E)-4,4-Dimethyl-1-(5-methylfuran-2-yl)pent-1-en-3-one (5f): Yellow oil. Yield: 163 mg, 85%. IR (atr) v 3113, 2967, 2869, 1676, 1608, 1571, 1476 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.14 (s, 9H, CH₃), 2.29 (s, 3H, CH₃), 6.05 (dd, *J* = 3.5, 1.2 Hz, 1H, furan), 6.46 (d, *J* = 3.5 Hz, 1H, furan), 6.84 (d, *J* = 15.2 Hz, 1H, =CH), 7.29 (d, *J* = 15.2 Hz, 1H, =CH); Anal. Calcd for C₁₂H₁₆O₂ (192.25): C, 74.97; H, 8.39. Found: C, 74.91; H, 8.33.

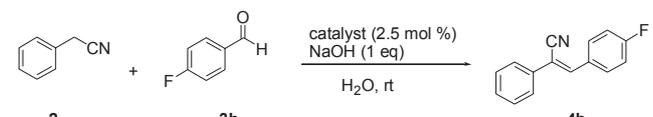
Results and Discussion

The ammonium salts having different spacer lengths were synthesized by the reaction of dibromoalkanes with *N,N*-dimethyldodecylamine according to literature procedure (Scheme 1). The structures of compounds were determined by their spectroscopic data and were in accordance with the literature.^{5b}

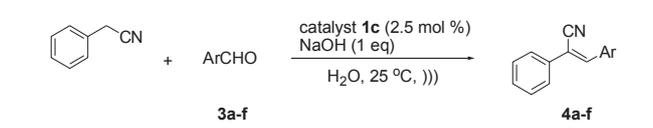
We started the study by investigation of the condensation reaction of benzyl cyanide with *p*-fluorobenzaldehyde to see how the long chain aliphatic dicationic ammonium salts effected the reaction as phase transfer catalysts. The reactions were carried out in water-reagent/substrate biphasic system without any other organic solvent. Several different bases such as sodium hydroxide, triethylamine, potassium carbonate were tried as base in the presence of catalysts **1a-c** and it was decided that

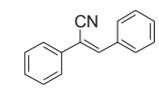
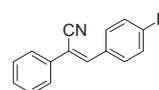
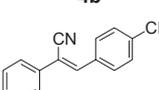
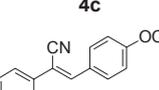
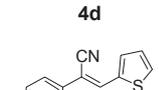
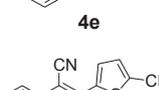


Scheme 1. The synthesis of dicationic phase transfer catalysts

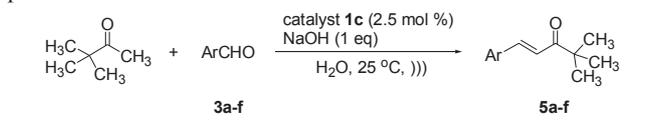
Table 1. The comparison of the activity of catalysts


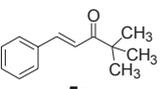
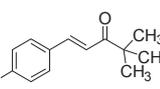
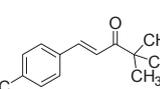
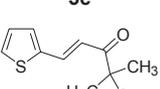
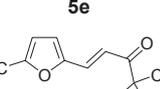
Catalyst	Without ultrasonic effect		Under ultrasonic effect	
	Reaction time (min)	Yield (%)	Reaction time (min)	Yield (%)
TBAB	50	45	20	55
1a	50	51	20	63
1b	30	65	20	80
1c	20	95	10	99

Table 2. The synthesis of acrylonitrile derivatives


Aldehyde 3	Product 4	Reaction time (min)	Yield (%)
		10	99
		10	99
		95	55
		180	67
		10	90
		40	95

sodium hydroxide was the good base in one equimolar amount. Then different catalyst amounts such as 10, 5, 2.5, and 1% were tried and the obtained yields were 95, 94, 95, and 57%, respectively for the catalyst **1c** as an example, so 2.5% mol catalyst was the best amount. Under these optimum conditions, the reaction was carried out with catalysts **1a-c** and also tetrabutylammonium bromide (TBAB) which is monocationic short chain ammonium salt at room temperature with or without ultrasonic irradiation for comparison. As one can see from the yields given in the Table 1, the catalyst **1c** having longest aliphatic

Table 3. The synthesis of 1-aryl-4,4-dimethylpent-1-en-3-one compounds


Aldehyde 3	Product 5	Reaction time (min)	Yield (%)
		70	99
		90	95
		180	40
		150	93
		120	85

chain was the most effective one. This can be interpreted as the catalyst cation having long alkyl group is easily dispersed into the organic substrate phase because of the lipophilicity of the cation. Beside, it is possible to think that the cationic centers separated by short aliphatic chain may interact with the anion more tightly than those separated by long chain, and exhibit a lower activity in activating anions by preventing exchange the anions for the reaction. So the electronic factors might not be important with the quaternary salts having longer distances between the cation centers, and these salts exhibit higher activity in activating anions.⁹

Using this procedure, the condensation reactions of various aromatic aldehydes with benzyl cyanide and 3,3-dimethylbutan-2-one were carried out in good yields and short reaction times as summarised in Table 2 and 3. All of the compounds except **4f** were known in the literature and all the spectroscopic data are in full agreement with their structures. Under ultrasonic irradiation, all hydroxy compounds, which formed according to the reaction mechanism were converted to unsaturated compounds immediately by the elimination of water, so no hydroxy product was isolated.

Conclusion

Long chain dicationic ammonium salts, which are prepared easily from cheap, commercially available materials, are very effective as phase transfer catalysts in the condensation reactions of aromatic aldehydes. When the aliphatic chain between the cationic centers is longer, the phase transfer activity in-

creases. Besides, the method used for the condensation reactions provides several advantages such as using environmentally friendly solvent water, short reaction times under ultrasonic irradiation and high yielded clean products.

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