A Novel Approach to the Synthesis of α-Aminonitriles Using Triphenylphosphine Dibromide under Solvent-Free Conditions

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Abstract: A quick and highly efficient, one-pot, three-component, solvent-free method for the synthesis of α-aminonitriles starting from the corresponding carbonyl compounds, amines, and trimethylisocyanide using triphenylphosphine dibromide, has been developed. Diverse α-aminonitriles have been synthesized in good to excellent yields (80–99%) using a range of aldehydes, ketones and amines.

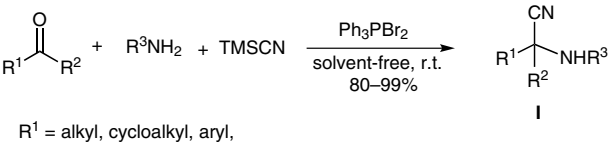
Key words: multicomponent reactions, Strecker synthesis, aminonitriles, carbonyl compounds

α-Aminonitriles constitute a major class of naturally occurring compounds that display remarkable biological activities[1] (anticancer, antibacterial, antifungal, antibiotic, and antiviral) and also serve as efficient precursors for the synthesis of natural and unnatural α-amino acids.[2] They have also been widely used as essential building blocks in peptide and protein synthesis.[3] Their synthetic utility has further been applied as a versatile synthon for the syntheses of amides, diamines, and various kinds of structurally diverse nitrogen and sulfur heterocycles[4] such as imidazoles and thiadiazoles. Furthermore, their synthetic utility has also been extended through carbanion-induced nucleophilic attack on the α-carbon atom with a variety of electrophiles, offering the possibility of further synthetic transformations.[5]

Among the reported methods, nucleophilic addition of cyanide ion to imines (Strecker reaction) offers one of the most direct approaches to the synthesis of α-aminonitriles.[6] The cyanide sources used during the course of this reaction include HCN, KCN, TMSCN, $(EtO)_2P(O)CN$, Et_2AlCN, Bu_3SnCN, MeCOCN, acetone cyanohydrin, acyl cyanides, ethyl cyanoformate, bis(dialkyl)aminocyanoboranes, and $K_4[Fe(CN)_6]$,[7] the majority of which are hazardous, toxic, and require harsh reaction conditions. In recent years, in the search for novel and efficient protocols for the synthesis of α-aminonitriles, a broad spectrum of metal complexes, Lewis acids, solid acids, bases, and organic catalysts have been developed to promote this reaction.[8,9] The majority of these catalysts are only efficient for the synthesis of α-aminonitriles from active aldehydes and are not suitable for ketone substrates. Therefore, there is continuing interest in developing new, efficient and safer protocols employing mild reaction conditions.

In recent years, triphenylphosphine dibromide (Ph_3PBr_2) has emerged as a versatile reagent in organic synthesis.[10] Our group has been engaged in the development of novel and efficient synthetic methodologies.[11] In the present communication, we wish to report an efficient method for the synthesis of α-aminonitriles through reaction of the corresponding carbonyl compounds, amines, and TMSCN using a catalytic amount of triphenylphosphine dibromide (TPPDB) under solvent-free conditions.[12] Triphenylphosphine dibromide was synthesized by the reported procedure.[10]

To optimize the protocol, the reaction of an equimolar amount of aniline, benzaldehyde, and trimethysilylcyanide, using a catalytic amount of TPPDB, was studied in a range of anhydrous solvents (CH_2Cl_2, THF, Et_2O, MeCN, DMF, $MeNO_2$, and MeOH) at room temperature and the corresponding α-aminonitrile was isolated. The best yields (99%) of the desired α-aminonitrile were achieved using at least 10 mol% TPPDB in the absence of solvent (Scheme 1).



R^1 = alkyl, cycloalkyl, aryl, naphthyl, anthracenyl, heteroaryl
R^2 = H, Me, Et, Ph
R^3 = alkyl, Ph, aryl

Scheme 1

It was subsequently observed that the desired α-aminonitrile could be achieved without using TPPDB under solvent-free conditions; although the reaction took longer (4 h) and afforded a lower yield (92%). However, although acetophenone reacted with aniline and TMSCN using a catalytic amount of TPPDB to afford a high-yield of the desired α-aminonitrile under solvent-free conditions at room temperature (Table 1), when this reaction was repeated without using TPPDB, the corresponding α-aminonitrile could not be achieved even after extended periods (4 h). When this reaction was repeated employing

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TPPDB without using TMSCN, the corresponding imine was obtained; without TPPDB no imine was observed. This implies a role for TPPDB in the generation of the corresponding imines in situ, particularly from ketones.

