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Solvent-Free Chemoselective Cyanation of α,α-Dibromoacetophenones Using Potassium Hexacyanoferrate(II) as an Eco-Friendly Cyanide Source

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A chemoselective route for the synthesis of 2-aryl-3,3-dibromoacrylonitriles by solvent-free cyanation of α,α-dibromoacetophenones by using potassium hexacyanoferrate(II) as an eco-friendly cyanide source is developed. The merits of this procedure include avoiding the use of a strong toxic cyanide source, a catalyst, and volatile organic solvents and the high yields of the products.

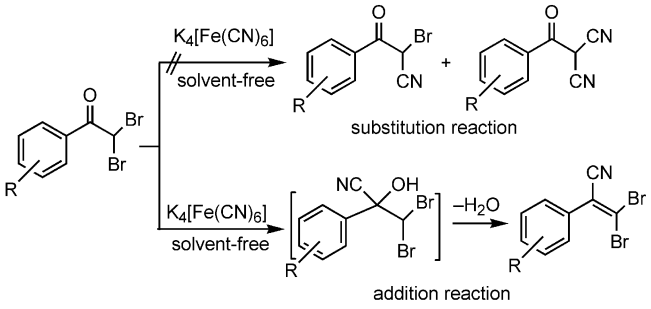
Introduction

Nucleophilic addition of carbonyl compounds with cyanating agents is a very important way to access nitriles, hydroxy acids, and amino acids, which are important intermediates for medicine and agrochemicals. Many cyanating agents were used in these nucleophilic additions, such as HCN,[1] NaCN,[2] TMSCN,[3] $(R_2N)_2BCN$,[4] cyanoformate,[5] acetone cyanohydrin,[6] and acetyl cyanide.[7] However, these cyanating agents are strongly toxic chemicals, which render nucleophilic addition of carbonyl compounds unsafe and environmentally unfriendly. Therefore, there is a need to explore eco-friendly cyanating agents for the corresponding cyanation reactions.

Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, is nontoxic and is even used in the food industry for metal precipitation. In addition, it has been described as an antiagglutinating auxiliary for table salt (NaCl). $K_4[Fe(CN)_6]$ is a byproduct of the coal chemical industry and commercially available on a ton scale, and it is even cheaper than KCN. Very recently, $K_4[Fe(CN)_6]$ has been proved to be an efficient cyanide source for the cyanation of halogenated arenes and aroyl chlorides to prepare benzonitriles[8] and aroyl cyanides.[9] In this paper, we report chemoselective nucleophilic addition reactions of α,α-dibromoacetophenones by using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source under solvent-free and catalyst-free conditions.

Results and Discussion

Initially, α,α-dibromoacetophenone was selected as a substrate to examine the feasibility of cyanation by using $K_4[Fe(CN)_6]$ under different conditions (Scheme 1, R = H). Generally, there are two possible reaction paths for this system. One pathway is the substitution of the two bromide groups of α,α-dibromoacetophenone with the cyanide group of $K_4[Fe(CN)_6]$. The other pathway involves an addition reaction at the carbonyl group of α,α-dibromoacetophenone by the cyanide group of $K_4[Fe(CN)_6]$. Fortunately, it was found that α,α-dibromoacetophenone chemoselectively reacted with $K_4[Fe(CN)_6]$ only by the addition reaction, followed by dehydration to give 2-phenyl-3,3-dibromoacrylonitrile. Substitution products were not observed. Furthermore, the optimal ratio of α,α-dibromoacetophenone to $K_4[Fe(CN)_6]$ was 4:1 for the synthesis of 2-phenyl-3,3-dibromoacrylonitrile. That indicated four cyanide ions bound to Fe in $K_4[Fe(CN)_6]$ were transferred to 2-phenyl-3,3-dibromoacrylonitrile. To select the other optimal conditions, the reaction was also tested at different temperatures for different times. It was found that the reaction of α,α-dibromoacetophenone with 0.25 equiv. of $K_4[Fe(CN)_6]$ at 160 °C for 20 min gave the best yield of 2-phenyl-3,3-dibromoacrylonitrile (Table 1, Entry 3; Table 2, Entry 4). The reaction at higher temperature for a prolonged time could cause carbonization of the substrate.



