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Synthesis of α-aminonitriles catalyzed by montmorillonite K10 in the presence of dicationic phosphonium salt in water under ultrasonic effect

Çiğdem YILDIRIM, Çiğdem YOLAÇAN, Feray AYDOĞAN*
Department of Chemistry, Yıldız Technical University, Davutpaşa Campus, 34010, Esenler, İstanbul - TURKEY
e-mail: feray_aydogan@yahoo.com

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The synthesis of α-aminonitriles was successfully accomplished by the 1-pot 3-component reaction of several aldehydes with $(S)-\alpha$-phenylethylamine and sodium cyanide in water in the presence of montmorillonite K10 and dicationic phosphonium salt under ultrasonic effect with good yields and moderate diastereoselectivities.

Key Words: α-Aminonitrile, Strecker synthesis, montmorillonite K10, dicationic phosphonium salt

Introduction

Three-component reaction of aldehydes, amines, and cyanide, known as the Strecker reaction, provides a traditional way to α-aminonitriles. These compounds are useful acyl anion and iminium ion equivalents[1] and very versatile intermediates for the synthesis of α-amino acids,[2] 1,2-diamines,[3] and various nitrogen containing heterocycles such as imidazoles, pyrroles, quinolones, and pyrazinones,[4] and several biologically active compounds.[5] Since Strecker's first report,[6] many modifications have been developed to enhance the efficiency of the original method. Generally, α-aminonitriles are prepared by nucleophilic addition of cyanide ion to the imines that are generated from the condensation of aldehydes with amines, in the presence of Lewis acid catalysts.[7] Beside the Lewis acid catalysts such as $NiCl_2$,[8] $Cu(OTf)_2$,[9] $RuCl_3$,[10] iodine,[11] $La(NO_3)_3.6H_2O$, $GdCl_3.6H_2O$,[12] $InCl_3$,[13] $Zr(HSO_4)_4$,[7] and Fe_3O_4,[14] solid catalysts such as silica supported heteropoly

*Corresponding author

acids,[15] cellulose sulfuric acid,[16] and mesoporous aluminosilicate[17] have been used to promote the reaction in organic solvents or solvent-free conditions.

Clays are solid acidic catalysts that can function as both Bronsted and Lewis acids in their natural and ion-exchanged form. A variety of organic reactions that are catalyzed by Bronsted or Lewis acids have been shown to take place in clays, especially montmorillonite, more efficiently, i.e. under milder conditions, with greater selectivity, better yields, shorter reaction times, and so on. Moreover, the work up and purification procedures are simpler as the catalyst is separated easily from the reaction mixture. Because of these reasons, and the fact that the catalyst can be reused or regenerated, the entire synthetic activity is not only economical but also environmentally benign.[18] Although montmorillonite clays have been successfully used as catalysts for a number of organic reactions,[19] as far as we know, there is only one report on the synthesis of α-aminonitriles in the presence of clay catalyst, [20] in which montmorillonite KSF was used as catalyst in a toxic solvent dichloromethane.

Here we wish to report a new synthetic method for the synthesis of α-aminonitriles from the 1-pot montmorillonite K10 catalyzed reaction of several aldehydes with $(S)-\alpha$-phenylethylamine and sodium cyanide in water as an environmentally benign solvent, in the presence of dicationic phosphonium salts as phase transfer catalyst under ultrasonic effect.

Experimental

All reagents were of commercial quality and reagent quality solvents were used without further purification. IR spectra were determined on a PerkinElmer, Spectrum One FT-IR spectrometer. NMR spectra were recorded on a Mercury VX-400 MHz spectrometer. Chemical shifts, δ, are reported in ppm relative to $CHCl_3$ (^{1}H: δ = 7.27) 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 $60F_{254}$ (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, 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 dicationic salts

A mixture of dihaloalkane (1.0 mmol) and triphenylphosphine (2.0 mmol) or N,N-dimethyldodecylamine (2.0 mmol) in absolute ethanol (10 mL) was refluxed for 48 h. After evaporation of the solvent, the crude product was washed with acetone and recrystallized from ethanol/diethyl ether (1:2).