Table 1 Effect of Triphenylphosphine Dibromide on the Formation of α-Aminonitriles **I**

R^1	R^2	R^3	Time	TPPDB (mol%)	Yield (%)
Ph	H	Ph	20 min	10	98
Ph	H	Ph	4 h	absent	92
Ph	Me	Ph	25 min	10	98
Ph	Me	Ph	4 h	absent	–

Comparing the catalytic activity of TPPBD with some reported catalysts such as I_2, guanidine hydrochloride, and cellulose sulfuric acid for the synthesis of α-aminonitriles under solvent-free conditions, it was found that TPPDB was superior, achieving high yields of the desired products in shorter reaction times (Table 2).

Table 2 Effect of Catalysts on the Formation of α-Aminonitriles **I**

R^1	R^2	R^3	Time (h)	Catalyst (10 mol%)	Yield (%)
Ph	H	Ph	4	I_2	58
Ph	Me	Ph	8	I_2	52
Ph	H	Ph	2	GuHCl	78
Ph	Me	Ph	4	GuHCl	64
Ph	H	Ph	2	cellulose sulfuric acid	66
Ph	Me	Ph	4	cellulose sulfuric acid	53
Ph	H	Ph	25 min	TPPBD	98
Ph	Me	Ph	30 min	TPPBD	98

The scope of this reaction was further explored with a range of aliphatic and aromatic substituted aldehydes and ketones bearing electron-releasing and electron-withdrawing functionalities and primary aliphatic and aromatic amines having electron-releasing and electron-withdrawing functional groups. Best yields of the products were obtained when an electron-releasing group was present at the *para*-position of the aromatic aldehydes, ketones, and amines (Table 3).

Table 3 Synthesis of α-Aminonitriles of General Formula **I**

Entry	R^1	R^2	R^3	Time (min)	Yield (%)	Ref.
1	Ph	H	Ph	25	98	[8d]
2	4-ClC_6H_4	H	Ph	25	97	[8m]
3	4-$O_2NC_6H_4$	H	Ph	30	94	[8i]
4	4-BrC_6H_5	H	Ph	30	94	[9i]
5	3,4-$Cl_2C_6H_3$	H	Ph	30	95	[9i]
6	4-FC_6H_4	H	Ph	35	91	[9b]
7	4-MeC_6H_4	H	Ph	30	90	[9a]
8	4-$MeOC_6H_4$	H	Ph	35	91	[9a]
9	3-pyridyl	H	Ph	30	89	[8i]
10	C_9H_{19}	H	Ph	60	80	[8p]
11	Et	H	Ph	60	89	[8q]
12	Ph	H	4-MeC_6H_4	25	95	[8m]
13	Ph	H	4-$MeOC_6H_4$	25	96	[8p]
14	Ph	Me	Ph	30	98	[9b]
15	Ph	Me	4-$MeOC_6H_4$	30	99	[8n]
16	Ph	Me	4-ClC_6H_4	30	92	[8n]
17	Ph	H	Bn	25	95	[9b]
18	1-naphthyl	H	Ph	30	93	[8o]
19	9-anthryl	H	Ph	35	91	[8r]
20	*c*-Pr	H	Ph	30	90	[8o]
21	Ph	Me	Bn	30	93	[9b]
22	$–(CH_2)_4–$		Ph	94		[8n]
23	$–(CH_2)_5–$		Ph	98		[8n]
24	$–(CH_2)_6–$		Ph	96		[9a]
25	Ph	Et	Ph	30	92	[9b]
26	Ph	Et	Bn	30	88	[9b]
27	Ph	Ph	Ph	35	85	[9b]
28	2-naphthyl	Me	Ph	35	84	[9b]
29	*i*-Pr	Me	Ph	45	82	[9b]
30	PhCH=CH	H	Ph	45	80	[9b]
31	Ph	H	*n*-Bu	35	81	[8i]
32	4-MeC_6H_4	H	*n*-Bu	35	83	–
33	*c*-Hex	H	Bn	35	81	–
34	*c*-Hex	H	Ph	35	80	–
35	*n*-Bu	*n*-Bu	Ph	45	86	[8r]
36	2-naphthyl	Ph	Ph	50	83	[8r]
37	4-$O_2NC_6H_4$	Me	Ph	55	81	[9b]
38	3-Me-2-HSC_6H_3	Me	Ph	55	83	[8o]
39	3-pyridyl	Me	4-$MeOC_6H_4$	45	87	[8n]
40	3,4-$(OCH_2O)C_6H_3$	Me	4-$MeOC_6H_4$	50	82	[8n]