Scheme 1. The reactions of α,α-dibromoacetophenones with $K_4[Fe(CN)_6]$.

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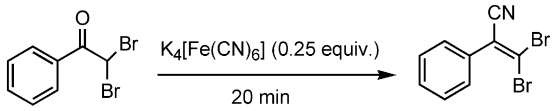
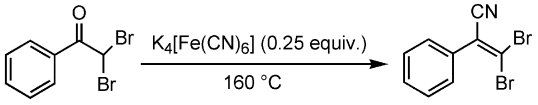
Table 1. The reactions of α,α-dibromoacetophenone with $K_4[Fe(CN)_6]$ at different temperatures.[a]



Entry	Temperature [°C]	Yield [%][b]
1	120	NR[c]
2	140	30
3	160	88
4	180	70
5	190	62
6	200	34

[a] All reactions were carried out by using α,α-dibromoacetophenone (10 mmol) and $K_4[Fe(CN)_6]$ (2.5 mmol). [b] Isolated yield. [c] No reaction.

Table 2. The reactions of α,α-dibromoacetophenone with $K_4[Fe(CN)_6]$ for different times.[a]



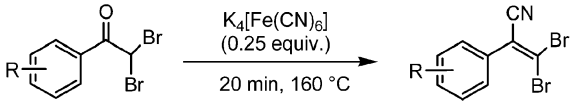
Entry	Reaction time [min]	Yield [%][b]
1	5	30
2	10	50
3	15	65
4	20	88
5	25	70
6	30	62

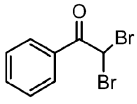
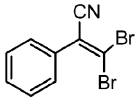
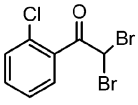
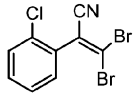
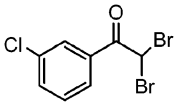
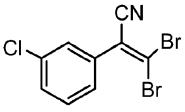
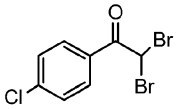
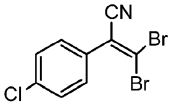
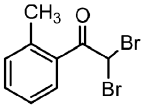
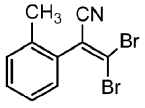
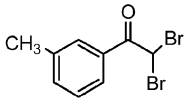
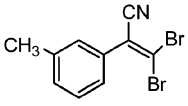
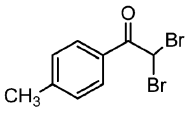
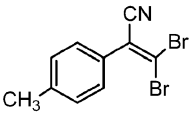
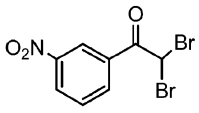
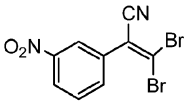
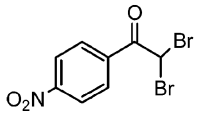
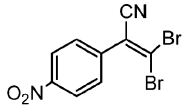
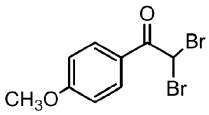
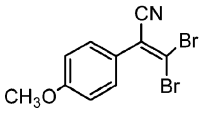
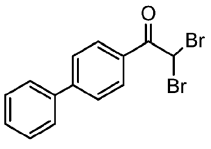
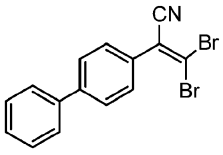
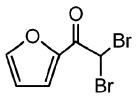
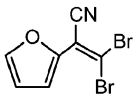
[a] All reactions were carried out by using α,α-dibromoacetophenone (10 mmol) and $K_4[Fe(CN)_6]$ (2.5 mmol). [b] Isolated yield.

