

One-Pot Four-Component Synthesis of 2-Aryl-3,3-Dihaloacrylonitriles using Potassium Hexacyanoferrate(II) as Environmentally Benign Cyanide Source

Zhouxing Zhao and Zheng Li*

Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China

Foi descrita uma rota eficiente para reações em uma etapa com quatro componentes incluindo cloretos de aroila, hexacianoferrato(II) de potássio, trifenilfosfina e tetrahaletos de carbono para sintetizar 2-aril-3,3-dicloroacrilonitrilas e 2-aril-3,3-dibromoacrilonitrilas. Este protocolo tem como vantagens o uso de uma fonte não-tóxica de cianeto, alto rendimento e procedimento experimental simples.

An efficient route to one-pot four-component reactions of aroyl chlorides, potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrahalides to synthesize 2-aryl-3,3-dichloroacrylonitriles and 2-aryl-3,3-dibromoacrylonitriles was described. This protocol has advantages of use of non-toxic cyanide source, high yield and simple work-up procedure.

Keywords: cyanation, four-component synthesis, potassium hexacyanoferrate(II), cyanide source, triphenylphosphine, 2-aryl-3,3-dichloroacrylonitriles, 2-aryl-3,3-dibromoacrylonitriles

Introduction

3,3-Dichloroacrylonitriles and 3,3-dibromoacrylonitriles are well-known as the most important synthetic intermediates.¹ Although 2-aryl-3,3-dichloroacrylonitriles and 2-aryl-3,3-dibromoacrylonitriles could be prepared directly from phosphorus ylides with aroyl cyanides,² the commercially available aroyl cyanides are limited and comparatively expensive. Especially, synthesis of aroyl cyanides had to utilize strong toxic reagents as original cyanide sources, such as HgCN,³ NaCN,⁴ CuCN,⁵ KCN,⁶ and TMSCN,⁷ which render the cyanation of aroyl chlorides unsafe and environmentally unfriendly. In addition, the corresponding phosphorus ylides, which are unstable to oxygen and moisture, also required to synthesize by reactions of triphenylphosphine with carbon tetrahalides prior to use. Therefore, there is a need to explore environmentally benign cyanating agents and simple procedure for the synthesis of 2-aryl-3,3-dichloroacrylonitriles and 2-aryl-3,3-dibromoacrylonitriles.

Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, is non-toxic 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 commercially available on a ton scale and

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

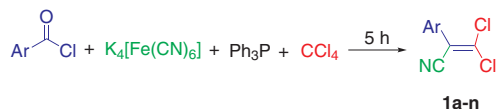
Herein, we wish to report an efficient one-pot four-component synthesis of 2-aryl-3,3-dichloroacrylonitriles and 2-aryl-3,3-dibromoacrylonitriles using potassium hexacyanoferrate(II) as an environmentally benign cyanide source.

Results and Discussion

Initially, the reaction of benzoyl chloride, potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrachloride was selected as a model reaction to examine the feasibility of one-pot four-component synthesis of 2-phenyl-3,3-dichloroacrylonitrile under different conditions (Scheme 1). It was found that the optimal mole ratio of benzoyl chloride to potassium hexacyanoferrate(II) and triphenylphosphine was 1:0.2:2 for the reaction, and the excess carbon tetrachloride were required because it acted both as a reactant and a solvent in this reaction. The 0.2 equivalent of potassium hexacyanoferrate(II) used in the reaction indicated that a small excess of CN^- was utilized in the reaction. The best yield was obtained by the procedure of first conducting the reaction of benzoyl chloride and potassium hexacyanoferrate(II) at 160 °C for 3 h, then further

*e-mail: lizheng@nwnu.edu.cn

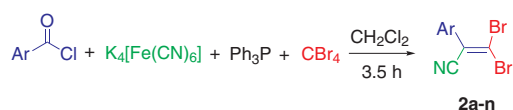
reacting the resulting mixture with triphenylphosphine and carbon tetrachloride at 80 °C for 2 h.



Scheme 1. One-pot synthesis of 2-aryl-3,3-dichloroacrylonitriles.

