

C-Cyanation with 1-Cyanobenzotriazole

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Dedicated to Professor Ernst Anders on the occasion of his 65th birthday

Abstract

1-Cyanobenzotriazole is a convenient source of NC^+ for C-cyanation with *in situ*-generated sp^3 and sp^2 carbanions providing α -cyano-sulfones, -ketones, -alkanecarboxylate esters, -cyanides, -alkylheterocycles, -diarylmethanes and heterylcarbonitriles in good to high yields (55–78%).

Keywords: Nitriles, 1-cyanobenzotriazole, C-cyanation, electrophilic substitution reaction

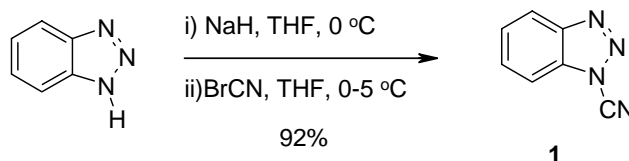
Introduction

Most reactions to introduce the cyano group employ the cyanide anion NC^- . Electrophilic reaction with NC^+ donors are more rare: most are electrophilic substitution reactions of organometallic reagents¹ with tosyl cyanide,^{2a,b} 2-chlorobenzyl thiocyanate,³ thiocyanogen,⁴ 2-cyanopyridazin-3(2*H*)-ones,⁵ cyanogen halides,⁶ and 1-cyanoimidazole.⁷ These show problems with stability, lack of reactivity, poor solubility, corrosiveness, availability, toxicity, cost, and/or complicated preparative procedures.

1-Cyanobenzotriazole **1** has been used previously in our group for cyanation of amines and thiols.⁸ More recently, Cava's group reported the C-cyanating ability of **1** for arylacetonitriles⁹ and aromatic and heteroaromatic compounds,¹ where moderate to good yields were obtained for cyanation of simple alkyl- and arenyl- carbanions and the thiophene ring system. In the present work, we have expanded the application of 1-cyanobenzotriazole to the preparation of α -cyano-sulfones, -ketones, -alkanecarboxylate esters, -cyanides, -alkylheterocycles, -diarylmethanes and heterylcarbonitriles.

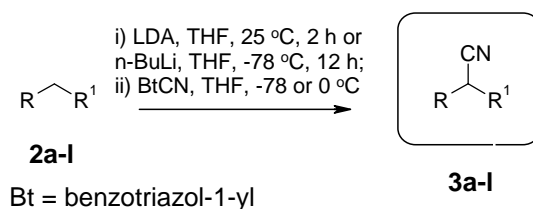
Results and Discussion

1-Cyanobenzotriazole **1** was readily prepared in high yield (92%) following a slightly modified literature procedure⁸ by the treatment of benzotriazole with sodium hydride followed by addition of cyanogen bromide (Scheme 1). Use of the sodium salt of benzotriazole, prepared *in situ*, affords the pure 1-cyanobenzotriazole **1** after simple filtration and evaporation of solvent. Alternative procedures require purification by sublimation.^{8,9}



Scheme 1

Synthesis of nitriles derivatives. The general utility of 1-cyanobenzotriazole for incorporation of the nitrile functional group into a diverse series of functionalized compounds **2** was investigated by reaction of the corresponding carbanions, again generated *in situ*, with cyanating reagent **1**. For optimum yields, reactions of lithium diisopropylamide (LDA, prepared as detailed in method A) with substrates **2a–j** required room temperature for 2 h followed by the addition of 1-cyanobenzotriazole at 0 °C. Then the reaction mixture was allowed to react at room temperature overnight and was quenched with a saturated solution of ammonium chloride. Extraction with ethyl acetate and purification by silica gel column chromatography provided α -cyanoalkyl derivatives in average 65 % yield (Scheme 2, Table 1). Nitriles **3k,l** were prepared by method B, which requires 2.2 molar equiv of *n*-BuLi and 12 h at room temperature for generation of the corresponding lithio derivatives. Treatment with 1-cyanobenzotriazole **1** gave the desired products **3k,l** in 65 and 70% yields.

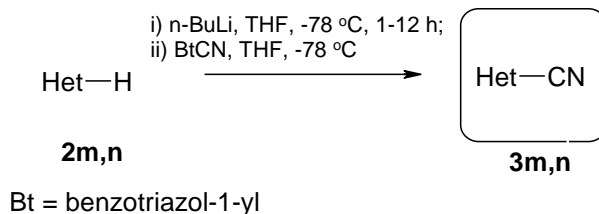


^a For designation of R and R¹ in **2** and **3** see Table 1.