1,6-Bis(triphenylphosphonium)hexane dibromide (P-6-P): White solid, (mp 311-312 °C). IR (atr): ν 3047, 3000, 2984, 2928, 2855, 1483, 1435 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.67 (brs, 4H, CH_2), 1.83 (brs, 4H, CH_2), 3.74-3.81 (m, 4H, CH_2), 7.66-7.84 (m, 30H, ArH).

1,12-Bis(triphenylphosphonium)dodecane dibromide (P-12-P): Orange oil. IR (atr): ν 3055, 2924, 2853, 1484, 1464, 1436 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.11 (brs, 8H, CH_2), 1.44 (brs, 8H, CH_2), 3.44-3.51 (m, 8H, CH_2), 7.52-7.60 (m, 12H, ArH), 7.61-7.70 (m, 18H, ArH).

1,12-Bis(dodecyldimethylamino)dodecane dibromide (12-12-12): White solid (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).

1,6-Bis(hexadecyldimethylamino)hexane dibromide (16-6-16): White solid (mp 185-186 °C). IR (atr): ν 2916, 2850, 1485, 1464, 1399, 1376 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.81 (t, J= 6.8 Hz, 6H, CH_3), 1.20 (m, 44H, CH_2), 1.28 (brs, 8H, CH_2), 1.49 (brs, 4H, CH_2), 1.65 (brs, 4H, CH_2), 1.92 (brs, 4H, CH_2), 3.32 (s, 12H, N-CH_3), 3.44 (m, 4H, CH_2), 3.64 (m, 4H, CH_2).

General procedure for the synthesis of α-aminonitriles

Aldehyde (1.0 mmol), (S)-α-phenylethylamine (1.0 mmol), montmorillonite K10 (0.25 g), and P-6-P (10 mol%) were added to the solution of NaCN (1.0 mmol) in water (20 mL). The reaction mixture was sonicated in an ultrasonic cleaner at 25 °C for a period long enough to complete the reaction (TLC). Then the crude product was extracted from the mixture by diethyl ether and purified by column chromatography over silica gel.

(*S,S*) and (*R,S*)-2-Phenyl-2-(1-phenylethylamino)acetonitrile (4a and 5a): Colorless oil. IR (atr): ν 3324, 3031, 2963, 2925, 2852, 2225, 1602, 1494, 1451 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): S,S-isomer (**4a**) δ 1.45 (d, J = 6.25 Hz, 3H, CH_3), 1.81 (brs, 1H, NH), 4.26 (q, J = 6.25 Hz, 1H, CHCH_3), 4.40 (brs, 1H, CHCN), 7.30-7.51 (m, 10H, ArH); R,S-isomer (**5a**) δ 1.43 (d, J = 6.64 Hz, 3H, CH_3), 1.81 (brs, 1H, NH), 4.01 (q, J = 6.64 Hz, 1H, CHCH_3), 4.71 (brs, 1H, CHCN), 7.30-7.51 (m, 10H, ArH).

(*S,S*) and (*R,S*)-2-(4-Fluorophenyl)-2-(1-phenylethylamino)acetonitrile (4b and 5b): Light yellow oil. IR (atr): ν 3321, 3064, 3030, 2972, 2928, 2864, 2228, 1602, 1509, 1494, 1452 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): S,S-isomer (**4b**) δ 1.45 (d, J = 6.64 Hz, 3H, CH_3), 4.25 (q, J= 6.40 Hz, 1H, CHCH_3), 4.38 (brs, 1H, CHCN), 7.07-7.12 (m, 2H, ArH), 7.25-7.50 (m, 6H, ArH), 7.78-7.81 (m, 1H, ArH); R,S-isomer (**5b**) δ 1.43 (d, J = 6.65 Hz, 3H, CH_3), 3.99 (q, J = 6.40 Hz, 1H, CHCH_3), 4.71 (brs, 1H, CHCN), 7.07-7.12 (m, 2H, ArH), 7.25-7.50 (m, 6H, ArH), 7.78-7.81 (m, 1H, ArH)