Under these optimal conditions, various substituted α,α-dibromoacetophenones were examined for the reactions. The results are summarized in Table 3. It was found that α,α-dibromoacetophenones bearing electron-withdrawing substituents such as chloride and nitro groups on the aromatic ring gave the corresponding products in higher yield (Table 3, Entries 2–4, 8, and 9). In contrast, α,α-dibromoacetophenones bearing electron-donating substituents such as methyl and methoxy groups on the aromatic ring gave the corresponding products in slightly lower yield under similar conditions (Table 3, Entries 5–7, 10). For *ortho*-substituted α,α-dibromoacetophenones (Table 3, Entries 2 and 5), the corresponding products were obtained in slightly lower yield than *para*-substituted α,α-dibromoacetophenones (Table 3, Entries 4 and 7), presumably due to steric effects. The substrate including a heterocycle such as 2,2-dibromo-1-(furan-2-yl)ethanone was also effective for the nucleophilic addition reactions (Table 3, Entry 12).

To examine the effect of the α-bromo group of acetophenone on the reaction rate and reaction yield, the reactions of acetophenone, α-bromoacetophenone, and α,α-dibromoacetophenone with $K_4[Fe(CN)_6]$ were investigated. The results showed that the bromide group played a very important role in the reaction rate and yield. Acetophenone failed to react with $K_4[Fe(CN)_6]$ under the studied condi-

Table 3. Synthesis of 2-aryl-3,3-dibromoacrylonitriles under solvent-free and catalyst-free conditions.

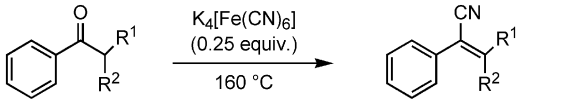


Entry	Substrate	Product	Yield [%][a]
1			88
2			82
3			85
4			90
5			71
6			74
7			78
8			81
9			85
10			76
11			70
12			87

[a] Isolated yield.

tions, even with a prolonged reaction time (Table 4, Entry 1). α-Bromoacetophenone could react with $K_4[Fe(CN)_6]$ to give a mixture of (*E*)- and (*Z*)-2-phenyl-3-bromoacrylonitriles in moderate yield (*E:Z* = 87:13; Table 4, Entry 2). In contrast, α,α-dibromoacetophenone could react with $K_4[Fe(CN)_6]$ more quickly than α-bromoacetophenone to give 2-phenyl-3,3-dibromoacrylonitrile in higher yield (Table 4, Entry 3). This indicated that the more bromide substituents on the methyl group of acetophenone, the more favorable the reactions. This is possibly because the electron-withdrawing effect of the bromide group renders the carbon atom of the carbonyl group more active to the cyanide reagent.

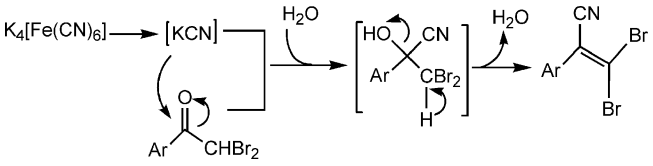
Table 4. The reactions of acetophenone, α-bromoacetophenone, and α,α-dibromoacetophenone with $K_4[Fe(CN)_6]$.[a]



Entry	R^1	R^2	Reaction time [min]	Yield [%][b]
1	H	H	120	NR
2	H	Br	120	42 (*E:Z* = 87:13)
3	Br	Br	20	88

[a] All reactions were carried out by using the substrate (10 mmol) and $K_4[Fe(CN)_6]$ (2.5 mmol). [b] Isolated yield.

The possible mechanism for the nucleophilic addition of α,α-dibromoacetophenones with $K_4[Fe(CN)_6]$ might involve thermal decomposition of $K_4[Fe(CN)_6]$ to form metal cyanides; then, a cyanide anion can selectively attack the carbon atom of the carbonyl of α,α-dibromoacetophenone to yield a cyanohydrin intermediate, which can undergo dehydration to produce 2-aryl-3,3-dibromoacrylonitrile (Scheme 2).



Scheme 2. Possible mechanism for the reaction of α,α-dibromoacetophenones with $K_4[Fe(CN)_6]$.