Scheme 2

Lithio derivatives (generated *in situ* by treating the corresponding heterocycles **2m,n** with 1 molar equiv of *n*-BuLi for 1 h (for **3m**) or for 12 h (for **3n**)) were treated with 1-

cyanobenzotriazole **1** in dry THF at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to room temperature while stirring overnight and afforded, after workup, heterylcarbonitriles **3m,n** in 55–65% isolated yields (Scheme 3 and Table 1).



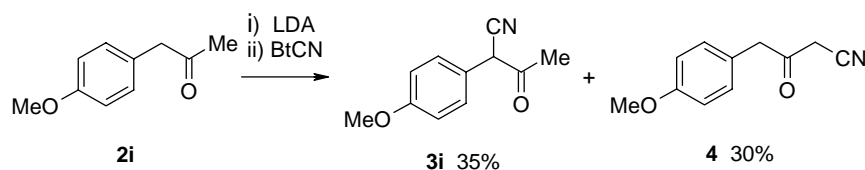
^a For designation of Het in **2** and **3** see Table 1.

Scheme 3

Table 1. Preparation nitriles **3a–n**

| Product | R or Het of 2 and 3 | R ¹ of 2 and 3 | Yield (%) of 3 | Method |
|-----------|-----------------------------------|---|-----------------------|--------|
| 3a | Ph | CN | 70 | A |
| 3b | Bz | CN | 65 | A |
| 3c | Ph | CO ₂ Et | 70 | A |
| 3d | Bz | CO ₂ Et | 67 | A |
| 3e | 1-naphthyl | CO ₂ Me | 65 | A |
| 3f | 2-tolyl | SO ₂ Ph | 75 | A |
| 3g | Ph | SO ₂ Ph | 78 | A |
| 3h | Bz | SO ₂ Ph | 65 | A |
| 3i | 4-anisyl | COMe | 35 | A |
| 3j | Ph | COPh | 62 | A |
| 3k | Ph | Ph | 65 | B |
| 3l | 2-pyridyl | Me | 70 | B |
| 3m | 2-ethyl-5-furyl | - | 65 | B |
| 3n | 1-methyl-2-pyrrolyl | - | 55 | B |

The cyanation of ketone **2i** under the standard lithiation conditions (method A) provided a mixture of two isomers **3i** and **4** due to the generation of the two corresponding anions on treatment of methyl 2-(4-methoxyphenyl)acetate **2i** with LDA¹⁰ (Scheme 4). Our attempts to improve the yield of methyl 2-cyano-2-(4-methoxyphenyl)acetate **3i** using shorter reaction times, lower temperatures and *n*-BuLi were unsuccessful. A variable amount of cyanomethyl 2-(4-methoxyphenyl)acetate **4** beside the major product **3i** was always detected in the reaction mixture.



Scheme 4

In summary, the utility of 1-cyanobenzotriazole for preparation of a broad variety of heterocyclic and functionalized α -nitriles has been established as a general and efficient methodology. 1-Cyanobenzotriazole is an advantageous cyanation reagent because it is a stable, non-volatile, crystalline solid that limits the risk of possible toxic exposure.

Experimental Section

General Procedures. Melting points were determined using a Bristoline hot-stage microscope and are uncorrected. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a 300 MHz NMR spectrometer in chloroform-*d* solution. Elemental and mass spectroscopy analyses were performed by the Analytical Laboratories, Dept. of Chem., University of Florida. THF was distilled from sodium-benzophenone ketal prior to use. All the reactions were performed under a nitrogen atmosphere. Column chromatography was conducted with silica gel (200–425 mesh).

1-Cyano-1H-1,2,3-benzotriazole (1). Benzotriazole (10 g, 84 mmol) was dissolved in anhydrous THF (150 ml). The solution was cooled to 0 °C and 60% sodium hydride (3.36 g, 92.4 mmol) was added. The mixture was allowed to react at the same temperature for 30 minutes. A solution of cyanogen bromide (9.7 g, 92.4 mmol) in dry THF (25 mL) was added rapidly to a vigorously stirred solution of sodium benzotriazole. The reaction mixture was allowed to react at ambient temperature for 1.5 h. The precipitate was filtered off and washed with THF. The filtrate was evaporated and the residue was dissolved in ethyl acetate and washed with water. The organic phase was dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure to afford 1-cyanobenzotriazole as a colorless powder (92%), mp 74–76 °C (lit.⁸ mp 73–76 °C); ^1H NMR δ 8.23 (d, J = 8.4 Hz, 1H), 7.76–7.87 (m, 2H), 7.58–7.68 (m, 1H); ^{13}C NMR δ 143.3, 132.7, 131.6, 126.8, 121.4, 109.5, 103.7.