Under the optimal conditions, various substituted aryl chlorides were examined for the one-pot four-component reactions. The results are summarized in Table 1. It was found that aryl chlorides bearing electron-withdrawing substituents such as chloro, iodo and nitro groups on the aromatic ring gave the corresponding products in high yield (**1b-1d**, **1i**, **1j** and **1m**). In contrast, aryl chlorides bearing electron-donating substituents such as methyl, ethyl, methoxy and ethoxy groups on the aromatic ring gave the corresponding products in slightly lower yield under similar conditions (**1e-1h**, **1k** and **1l**). For *ortho*-substituted aryl chlorides, the corresponding products were obtained in slightly lower yield than *para*-substituted ones, presumably due to the steric effect (**1b**, **1e** and **1h**). Heteroaryl chloride, furyl chloride, was also very efficient for the one-pot four-component reaction (**1n**).

In addition, one-pot four-component reactions of aryl chlorides, potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrabromide to synthesize various 2-aryl-3,3-dibromoacrylonitriles were also investigated (Scheme 2). In comparison with carbon tetrachloride, carbon tetrabromide is more active for the one-pot four-component reaction. Therefore milder conditions are required, such as lower reaction temperature and short reaction time although solvent is needed because carbon tetrabromide can not act as a solvent at low temperatures. The optimal conditions for the selected four-component reaction of benzoyl chloride, potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrabromide were also investigated. It was found that the optimal mole ratio of benzoyl chloride to potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrabromide was 1:0.2:2:1 for the reaction, and the best yield was obtained by the procedure of first conducting the reaction of benzoyl chloride and potassium hexacyanoferrate(II) at 160 °C for 3 h, then further reacting the resulting mixture with triphenylphosphine and carbon tetrabromide in methylene chloride at 10 °C for 0.5 h.



Scheme 2. One-pot synthesis of 2-aryl-3,3-dibromoacrylonitriles.

Table 1. One-pot four-component synthesis of various 2-aryl-3,3-dichloroacrylonitriles

Compd.	Aroyl chloride	Product	Yield ^a (%)	mp (lit.) (°C)
1a			75	Oil (Oil) ²
1b			78	104-105
1c			80	54-56
1d			81	83-84 (84.5-85) ²
1e			67	Oil
1f			71	Oil (Oil) ²
1g			73	Oil
1h			68	Oil
1i			79	137-139
1j			80	128-130
1k			75	102-104
1l			72	106-108 (107.5-108) ²
1m			79	68-69
1n			81	100-102

^a Isolated yields.

Under the optimal conditions, various substituted aroyl chlorides were examined for the reactions. The results are summarized in Table 2. The various substituted aroyl chlorides including electron-withdrawing groups and electron-donating groups are effective for the reactions, which have the similar effect on the yield to carbon tetrachloride. It is noteworthy to mention that 4-phenylbenzoyl chloride and isophthaloyl dichloride could also efficiently participate in the one-pot four-component reactions of carbon tetrabromide, but not for the reactions of carbon tetrachloride under the studied conditions (**2l** and **2m**). Heteroaroyl chloride, furoyl chloride, was also very efficient for the one-pot four-component reaction to obtain 2-(furan-2-yl)-3,3-dibromoacrylonitrile (**2n**).

Conclusions

An efficient route to the one-pot four-component reactions of aroyl chlorides, potassium hexacyanoferrate(II), triphenylphosphine and carbon tetrahalides to synthesize 2-aryl-3,3-dichloroacrylonitriles and 2-aryl-3,3-dibromoacrylonitriles has been developed. The protocol has the advantages of using non-toxic potassium hexacyanoferrate(II) as an environmentally benign cyanide source instead of traditional strong toxic cyanating agents, high yield and simple work-up procedure.