Conclusions

An efficient and convenient method for the chemoselective cyanation of various substituted α,α-dibromoacetophenones using inexpensive and nontoxic $K_4[Fe(CN)_6]$ as an environmentally benign cyanide source under solvent-free and catalyst-free conditions has developed. A series of 2-aryl-3,3-dibromoacrylonitriles were efficiently synthesized by these nucleophilic additions. These compounds are important intermediates for the further synthesis of various fine chemicals because of their many functional groups, which include cyano and bromide groups, a double bond, and an aromatic ring.[10]

Experimental Section

General Methods: IR spectra were recorded by using KBr pellets with an Alpha Centauri FTIR spectrophotometer, ^1H NMR and ^{13}C NMR spectra were recorded with a Mercury-400BB instrument by using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Elemental analyses were performed with a Vario El Elemental Analysis instrument. Melting points were observed in an electrothermal melting point apparatus. Potassium hexacyanoferrate(II) was dried at 80 °C under vacuum for 24 h and finely powdered prior to use. All reactions were monitored by TLC. Flash column chromatography was carried out by using 200–300 mesh silica gel at increased pressure. α,α-Dibromoacetophenones were synthesized according to standard methods.[11]

General Procedure for the Preparation of 2-Aryl-3,3-dibromoacrylonitriles: A round-bottomed flask equipped with an air condenser was charged with the (un)substituted α,α-dibromoacetophenone (10 mmol) and $K_4[Fe(CN)_6]$ (2.5 mmol). Then, the mixture was heated at 160 °C for 20 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the resulting mixture was extracted with dichloromethane (3 × 10 mL), and the extract was concentrated under reduced pressure. The residue was subjected to silica gel flash column chromatography (petroleum ether/EtOAc, 30:1) to obtain the pure product.

2-Phenyl-3,3-dibromoacrylonitrile (Table 3, Entry 1): White solid. M.p. 62–64 °C. IR (KBr): $\tilde{\nu}$ = 3062, 2923, 2216, 1579, 1487, 1247, 842, 752, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 5 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.3, 130.0, 128.9, 128.5, 122.6, 117.0, 109.7 ppm. $C_9H_5Br_2N$ (286.95): calcd. C 37.67, H 1.76, N 4.88; found C 37.71, H 1.77, N 4.86.

2-(2-Chlorophenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 2): White solid. M.p. 84–86 °C. IR (KBr): $\tilde{\nu}$ = 3069, 2924, 2218, 1554, 1467, 1435, 1287, 1038, 853, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.25 (m, 4 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.8, 132.4, 131.5, 130.4, 130.2, 127.4, 120.3, 115.5, 113.9 ppm. $C_9H_4Br_2ClN$ (321.40): calcd. C 33.63, H 1.25, N 4.36; found C 33.69, H 1.25, N 4.34.

2-(3-Chlorophenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 3): White solid. M.p. 78–80 °C. IR (KBr): $\tilde{\nu}$ = 3061, 2924, 2218, 1570, 1469, 1254, 852, 785 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.35 (m, 4 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 134.7, 130.3, 130.2, 128.6, 126.7, 121.2, 116.6, 111.1 ppm. $C_9H_4Br_2ClN$ (321.40): calcd. C 33.63, H 1.25, N 4.36; found C 33.59, H 1.26, N 4.35.

2-(4-Chlorophenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 4): White solid. M.p. 103–104 °C. IR (KBr): $\tilde{\nu}$ = 2922, 2213, 1590, 1482, 1396, 1095, 831 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 4 H, Ph-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.2, 131.6, 129.9, 129.2, 121.5, 116.7, 110.4 ppm. $C_9H_4Br_2ClN$ (321.40): calcd. C 33.63, H 1.25, N 4.36; found C 33.65, H 1.25, N 4.37.

2-(2-Methylphenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 5): White solid. M.p. 74–76 °C. IR (KBr): $\tilde{\nu}$ = 3062, 2920, 2214, 1546, 1453, 1251, 852, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.18 (m, 4 H, Ar-H), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 133.3, 130.8, 130.2, 128.8, 126.6, 122.4, 116.1, 111.9, 19.3 ppm. $C_{10}H_7Br_2N$ (300.98): calcd. C 39.91, H 2.34, N 4.65; found C 39.86, H 2.35, N 4.63.

2-(3-Methylphenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 6): White solid. M.p. 40–41 °C. IR (KBr): $\tilde{\nu}$ = 3018, 2921, 2214, 1600, 1554, 1095, 850, 789 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 4 H, Ar-H), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 138.8, 133.2, 130.8, 128.9, 128.8, 125.6, 122.7, 117.1, 109.4, 21.3 ppm. $C_{10}H_7Br_2N$ (300.98): calcd. C 39.91, H 2.34, N 4.65; found C 39.95, H 2.34, N 4.67.