General procedure of preparation of sulfones 2f–h

To ethanol (100 mL) was added phenyl sulfonyl sodium salt (60.9 mmol) and the respective benzylbromide (60.9 mmol). The mixture was refluxed for 3 hours. The solvent was evaporated and the solid was washed with water and with isopropyl ether to afford compounds 2f–h.

2-Methylbenzyl phenyl sulfone (2f). White prisms (75%), mp 73–74 °C (lit.¹¹ mp 73–75 °C); ¹H NMR δ 7.58–7.66 (m, 3H), 7.43–7.48 (m, 2H), 7.12–7.14 (m, 2H), 6.83–6.90 (m, 2H), 4.27 (s, 2H), 2.26 (s, 3H); ¹³C NMR δ 138.2, 137.8, 133.6, 131.5, 129.4, 128.7, 128.5, 128.3, 127.73, 127.72, 62.8, 21.1. Anal. Calcd for C₁₄H₁₄O₂S: C, 68.26; H, 5.73; Found: C, 68.14; H, 5.75.

Benzyl phenyl sulfone (2g). Colorless prisms (70%), mp 148–150 °C (lit.¹² mp 146–147 °C); ¹H NMR δ 7.63–7.76 (m, 3H), 7.43 (m, 2H), 7.33–7.22 (m, 3H), 7.07 (m, 2H), 4.31 (s, 2H); ¹³C NMR δ 137.7, 133.6, 130.7, 128.8, 128.7, 128.5, 128.4, 128.0, 62.7. Anal. Calcd for C₁₃H₁₂O₂S: C, 67.22; H, 5.21; Found: C, 66.85; H, 5.21.

Phenethyl phenyl sulfone (2h). White prisms (65%), mp 53–54 °C (lit.¹² mp 53–56 °C); ¹H NMR δ 7.96–7.93 (m, 2H), 7.67 (m, 1H), 7.58 (m, 2H), 7.30–7.18 (m, 3H), 7.11 (m, 2H), 3.40–3.33 (m, 2H), 3.10–3.01 (m, 2H); ¹³C NMR δ 138.9, 137.4, 133.8, 129.3, 128.8, 128.2, 128.1, 126.9, 57.5, 28.7. Anal. Calcd for C₁₄H₁₄O₂S: C, 68.26; H, 5.73; Found: C, 67.94; H, 5.76.

General procedures for C-cyanation

Method A. A solution of diisopropylamine (12.0 mmol, 1.68 mL) in THF (15.0 mL) was treated with *n*-butyllithium (2.5 M in *n*-hexane, 12.0 mmol, 4.8 mL), at 0 °C, under a nitrogen atmosphere. After 30 min at 0 °C, a solution of **2** (6 mmol) in THF (15 mL) was added dropwise. The mixture was stirred at room temperature for 2 h, cooled to 0 °C and then a solution of 1-cyanobenzotriazole (0.91 g, 6.3 mmol) in THF (10 mL) was slowly added. The mixture was allowed to warm to room temperature while stirring overnight and then was poured into a saturated solution of ammonium chloride (60 mL). The product was extracted with ethyl acetate (30 mL x 3). The combined organic extracts were washed with brine and dried over MgSO₄. After evaporation under vacuum, the residue was purified by column chromatography (CH₂Cl₂ or heptane/ethyl acetate: 10/1) to afford the desired functionalized α-nitriles **3a–j** and **4**.

2-Phenylmalononitrile (3a). Colorless prisms (70%), mp 65–67 °C, (lit.³ mp 67–68 °C); ¹H NMR δ 7.50 (s, 5H), 5.09 (s, 1H); ¹³C NMR δ 130.4, 130.1, 127.2, 126.2, 111.9, 28.1. Anal. Calcd for C₉H₆N₂: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.99; H, 4.05; N, 19.59.