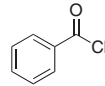
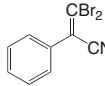
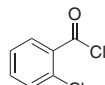
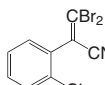
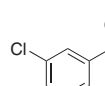
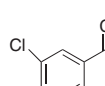
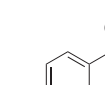
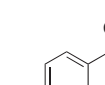
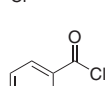
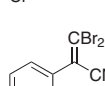
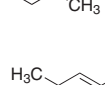
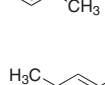
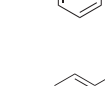
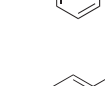
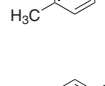
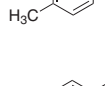
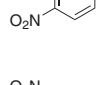
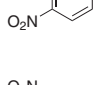
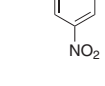
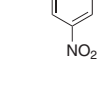
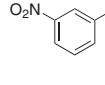
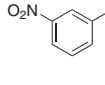
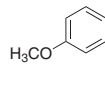
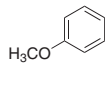
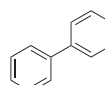
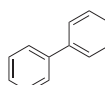
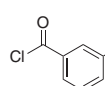
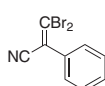
Experimental

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer and ^1H NMR and ^{13}C NMR spectra on a Mercury-400BB instrument using CDCl_3 as solvent and Me_4Si as internal standard. Melting points were observed in an electrothermal melting point apparatus. Potassium hexacyanoferrate(II) 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 using 200-300 mesh silica gel at increased pressure.

General procedure for the preparation of 2-aryl-3,3-dichloroacrylonitriles

The mixture of aroyl chloride (10 mmol) and potassium hexacyanoferrate(II) (0.84 g, 2 mmol) was heated at 160°C for 3 h. After cooling to room temperature, triphenylphosphine (5.24 g, 20 mmol) and carbon tetrachloride (10 mL) were added. The resulting mixture was further stirred at 80°C for 2 h. Then the solid was removed by filtration, and the filtrate was evaporated to

Table 2. One-pot four-component synthesis of various 2-aryl-3,3-dibromoacrylonitriles

Compd.	Aroyl chloride	Product	Yield ^a (%)	mp ($^\circ\text{C}$)
2a			75	62-64
2b			78	84-86
2c			80	78-80
2d			82	103-104
2e			72	74-76
2f			75	40-41
2g			77	74-76
2h			80	130-132
2i			83	88-90
2j			78	158-160
2k			77	136-138
2l			68	74-76
2m			84	156-158
2n			82	52-53

^a Isolated yields.

remove solvent under reduced pressure, and the residue was subjected to silica gel flash column chromatography (ethyl acetate, petroleum ether, 1:40, v/v) to obtain pure product. The analytical and spectral data for products are given below; melting points are given in Table 1.

2-Phenyl-3,3-dichloroacrylonitrile (**Ia**)

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.52-7.41 (m, 5H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 137.1, 130.6, 130.0, 128.8, 128.6, 115.5, 108.2; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3061, 2922, 2223, 1563, 1445, 930, 824, 759, 695. Found: C, 54.65; H, 2.53; N, 7.10. Calc. for $\text{C}_9\text{H}_5\text{Cl}_2\text{N}$: C, 54.58; H, 2.54; N, 7.07%.

2-(2-Chlorophenyl)-3,3-dichloroacrylonitrile (**Ib**)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.60-7.31 (m, 4H, Ar-H), $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 132.9, 132.4, 131.5, 130.4, 130.2, 127.4, 120.4, 115.6, 113.9; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3042, 2999, 2219, 1604, 1510, 1256, 927, 825. Found: C, 46.55; H, 1.72; N, 6.04. Calc. for $\text{C}_9\text{H}_4\text{Cl}_3\text{N}$: C, 46.49; H, 1.73; N, 6.02%.

2-(3-Chlorophenyl)-3,3-dichloroacrylonitrile (**Ic**)

Light yellow solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.52 (s, 1H, Ar-H), 7.44-7.39 (m, 3H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 138.6, 134.9, 132.2, 130.3, 130.2, 128.8, 126.9, 115.1, 114.3; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3062, 2926, 2220, 1571, 1471, 1262, 943, 850. Found: C, 46.42; H, 1.73; N, 5.99. Calc. for $\text{C}_9\text{H}_4\text{Cl}_3\text{N}$: C, 46.49; H, 1.73; N, 6.02%.