In conclusion, we have developed a simple and efficient method for the synthesis of α-aminonitriles starting from their corresponding carbonyl compounds, amines, and trimethylsilyl cyanide, by employing a catalytic amount of TPPDB under solvent-free conditions.

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(12) **Synthesis of α-Aminonitriles; Typical Procedure:** A mixture of aldehyde (1 mmol), amine (1 mmol), triphenylphosphine dibromide (10 mol%), and trimethylsilylcyanide (1.2 mmol) was stirred at room temperature until the reaction was complete (monitored by TLC). The reaction mixture was then extracted with EtOAc (×3), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification of the crude product by chromatography on silica gel (60–120 mesh; petroleum ether–EtOAc, 5:1) gave the pure product.

2-Anilino-2-phenylacetonitrile (Table 3, Entry 1): Light-yellow solid; mp 85–86 °C; IR ($CHCl_3$): 3368, 3055, 2233, 1602, 1502 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 4.03 (d, *J* = 9 Hz, 1 H), 5.41 (d, *J* = 9 Hz, 1 H), 6.76 (d, *J* = 9 Hz, 2 H), 6.90 (t, *J* = 6 Hz, 1 H), 7.30 (t, *J* = 9 Hz, 2 H), 7.44 (m, 3 H), 7.59 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.8, 114.0, 118.1, 119.9, 127.0, 128.3, 129.4, 129.8, 133.6, 144.6; MS (ESI): *m*/*z* = 208.2 $[M]^+$; Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.80; H, 5.76; N, 13.47.

2-Anilino-2-(4-chlorophenyl)acetonitrile (Table 3, Entry 2): White solid; mp 96–98 °C; IR ($CHCl_3$): 3365, 3055, 2235, 1603, 1504 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 4.02 (d, *J* = 6 Hz, 1 H), 5.41 (d, *J* = 9 Hz, 1 H), 6.75 (d, *J* = 9 Hz, 2 H), 6.92 (t, *J* = 6 Hz, 1 H), 7.28 (m, 2 H), 7.42 (d, *J* = 9 Hz, 2 H), 7.53 (d, *J* = 6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.5, 114.2, 117.8, 120.4, 128.4, 129.2, 129.6, 132.8, 135.4, 144.3; MS (ESI): *m*/*z* = 242.1 $[M]^+$; Anal. Calcd for $C_{14}H_{11}ClN_2$: C, 69.28; H, 4.57; N, 11.54; Found: C, 69.19; H, 4.63; N, 11.56.

2-Anilino-2-(4-nitrophenyl)acetonitrile (Table 3, Entry 3): Gummy solid; IR ($CHCl_3$): 3381, 3063, 2225, 1601, 1550, 1502 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 4.08 (d, *J* = 9 Hz, 1 H), 5.57 (d, *J* = 9 Hz, 1 H), 6.68 (d, *J* = 9 Hz, 2 H), 6.78 (t, *J* = 8 Hz, 1 H), 7.29 (t, *J* = 9 Hz, 2 H), 7.8 (d, *J* = 9 Hz, 2 H), 8.1 (d, *J* = 9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.8, 115.3, 118.0, 127.0, 127.7, 127.8, 128.6, 129.0, 133.8, 144.1, 145.0; MS (ESI): *m*/*z* = 276.2 $[M + Na]^+$; Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59; Found: C, 66.46; H, 4.40; N, 16.51.