2-Benzylmalononitrile (3b). Colorless prisms (65%), mp 86–88 °C, (lit.¹³ mp 80–81 °C); ¹H NMR δ 7.45–7.40 (m, 3H), 7.36–7.30 (m, 2H), 3.91 (t, *J* = 7.0 Hz, 1H), 3.29 (d, *J* = 7.0 Hz, 2H); ¹³C NMR δ 132.9, 129.3, 129.1, 128.8, 112.1, 36.7, 25.0. Anal. Calcd for C₁₀H₈N₂: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.65; H, 5.12; N, 18.04.

Ethyl 2-cyano-2-phenylacetate (3c).¹⁴ Yellow oil (70%); ¹H NMR δ 7.45–7.46 (m, 5H), 4.72 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR δ 164.9, 129.9, 129.2, 129.1, 127.8, 115.6, 63.2, 43.6, 13.8. Anal. Calcd for C₁₁H₁₁NO₂: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.14; H, 6.18; N, 7.13.

Ethyl 2-cyano-3-phenylpropanoate (3d).¹³ Yellow oil (67%); ¹H NMR δ 7.37–7.28 (m, 5H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.72 (dd, *J* = 8.5, 5.9 Hz, 1H), 3.20 (dd, *J* = 13.9, 8.5 Hz, 1H), 3.27 (dd, *J* = 13.9, 8.5 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR δ 165.5, 135.2, 129.1, 129.0, 128.8, 127.8, 116.1, 62.9, 39.7, 35.7, 13.9. Anal. Calcd for C₁₂H₁₃NO₂: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.24; H, 6.83; N, 7.24.

Methyl 2-cyano-2-(1-naphthyl)acetate (3e). Colorless prisms (65%), mp 90–92 °C (lit.¹⁵ mp 89–90 °C); ¹H NMR δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.64–7.49 (m, 3H), 5.39 (s, 1H), 3.78 (s, 3H); ¹³C NMR δ 165.5, 133.9, 130.3, 130.2, 129.1, 127.6, 127.5, 126.4, 126.0, 125.4, 122.4, 115.7, 53.9, 41.2. Anal. Calcd for C₁₄H₁₁NO₂: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.40; H, 4.92; N, 6.19.

2-(2-Methylphenyl)-2-(phenylsulfonyl)acetonitrile (3f). Colorless prisms (75%), mp 130–132 °C (lit.¹⁶ mp 133–134 °C); ¹H NMR δ 7.71–7.75 (m, 3H), 7.51–7.57 (m, 2H), 7.23–7.26 (m, 2H), 7.04–7.09 (m, 2H), 5.09 (s, 1H), 2.32 (s, 3H); ¹³C NMR δ 139.0, 135.2, 134.3, 131.3, 130.3, 130.1, 129.1, 128.8, 126.8, 125.1, 113.5, 63.0, 21.2. Anal. Calcd for C₁₅H₁₃NO₂S: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.39; H, 4.73; N, 5.04.

2-Phenyl-2-(phenylsulfonyl)acetonitrile (3g). Colorless prisms (70%), mp 151–152 °C (lit.¹⁴ mp 147–148 °C); ¹H NMR δ 7.74–7.71 (m, 3H), 7.53 (m, 2H), 7.44 (m, 1H), 7.37 (m, 2H), 7.27 (m, 2H), 5.14 (s, 1H); ¹³C NMR δ 135.3, 134.2, 130.5, 130.0, 129.7, 129.2, 129.0, 125.3, 113.4, 63.0. Anal. Calcd for C₁₄H₁₁NO₂S: C, 65.35; H, 4.31; 5.44. Found: C, 65.42; H, 4.30; N, 5.43.

3-Phenyl-2-(phenylsulfonyl)propanenitrile (3h). Yellow prisms (65%), mp 80–82 °C (lit.¹⁷ mp 76–78 °C); ¹H NMR δ 8.10–8.05 (m, 2H), 7.82–7.77 (m, 1H), 7.70–7.65 (m, 2H), 7.38–7.26 (m, 5H), 4.07 (dd, *J* = 11.8, 3.7 Hz, 1H), 3.60 (dd, *J* = 13.6, 3.7 Hz, 1H), 3.09 (dd, *J* = 13.3, 11.8 Hz, 1H); ¹³C NMR δ 135.5, 133.5, 129.8, 129.7, 129.4, 129.1, 128.2, 113.7, 59.5, 32.7. Anal. Calcd for C₁₅H₁₃NO₂S: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.45; H, 4.80; N, 5.10.