2-(4-Chlorophenyl)-3,3-dichloroacrylonitrile (**Id**)

Light yellow solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.48-7.40 (m, 4H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 137.7, 136.2, 130.0, 129.1, 129.0, 115.2, 114.5; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3084, 2924, 2220, 1555, 1481, 1279, 927, 809. Found: C, 46.45; H, 1.72; N, 6.01. Calc. for $\text{C}_9\text{H}_4\text{Cl}_3\text{N}$: C, 46.49; H, 1.73; N, 6.02%.

2-(2-Methylphenyl)-3,3-dichloroacrylonitrile (**Ie**)

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.22-7.00 (m, 4H, Ar-H), 2.16 (s, 3H, CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 138.5, 136.1, 130.4, 130.0, 129.9, 128.7, 126.2, 114.7, 114.2, 18.8; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3067, 2925, 2219, 1571, 1485, 1258, 930, 753. Found: C, 56.53; H, 3.32; N, 6.62. Calc. for $\text{C}_{10}\text{H}_7\text{Cl}_2\text{N}$: C, 56.63; H, 3.33; N, 6.60%.

2-(3-Methylphenyl)-3,3-dichloroacrylonitrile (**If**)

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.28-7.20 (m, 4H, Ar-H), 2.35 (s, 3H, CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 138.5, 136.6, 130.6, 130.4, 128.9, 128.5, 125.5, 115.5, 115.4, 21.0; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3039, 2923, 2222, 1565, 1485, 1267,

931, 877, 791, 697. Found: C, 56.56; H, 3.34; N, 6.56. Calc. for $\text{C}_{10}\text{H}_7\text{Cl}_2\text{N}$: C, 56.63; H, 3.33; N, 6.60%.

2-(4-Methylphenyl)-3,3-dichloroacrylonitrile (**Ig**)

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.37 (d, 2H, J 8.4 Hz, Ar-H), 7.19 (d, 2H, J 8.4 Hz, Ar-H), 2.32 (s, 3H, CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 140.0, 135.7, 129.2, 128.2, 127.4, 115.3, 115.2, 20.9; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3031, 2923, 2222, 1573, 1509, 1258, 929, 815, 771. Found: C, 56.70; H, 3.32; N, 6.57. Calc. for $\text{C}_{10}\text{H}_7\text{Cl}_2\text{N}$: C, 56.63; H, 3.33; N, 6.60%.

2-(2-Ethylphenyl)-3,3-dichloroacrylonitrile (**Ih**)

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.25-6.97 (m, 4H, Ar-H), 2.88 (q, 2H, J 6.4 Hz, CH_2), 1.26 (t, 3H, J 6.4 Hz, CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 143.1, 129.1, 129.0, 128.8, 124.7, 124.1, 121.6, 120.3, 119.2, 25.6, 14.3; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3032, 2918, 2224, 1589, 1497, 1234, 942, 842. Found: C, 58.50; H, 3.99; N, 6.20. Calc. for $\text{C}_{11}\text{H}_9\text{Cl}_2\text{N}$: C, 58.43; H, 4.01; N, 6.19%.

2-(3-Nitrophenyl)-3,3-dichloroacrylonitrile (**Ii**)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.45 (s, 1H, Ar-H), 8.33 (d, 1H, J 8.0 Hz, Ar-H), 7.87 (d, 1H, J 8.0 Hz, Ar-H), 7.70 (t, 1H, J 8.0 Hz, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 148.2, 140.1, 134.6, 132.2, 130.2, 124.9, 123.9, 114.7, 113.4; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3081, 2924, 2223, 1614, 1532, 1348, 1263, 947. Found: C, 44.55; H, 1.67; N, 11.57. Calc. for $\text{C}_9\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$: C, 44.48; H, 1.66; N, 11.53%.

2-(4-Nitrophenyl)-3,3-dichloroacrylonitrile (**Ij**)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.33 (d, J 9.2 Hz, 2H, Ar-H), 7.74 (d, 2H, J 9.2 Hz, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 148.3, 140.2, 136.7, 130.0, 124.1, 114.7, 113.8; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3049, 2923, 2235, 1555, 1481, 1377, 1226, 1024, 939, 748. Found: C, 44.45; H, 1.66; N, 11.49. Calc. for $\text{C}_9\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$: C, 44.48; H, 1.66; N, 11.53%.