(*S,S*) and (*R,S*)-2-(4-Methylphenyl)-2-(1-phenylethylamino)acetonitrile (4c and 5c): Orange oil. IR (atr): ν 3314, 3063, 3026, 2970, 2924, 2853, 2228, 1603, 1512, 1489, 1448 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): S,S-isomer (**4c**) δ 1.42 (d, J = 6.64 Hz, 3H, CH_3), 1.95 (brs, 1H, NH), 2.35 (s, 3H, CH_3), 4.23 (q, J = 6.64 Hz, 1H, CHCH_3), 4.35 (s, 1H, CHCN), 7.18-7.47 (m, 7H, ArH), 7.77-7.79 (m, 2H, ArH); R,S-isomer (**5c**) δ 1.39 (d, J = 6.25 Hz, 3H, CH_3), 1.95 (brs, 1H, NH), 2.36 (s, 3H, CH_3), 3.97 (q, J= 6.25 Hz, 1H, CHCH_3), 4.64 (s, 1H, CHCN), 7.18-7.47 (m, 7H, ArH), 7.77-7.79 (m, 2H, ArH).

(*S,S*) and (*R,S*)-2-(4-Methoxyphenyl)-2-(1-phenylethylamino)acetonitrile (4d and 5d): Yellow oil. IR (atr): ν 3321, 3067, 3031, 2967, 2928, 2838, 2224, 1606, 1511, 1452 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): S,S-isomer (**4d**) δ 1.35 (d, J= 6.63 Hz, 3H, CH_3), 1.57 (brs, 1H, NH), 3.73 (s, 3H, OCH_3), 4.14 (q, J = 6.64 Hz, 1H, CHCH_3), 4.25 (s, 1H, CHCN), 6.82-6.85 (m, 2H, ArH), 7.21-7.39 (m, 5H, ArH), 7.75-7.79 (m, 2H, ArH); R,S-isomer (**5d**) δ 1.32 (d, J= 6.64 Hz, 3H, CH_3), 1.66 (brs, 1H, NH), 3.74 (s, 3H, OCH_3), 3.89 (q, J = 6.64 Hz, 1H, CHCH_3), 4.56 (s, 1H, CHCN), 6.82-6.85 (m, 2H, ArH), 7.21-7.39 (m, 5H, ArH), 7.75-7.79 (m, 2H, ArH)

(S,*S*) and (*R,S*)-2-(5-Methylfuran-2-yl)-2-(1-phenylethylamino)acetonitrile (4e and 5e): Yel-

low oil. IR (atr): ν 3318, 3027, 2972, 2926, 2863, 2228, 1587, 1531, 1492, 1451 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): *R,S*-isomer (**4e**) δ 1.36 (d, J = 6.64 Hz, 3H, CH_3), 1.60, (brs, 1H, NH), 2.22 (s, 3H, CH_3), 4.11 (q, J = 6.64 Hz, 1H, CHCH$_3$), 4.29 (brs, 1H, CHCN), 5.84-5.86 (m, 1H, HetarylH), 6.19 (d, J = 3.12 Hz, 1H, HetarylH), 7.14-7.34 (m, 5H, ArH); *S,S*-isomer (**5e**) δ 1.31 (d, J = 6.64 Hz, 3H, CH_3), 1.97 (brs, 1H, NH), 2.29 (s, 3H, CH_3), 3.86 (q, J = 6.64 Hz, 1H, CHCH$_3$), 4.55 (brs, 1H, CHCN), 5.99-6.00 (m, 1H, HetarylH), 6.54 (d, J = 3.52 Hz, 1H, HetarylH), 7.14-7.34 (m, 5H, ArH)