2-(4-Methylphenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 7): White solid. M.p. 62–64 °C. IR (KBr): $\tilde{\nu}$ = 3028, 2917, 2220, 1613, 1551, 1505, 1260, 849, 823, 742 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.0 Hz, 2 H, Ar-H), 7.25 (d, J = 8.0 Hz, 2 H, Ar-H), 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 130.4, 129.6, 128.4, 122.6, 117.1, 108.9, 21.4 ppm. $C_{10}H_7Br_2N$ (300.98): calcd. C 39.91, H 2.34, N 4.65; found C 39.96, H 2.35, N 4.66.

2-(3-Nitrophenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 8): White solid. M.p. 158–160 °C. IR (KBr): $\tilde{\nu}$ = 3088, 2924, 2218, 1615, 1531, 1346, 1255, 860, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, Ar-H), 8.33 (d, J = 8.4 Hz, 1 H, Ar-H), 7.84 (d, J = 8.4 Hz, 1 H, Ar-H), 7.69 (t, J = 8.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 134.7, 134.5, 130.3, 124.8, 123.8, 120.3, 116.2, 112.8 ppm. $C_9H_4Br_2N_2O_2$ (331.95): calcd. C 32.56, H 1.21, N 8.44; found C 32.61, H 1.20, N 8.46.

2-(4-Nitrophenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 9): White solid. M.p. 130–132 °C. IR (KBr): $\tilde{\nu}$ = 3104, 2924, 2216, 1600, 1518, 1350, 1294, 858 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 7.2 Hz, 2 H, Ar-H), 7.71 (d, J = 7.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 139.1, 129.9, 124.2, 120.6, 116.2, 112.7 ppm. $C_9H_4Br_2N_2O_2$ (331.95): calcd. C 32.56, H 1.21, N 8.44; found C 32.49, H 1.21, N 8.41.

2-(4-Methoxyphenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 10): White solid. M.p. 136–138 °C. IR (KBr): $\tilde{\nu}$ = 2999, 2939, 2214, 1605, 1508, 1259, 1182, 1021, 829 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.8 Hz, 2 H, Ar-H), 6.94 (d, J = 8.8 Hz, 2 H, Ar-H), 3.84 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 130.1, 125.4, 122.2, 117.1, 114.2, 108.0, 55.3 ppm. $C_{10}H_7Br_2NO$ (316.98): calcd. C 37.89, H 2.23, N 4.42; found C 37.95, H 2.24, N 4.40.

2-(4-Biphenyl)-3,3-dibromoacrylonitrile (Table 3, Entry 11): Brown solid. M.p. 74–76 °C. IR (KBr): $\tilde{\nu}$ = 3063, 2922, 2223, 1600, 1479, 1400, 842, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.42 (m, 9 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 139.1, 132.5, 132.4, 129.0, 128.6, 127.7, 127.2, 122.1, 118.9, 110.8 ppm. $C_{15}H_9Br_2N$ (363.05): calcd. C 49.62, H 2.50, N 3.86; found C 49.69, H 2.49, N 3.88.

2-(Furan-2-yl)-3,3-dibromoacrylonitrile (Table 3, Entry 12): White solid. M.p. 52–54 °C. IR (KBr): $\tilde{\nu}$ = 3153, 2227, 1634, 1534, 1476, 1030, 850, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 1.6 Hz, 1 H, Fu-H), 7.08 (d, J = 4.0 Hz, 1 H, Fu-H), 6.54 (dd, J = 3.6, 1.6 Hz, 1 H, Fu-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 144.2, 115.3, 114.5, 113.5, 112.1, 103.7 ppm. $C_7H_3Br_2NO$ (276.91): calcd. C 30.36, H 1.09, N 5.06; found C 30.29, H 1.08, N 5.08.

Supporting Information (see footnote on the first page of this article): Copies of the IR, ^1H NMR, and ^{13}C NMR spectra of the 2-aryl-3,3-dibromoacrylonitriles.

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