2-(4-Ethoxyphenyl)-3,3-dichloroacrylonitrile (**Ik**)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.46 (d, 2H, J 8.8 Hz, Ar-H), 6.93 (d, 2H, J 8.8 Hz, Ar-H), 4.06 (q, 2H, J 6.8 Hz, CH_2), 1.43 (t, 3H, J 6.8 Hz, CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.0, 135.3, 130.2, 122.6, 115.8, 115.2, 114.6, 63.6, 14.6; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3059, 2988, 2218, 1606, 1510, 1265, 924. Found: C, 54.50; H, 3.77; N, 5.80. Calc. for $\text{C}_{11}\text{H}_9\text{Cl}_2\text{NO}$: C, 54.57; H, 3.75; N, 5.79%.

2-(4-Methoxyphenyl)-3,3-dichloroacrylonitrile (**Il**)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.48 (d, 2H, J 9.2 Hz, Ar-H), 6.95 (d, 2H, J 9.2 Hz, Ar-H), 3.84

(s, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 160.7, 135.4, 130.2, 122.8, 115.7, 115.2, 114.2, 55.3; IR (KBr) ν_{\max} /cm⁻¹: 3067, 2988, 2218, 1589, 1465, 1287, 854, 765. Found: C, 52.59; H, 3.07; N, 6.17. Calc. for C₁₀H₇Cl₂NO: C, 52.66; H, 3.09; N, 6.14%.

2-(4-Iodophenyl)-3,3-dichloroacrylonitrile (**1m**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.79 (d, 2H, *J* 8.8 Hz, Ar-H), 7.26 (d, 2H, *J* 8.8 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.1, 137.8, 130.3, 130.1, 115.2, 114.7, 96.6; IR (KBr) ν_{\max} /cm⁻¹: 3065, 2220, 1572, 1481, 1288, 1276, 933, 834. Found: C, 33.41; H, 1.23; N, 4.31. Calc. for C₉H₄Cl₂IN: C, 33.37; H, 1.24; N, 4.32%.

2-(Furan-2-yl)-3,3-dichloroacrylonitrile (**1n**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.76 (d, 1H, *J* 1.6 Hz, Fu-H), 7.04 (d, 1H, *J* 4.4 Hz, Fu-H), 6.41 (dd, 1H, *J* 3.6 Hz, *J* 1.6 Hz, Fu-H), ¹³C NMR (CDCl₃, 100 MHz): δ 148.3, 140.2, 136.6, 130.0, 124.1, 114.7, 113.8; IR (KBr) ν_{\max} /cm⁻¹: 3109, 2923, 2220, 1520, 1350, 931, 858, 817, 698. Found: C, 44.66; H, 1.62; N, 7.43. Calc. for C₇H₃Cl₂NO: C, 44.72; H, 1.61; N, 7.45%.

General procedure for the preparation of 2-aryl-3,3-dibromoacrylonitriles

The mixture of aroyl chloride (10 mmol) and potassium hexacyanoferrate(II) (0.84 g, 2 mmol) was heated at 160 °C for 3 h. After cooling to 10 °C, triphenylphosphine (5.24 g, 20 mmol) and carbon tetrabromide (3.31 g, 10 mmol) in 10 mL of methylene chloride was slowly added dropwise with stirring. The resulting mixture was further stirred at 10 °C for 0.5 h. Then the solid was removed by filtration, and the filtrate was evaporated to remove solvent under reduced pressure, and the residue was subjected to silica gel flash column chromatography (ethyl acetate, petroleum ether, 1:40, v/v) to obtain pure product. The analytical and spectral data for products are given below; melting points are given in Table 2.

2-Phenyl-3,3-dibromoacrylonitrile (**2a**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.45 (m, 5H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 133.3, 130.0, 128.9, 128.5, 122.6, 117.0, 109.7; IR (KBr) ν_{\max} /cm⁻¹: 3062, 2923, 2216, 1443, 842. Found: C, 37.71; H, 1.77; N, 4.86. Calc. for C₉H₅Br₂N: C, 37.67; H, 1.76; N, 4.88%.