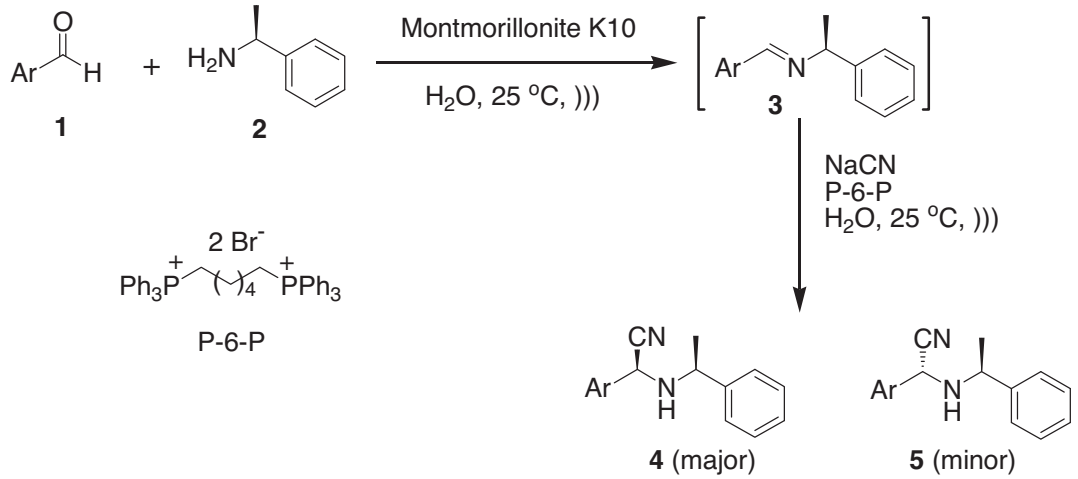
(S,*S*) and (*R,S*)-2-(1-phenylethylamino)-2-(pyridin-3-yl)acetonitrile (4f and 5f): Yellow oil. IR (atr): ν 3316, 3032, 2970, 2926, 2225, 1590, 1492, 1478, 1451, 1422 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): *S,S*-isomer (**4f**) δ 1.41 (d, J = 6.25 Hz, 3H, CH_3), 2.10 (brs, 1H, NH), 4.21 (q, J = 6.25 Hz, 1H, CHCH$_3$), 4.40 (brs, 1H, CHCN), 7.25-7.45 (m, 5H, ArH), 7.78 (m, 1H, HetarylH), 8.55 (dd, J = 4.68, 1.56 Hz, 1H, HetarylH), 8.68 (d, J = 2.34 Hz, 1H, HetarylH), 9.02 (d, J = 1.56 Hz, 1H, HetarylH); *R,S*-isomer (**5f**) δ 1.56 (d, J = 6.64 Hz, 3H, CH_3), 2.10 (brs, 1H, NH), 3.96 (q, J = 6.64 Hz, 1H, CHCH$_3$), 4.76 (brs, 1H, CHCN), 7.25-7.45 (m, 5H, ArH), 8.21 (m, 1H, HetarylH), 8.64 (d, J = 2.34 Hz, 1H, HetarylH), 8.79 (dd, J = 4.69, 1.56 Hz, 1H, HetarylH), 8.83 (d, J = 1.56 Hz, 1H, HetarylH)

(S,*S*) and (*R,S*)-3-Methyl-2-(1-phenylethylamino)butyronitrile (4g and 5g): Colorless oil. IR (atr): ν 3324, 3031, 2967, 2930, 2875, 2225, 1604, 1469, 1454, 1372 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): *S,S*-isomer (**4g**) δ 0.93 (d, J= 6.80 Hz, 3H, CH_3), 0.96 (d, J= 6.80 Hz, 3H, CH_3), 1.29 (d, J= 6.80 Hz, 3H, CH_3), 1.39 (brs, 1H, NH), 1.77-1.86 (m, 1H, CH(CH$_3$)$_2$), 2.89 (d, J= 6.00 Hz, 1H, CHCN), 3.98 (q, J= 6.40 Hz, 1H, CHCH$_3$), 7.15-7.25 (m, 5H, ArH); *R,S*-isomer (**5g**) δ 0.99 (d, J= 6.80 Hz, 6H, CH_3), 1.26 (d, J= 6.80 Hz, 3H, CH_3), 1.39 (brs, 1H, NH), 1.86-1.92 (m, 1H, CH(CH$_3$)$_2$), 3.37 (d, J= 6.00 Hz, 1H, CHCN), 3.94 (q, J= 6.40 Hz, 1H, CHCH$_3$), 7.15-7.25 (m, 5H, ArH).

(S,*S*) and (*R,S*)-2-(4-Methylthiophenyl)-2-(1-phenylethylamino)acetonitrile (4h and 5h): Light yellow oil. IR (atr): ν 3318, 3059, 3026, 2970, 2922, 2842, 2224, 1594, 1492, 1437, 1403 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): *S,S*-isomer (**4h**) δ 1.41 (d, J= 6.64 Hz, 3H, CH_3), 1.85 (brs, 1H, NH), 2.50 (s, 3H, CH_3), 4.21 (q, J = 6.64 Hz, 1H, CHCH$_3$), 4.33 (s, 1H, CHCN), 7.20-7.46 (m, 7H, ArH), 7.73-7.76 (m, 2H, ArH); *R,S*-isomer (**5h**) δ 1.38 (d, J= 6.25 Hz, 3H, CH_3), 1.85 (brs, 1H, NH), 2.45 (s, 3H, CH_3), 3.95 (q, J= 6.25 Hz, 1H, CHCH$_3$), 4.64 (s, 1H, CHCN), 7.20-7.46 (m, 7H, ArH) 7.73-7.76 (m, 2H, ArH)