Methyl 2-cyano-2-(4-methoxyphenyl)acetate (3i). Yellow microcrystals (35%), mp 80–82 °C (lit.¹⁸ mp 75–76 °C); ¹H NMR δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.63 (s, 1H), 3.83 (s, 3H), 2.25 (s, 3H); ¹³C NMR δ 196.8, 160.3, 129.2, 121.5, 116.4, 115.1, 55.4, 50.8, 26.8. Anal. Calcd for C₁₁H₁₁NO₂: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.83; H, 5.85; N, 7.32.

3-Oxo-2,3-diphenylpropanenitrile (3j). Colorless prisms (62%), mp 84–86 °C (lit.¹⁹ mp 89–90 °C); ¹H NMR δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.63–7.58 (m, 1H), 7.49–7.36 (m, 7H), 5.60 (s, 1H); ¹³C NMR δ 188.8, 135.5, 134.5, 133.6, 129.7, 129.3, 129.0, 128.3, 126.2, 116.5, 46.7. Anal. Calcd for C₁₅H₁₁NO: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.17; H, 5.15; N, 6.06.

Cyanomethyl 2-(4-methoxyphenyl)acetate (4). Yellow microcrystals (30%), mp 82–84 °C (lit.²⁰ mp 83.5–84.5 °C); ¹H NMR δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 2H), 3.45 (s, 2H). ¹³C NMR δ 195.6, 159.3, 130.5, 123.7, 114.7, 114.2, 55.3, 48.4, 30.9. Anal. Calcd for C₁₁H₁₁NO₂: C, 69.83; H, 5.86; N, 7.40. Found: C, 70.08; H, 5.78; N, 7.48.

Method B. *n*-Butyl lithium (7 mmol (for **3m**) or 13.2 mmol (for **3k, l, n**), 1.6 M in hexanes) was added to a cooled solution of **2** (6 mmol) in anhydrous THF (30 mL) at –78 °C under nitrogen. The mixture was stirred one hour (for **3m**) or overnight (for **3k, l, n**) at room temperature and then cooled to –78 °C. The solution of 1-cyanobenzotriazole (0.91 g, 6.3 mmol) was added dropwise. The mixture was allowed to warm to room temperature, stirred overnight and poured into a saturated solution of ammonium chloride (60 mL). The product was extracted with ethyl acetate (30 mL x 3), the organic extracts combined, washed with brine, and dried over MgSO₄. After evaporation, the residue was purified by column chromatography (CH₂Cl₂ or heptane/ethyl acetate: 10/1) to afford the desired nitriles **3k–n**.

2,2-Diphenylacetonitrile (3k). White microcrystals (60%), mp 73–74 °C (lit.²¹ mp 72.0–73.5 °C); ¹H NMR δ 7.41–7.26 (m, 10H), 5.15 (s, 1H); ¹³C NMR δ 135.8, 129.2, 128.2, 127.7, 119.7, 42.6. Anal. Calcd for C₁₄H₁₁N: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.83; H, 5.80; N, 7.22.

2-(2-Pyridinyl)propanenitrile (3l).²² Yellow oil (70%); ¹H NMR δ 8.60 (br d, *J* = 4.8 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 5.0 Hz, 1H), 4.08 (q, *J* = 7.3 Hz, 1H), 1.72 (d, *J* = 7.3 Hz, 3H); ¹³C NMR δ 156.0, 149.8, 137.4, 122.9, 121.0, 120.9, 33.7, 19.6; Anal. Calcd for C₈H₈N₂: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.46; H, 6.27; N, 21.25.

5-Ethyl-2-furonitrile (3m). Yellow oil (65%), bp 59–61 °C/1 mmHg (lit.²³ bp 59–60 °C/1 mmHg); ¹H NMR δ 7.01 (d, *J* = 3.6 Hz, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H); ¹³C NMR δ 163.6, 126.1, 124.3, 123.1, 106.2, 21.6, 11.6.

1-Methyl-1H-pyrrole-2-carbonitrile (3n). Yellow oil (55%), bp 60–62 °C/20 mmHg, (lit.²⁴ bp 60–62 °C/20 mmHg); ¹H NMR δ 6.81–6.78 (m, 2H), 6.16 (dd, *J* = 4.0, 1.4 Hz, 1H), 3.78 (s, 3H). ¹³C NMR δ 160.6, 127.4, 119.9, 113.7, 109.4, 35.2.

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