2-(2-Chlorophenyl)-3,3-dibromoacrylonitrile (**2b**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.31 (m, 4H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 132.8,

132.4, 131.5, 130.4, 130.2, 127.4, 120.3, 115.5, 113.9; IR (KBr) ν_{\max} /cm⁻¹: 3069, 2924, 2218, 1554, 1467, 11435, 1287, 1038, 853, 750. Found: C, 33.69; H, 1.25; N, 4.34. Calc. for C₉H₄Br₂CIN: C, 33.63; H, 1.25; N, 4.36%.

2-(3-Chlorophenyl)-3,3-dibromoacrylonitrile (**2c**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.35 (m, 4H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 134.9, 134.7, 130.3, 130.2, 128.6, 126.7, 121.2, 116.6, 111.1; IR (KBr) ν_{\max} /cm⁻¹: 3065, 2927, 2218, 1589, 1434, 1282, 981, 848, 751. Found: C, 33.59; H, 1.26; N, 4.35. Calc. for C₉H₄Br₂CIN: C, 33.63; H, 1.25; N, 4.36%.

2-(4-Chlorophenyl)-3,3-dibromoacrylonitrile (**2d**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.43 (s, 4H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 136.2, 131.6, 129.9, 129.2, 121.5, 116.7, 110.4; IR (KBr) ν_{\max} /cm⁻¹: 2922, 2213, 1590, 1482, 1095, 831. Found: C, 33.65; H, 1.25; N, 4.38. Calc. for C₉H₄Br₂CIN: C, 33.63; H, 1.25; N, 4.36%.

2-(2-Methylphenyl)-3,3-dibromoacrylonitrile (**2e**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.37-7.18 (m, 4H, Ar-H), 2.33 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 136.1, 133.3, 130.8, 130.2, 128.8, 126.6, 122.4, 116.1, 111.9, 19.3; IR (KBr) ν_{\max} /cm⁻¹: 3062, 2920, 2214, 1546, 1453, 1251, 852, 735. Found: C, 39.86; H, 2.35; N, 4.63. Calc. for C₁₀H₇Br₂N: C, 39.91; H, 2.34; N, 4.65%.

2-(3-Methylphenyl)-3,3-dibromoacrylonitrile (**2f**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.34-7.24 (m, 4H, Ar-H), 2.39 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 138.8, 133.2, 130.8, 128.9, 128.8, 125.6, 122.7, 117.1, 109.4, 21.3; IR (KBr) ν_{\max} /cm⁻¹: 3018, 2921, 2214, 1600, 1554, 1095, 850, 789. Found: C, 39.95; H, 2.34; N, 4.67. Calc. for C₁₀H₇Br₂N: C, 39.91; H, 2.34; N, 4.65%.

2-(4-Methylphenyl)-3,3-dibromoacrylonitrile (**2g**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.23 (m, 4H, Ar-H), 2.38 (s, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 140.4, 130.4, 129.6, 128.4, 122.6, 117.1, 108.9, 21.4; IR (KBr) ν_{\max} /cm⁻¹: 3028, 2917, 2220, 1613, 1551, 1505, 1260, 849, 823. Found: C, 39.96; H, 2.35; N, 4.66. Calc. for C₁₀H₇Br₂N: C, 39.91; H, 2.34; N, 4.65%.

2-(4-Nitrophenyl)-3,3-dibromoacrylonitrile (**2h**)

White solid; ¹H NMR (CDCl₃, 400 MHz): δ 8.32 (d, 2H, *J* 7.2 Hz, Ar-H), 7.71 (d, 2H, *J* 7.2 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 148.3, 139.1, 129.9, 124.2, 120.6, 116.2, 112.7; IR (KBr) ν_{\max} /cm⁻¹: 3104, 2924, 2216, 1600, 1518, 1350, 1294, 858. Found: C, 32.49; H, 1.21; N, 8.41. Calc. for C₉H₄Br₂N₂O₂: C, 32.56; H, 1.21; N, 8.44%.

2-(3,5-Dinitrophenyl)-3,3-dibromoacrylonitrile (2i)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 9.13 (s, 1H, Ar-H), 8.74 (s, 2H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 148.7, 136.3, 129.0, 128.9, 120.0, 118.4, 115.6; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3094, 2983, 2224, 1627, 1543, 1344, 1279, 918, 853, 729. Found: C, 28.73; H, 0.80; N, 11.11. Calc. for $\text{C}_9\text{H}_3\text{Br}_2\text{N}_3\text{O}_4$: C, 28.68; H, 0.80; N, 11.15%.