Results and discussion

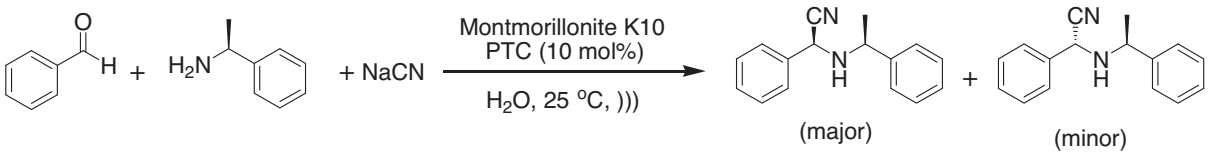
We started our study by investigation of the 1-pot 3-component reaction of benzaldehyde, $(S)-\alpha$-phenylethylamine, and NaCN in water with montmorillonite K10 and bentonite as catalysts to see how the reaction took place in water. The formation of α-aminonitriles was observed in water with the investigated clays; the yield was lower with bentonite (52%) than montmorillonite K10 (60%) with long reaction times such as 18-22 h. Then the reaction was carried out under ultrasonic effect in water in the presence of montmorillonite K10. The reaction time was 2 h and yield was slightly high under ultrasonic effect, but the TLC observations showed that the imine (**3**) formed as intermediate at the clay-organic phase interlayer (Scheme) was not completely reacted with cyanide ion.



Scheme. Synthesis of α-aminonitriles.

Therefore, we decided to use phase transfer catalysts to transfer cyanide ion into the organic phase. Several mono- and dicationic phase transfer catalysts such as benzyltriethylammonium bromide (TEBAB), 1,6-bis(hexadecyldimethylamino)hexane dibromide (16-6-16), 1,6-bis(triphenylphosphonium)hexane dibromide (P-6-P), 1,12-bis(dodecyldimethylamino)dodecane dibromide (12-12-12), and 1,12-bis(triphenylphosphonium)dodecane dibromide (P-12-P) were investigated for this purpose. We have successfully used long chain aliphatic dicationic ammonium salts as phase transfer catalyst in the condensation reactions of aromatic aldehydes in water under ultrasonic effect,[21] and so we especially chose dicationic salts. Indeed, all imine reacted in the presence of 10 mol% PTC and the yields were good with the dicationic salts, especially with phosphonium salts, as shown in Table 1. Then the reactions were carried out in the presence of 1,6-bis(triphenylphosphonium)hexane dibromide, which was easily prepared by the reflux of 1,6-dibromohexane, which was cheaper than 1,12-dibromododecane, with triphenylphosphine in dry ethanol for 48 h.

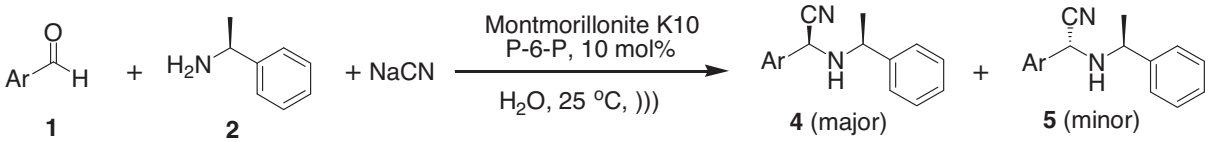
Table 1. The comparison of the effect of phase transfer catalysts.



PTC	Yield (%)	d.r.
-	60	28:72
TEBAB	65	28:72
16-6-16	73	27:73
12-12-12	76	28:72
P-6-P	85	27:73
P-12-P	84	27:73

Using these optimum conditions, the 1-pot 3-component reaction of several aldehydes with $(S)-\alpha$-phenylethylamine and NaCN was carried out in good yields, short reaction times, and moderate diastereos-

Table 2. The synthesis of α-aminonitriles.