2-(3-Nitrophenyl)-3,3-dibromoacrylonitrile (2j)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.41 (s, 1H, Ar-H), 8.33 (d, 1H, J 8.4 Hz, Ar-H), 7.84 (d, 1H, J 8.4 Hz, Ar-H), 7.69 (t, 1H, J 8.4 Hz, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 148.3, 134.7, 134.5, 130.3, 124.8, 123.8, 120.3, 116.2, 112.8; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3104, 2924, 2216, 1600, 1518, 1350, 1294, 858. Found: C, 32.61; H, 1.20; N, 8.46. Calc. for $\text{C}_9\text{H}_4\text{Br}_2\text{N}_2\text{O}_2$: C, 32.56; H, 1.21; N, 8.44%.

2-(4-Methoxyphenyl)-3,3-dibromoacrylonitrile (2k)

IR $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.44 (d, 2H, J 9.2 Hz, Ar-H), 6.94 (d, 2H, J 9.2 Hz, Ar-H), 3.84 (s, 3H, CH_3). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.6, 130.1, 125.4, 122.2, 117.1, 114.2, 108.0, 55.3. (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2999, 2939, 2214, 1605, 1508, 1259, 1182, 1021, 829. Found: C, 37.95; H, 2.22; N, 4.41. Calc. for $\text{C}_{10}\text{H}_7\text{Br}_2\text{NO}$: C, 37.89; H, 2.23; N, 4.42%.

2-(4-Biphenyl)-3,3-dibromoacrylonitrile (2l)

Brown solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.74-7.42 (m, 9H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.9, 127.7, 127.2, 122.1, 118.9, 110.8; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3063, 2922, 2223, 1600, 1479, 1400, 842, 767. Found: C, 49.69; H, 2.49; N, 3.87. Calc. for $\text{C}_{15}\text{H}_9\text{Br}_2\text{N}$: C, 49.62; H, 2.50; N, 3.86%.

1,3-bis(2,2-dibromo-1-cyanovinyl)benzene (2m)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.75-7.42 (m, 4H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 133.3, 132.4, 132.3, 132.2, 131.5, 128.5, 128.4; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3055, 2923, 2200, 1636, 1479, 1433, 1102, 713, 514. Found: C, 29.14; H, 0.81; N, 5.63. Calc. for $\text{C}_{12}\text{H}_4\text{Br}_4\text{N}_2$: C, 29.07; H, 0.81; N, 5.65%.

2-(Furan-2-yl)-3,3-dibromoacrylonitrile (2n)

White solid; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.58 (d, 1H, J 1.6 Hz, Fu-H), 7.08 (d, 1H, J 4.0 Hz, Fu-H), 6.54 (dd, 1H, J 3.6 Hz, J 1.6 Hz, Fu-H), $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 145.9, 144.2, 115.3, 114.5, 113.5, 112.1, 103.7. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3153, 2227, 1476, 1030, 850, 750. Found: C, 30.29; H, 1.08; N, 5.08. Calc. for $\text{C}_7\text{H}_3\text{Br}_2\text{NO}$: C, 30.36; H, 1.09; N, 5.06%.

Supplementary Information

Full set of IR, $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra are available free of charge at <http://jbc.ssbj.org.br>, as pdf file.

Acknowledgments

The authors thank the National Natural Science Foundation of China (20772096), and Key Laboratory of Eco-Environment-Related Polymer Materials (Northwest Normal University), Ministry of Education of China for the financial support of this work.