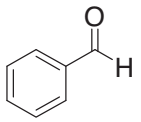
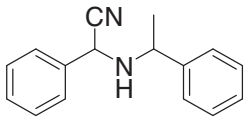
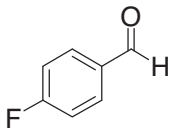
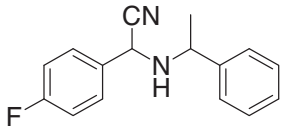
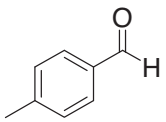
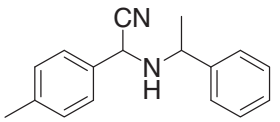
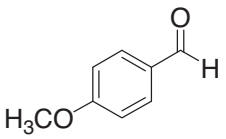
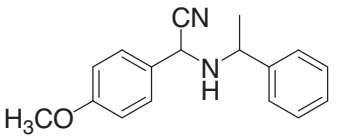
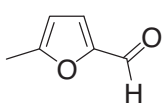
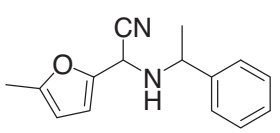
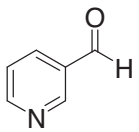
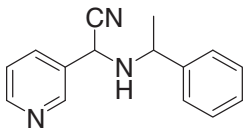
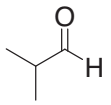
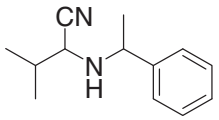
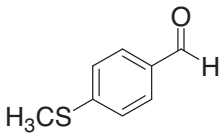
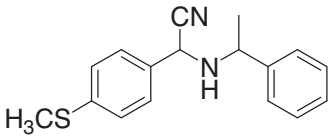
Aldehyde **1**	Product **4** and **5**	Reaction Time (h)	Yield (%)	d.r.
 **1a**	 (**4a** and **5a**)[22]	2	85	27:73
 **1b**	 (**4b** and **5b**)[23]	4	79	29:71
 **1c**	 (**4c** and **5c**)[24]	4	87	23:77
 **1d**	 (**4d** and **5d**)[24]	6	79	29:71
 **1e**	 (**4e** and **5e**)[25]	4	84	34:66

Table 2. Continued.

Aldehyde **1**	Product **4** and **5**	Reaction Time (h)	Yield (%)	d.r.
 **1f**	 (**4f** and **5f**)[25]	3	79	24:76
 **1g**	 (**4g** and **5g**)[23]	2.5	90	36:64
 **1h**	 (**4h** and **5h**)[26]	4	85	23:77

electivities, as summarized in Table 2. The products were easily separated from clay and phosphonium salt by a simple extraction of reaction mixture with diethyl ether, and purified by column chromatography. All of the compounds were known in the literature and all spectroscopic data were in full agreement with their structures. In the ^{1}H-NMR spectra the signals of C$\underline{\text{H}}$(CH_3)Ph protons appeared as quartets at δ 3.98-4.26 for major diastereomer 4, and δ 3.86-4.01 for minor diastreomer 5. The signals of C$\underline{\text{H}}$(CN)Ph protons appeared as broad singlets at δ 2.89-4.40 (major) and δ 3.37-4.76 (minor). These data were also in full agreement with the literature data.[22,25] The diastereomeric ratios were determined based on these benzylic protons in the ^{1}H-NMR spectra. The GC-MS spectra of compounds gave only one signal belonging to the corresponding imine because of the thermal instability of compounds under GC analysis conditions.

Conclusion

The synthesis of α-aminonitriles was successfully accomplished by the 1-pot 3-component reaction of several aldehydes with $(S)-\alpha$-phenylethylamine and NaCN in water in the presence of montmorillonite K10 and dicationic phosphonium salt under ultrasonic effect with good yield and moderate diastereoselectivity. The combination of clay, PTC, and ultrasonic effect for the synthesis of α-aminonitriles has been used for the first time. It is shown that the dicationic phosphonium salts are more effective than the ammonium salts in this

reaction. The phosphonium salts are useful phase transfer catalysts, because they are easily prepared from cheap and easily available starting materials, are stable, and easily separated from the product. This new method provides several advantages over the literature processes such as using water as an environmentally friendly solvent and clay as environmentally friendly catalyst, short reaction times under ultrasonic irradiation, and easy work-up procedure, and so it is also important procedure from the viewpoint of green chemistry.

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