References

- Shablykin, O. V.; Gakh, A. A.; Brovarets, V. S.; Rusanov, E. B.; Drach, B. S.; *Heteroat. Chem.* **2008**, *9*, 506; Shablykin, O. V.; Brovarets, V. S.; Drach, B. S.; *Russ. J. Gen. Chem.* **2007**, *77*, 1308; Brovarets, V. S.; Pilyo, S. G.; Chernega, A. N.; Romanenko, E. A.; Drach, B. S.; *Russ. J. Gen. Chem.* **1999**, *69*, 1577; Popil' nichenko, S. V.; Brovarets, V. S.; Chernega, A. N.; Poltorak, D. V.; Drach, B. S.; *Heteroat. Chem.* **2006**, *17*, 411; Golovchenko, O. V.; Pilyo, S. G.; Brovarets, V. S.; Chernega, A. N.; Drach, B. S.; *Heteroat. Chem.* **2004**, *15*, 454; Pilyo, S. G.; Brovarets, V. S.; Vinogradova, T. K.; Golovchenko, A. V.; Drach, B. S.; *Russ. J. Gen. Chem.* **2002**, *72*, 1714; Kozachenko, A. P.; Shablykin, O. V.; Vasilenko, A. N.; Brovarets, V. S.; *Russ. J. Gen. Chem.* **2010**, *80*, 127; Kozachenko, A. P.; Shablykin, O. V.; Rusanov, E. B.; Vasilenko, A. N.; Brovarets, V. S.; *Russ. J. Gen. Chem.* **2009**, *79*, 996.
- Soulen, R. L.; Carlson, S. C.; Lang, F.; *J. Org. Chem.* **1973**, *38*, 479; Clement, B. A.; Soulen, R. L.; *J. Org. Chem.* **1974**, *39*, 97; Clement, B. A.; Soulen, R. L.; *J. Org. Chem.* **1976**, *41*, 556; Sepiol, J. J.; Sepiol, J. A.; Soulen, R. L.; *J. Org. Chem.* **1984**, *49*, 1125.
- Haase, K.; Hoffmann, H. M.; *Angew. Chem., Int. Ed.* **1982**, *21*, 83.
- Kazuaki, S.; *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1085.
- Oakwood, T. S.; Weisgerber, C. A.; *Org. Synth.* **1955**, *24*, 14.
- Patricinio, A. F.; Moran, P. J. S.; *J. Braz. Chem. Soc.* **2001**, *12*, 7; Cao, Y. Q.; Du, Y. F.; Chen, B. H.; Li, J. T.; *Synth. Commun.* **2004**, *34*, 2951.
- Harle, H.; Jochims, J. C.; *Chem. Ber.* **1986**, *119*, 1400; Zeng, W.; Yang, J.; Meng, B.; Zhang, B.; Jiang, M.; Chen, F. X.; *Lett. Org. Chem.* **2009**, *6*, 637.
- Schareina, T.; Zapf, A.; Beller, M.; *J. Organomet. Chem.* **2004**, *689*, 4576; Schareina, T.; Zapf, A.; Beller, M.; *Chem. Commun.* **2004**, 1388; Schareina, T.; Zapf, A.; Beller, M.; *Tetrahedron Lett.* **2005**, *46*, 2585; Schareina, T.; Zapf, A.; Magerlein, W.; Muller, N.; Beller, M.; *Tetrahedron Lett.* **2007**, *48*, 1087; Weissman, S. A.; Zewge, D.; Chen, C.; *J. Org. Chem.* **2005**, *70*, 1508; Grossman,

O.; Gelman, D.; *Org. Lett.* **2006**, *8*, 1189; Li, L. H.; Pan, Z. L.; Duan, X. H.; Liang, Y. M.; *Synlett* **2006**, 2094; Velmathi, S.; Leadbeater, N. E.; *Tetrahedron Lett.* **2008**, *49*, 4693; Chen, G.; Weng, J.; Zheng, Z.; Zhu, X.; Cai, Y.; Cai, J.; Wan, Y.; *Eur. J. Org. Chem.* **2008**, 3524; Cheng, Y. N.; Duan, Z.; Yu, L. J.; Li, Z. X.; Zhu, Y.; Wu, Y. J.; *Org. Lett.* **2008**, *10*, 901; Franz, A. W.; Popa, L. N.; Muller, T. J. J.; *Tetrahedron Lett.* **2008**, *49*, 3300; Ren, Y.

L.; Liu, Z. F.; He, S. B.; Zhao, S.; Wang, J. J.; Niu, R. Q.; Yin, W. P.; *Org. Process Res. Dev.* **2009**, *13*, 764.
9. Li, Z.; Shi, S. Y.; Yang, J. Y.; *Synlett* **2006**, 2495.

Submitted: April 27, 2010

Published online: September 8, 2010