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One-Pot Multi-Component Synthesis of Triarylacrylonitriles Direct Using CaC_2 as a Concise Acetylene Source and $K_4[Fe(CN)_6]$ as an Eco-Friendly Cyanide Source

Geyang Song[a] and Zheng Li*[a]

Abstract: An efficient method for the one-pot multicomponent synthesis of triarylacrylonitriles from various aryl iodides direct using calcium carbide as a concise acetylene source and potassium hexacyanoferrate(II) as an eco-friendly cyanide source is described. This protocol has the features of use of safe, inexpensive and easy-to-handle starting materials, good substrate tolerance and simple work-up procedure.

Introduction

Triarylacrylonitriles are of importance in medicinal chemistry because of their biological activities and their applications in the synthesis of biologically active compounds.[1] For example, some triarylacrylonitriles can inhibit the growth of certain tumors (breast and prostate cancer), and can also be used to synthesize resveratrol, which suppresses the growth of a number of tumor cell lines including those derived from colorectal, liver, breast, pancreatic, and prostate tumors.[2] In addition, triarylacrylonitriles also have comprehensive synthetic applications in organic and material chemistry.[3] Over the years, various methods have been developed to synthesize triarylacrylonitriles.[4] The general methods include i) the reactions of diaryl ketones with arylacetonitriles. However, the arylacetonitriles used in this method must be synthesized using the strong toxic NaCN[5] and HCN,[6] etc.; ii) the reactions of diarylacetylenes, aryl bromides and potassium hexacyanoferrate(II). However, the diarylacetylenes were generally synthesized from highly flammable, complicated handling acetylene gas.[7] Therefore it is necessary to explore a more concise approach to synthesize triarylacrylonitriles.

Calcium carbide, CaC_2, is a stable and inexpensive solid, which is extensively used as a raw material to produce acetylene gas by hydrolysis in chemical industry. The recent reports have revealed that calcium carbide can be directly used as a sustainable, easy-to-handle, and low-cost feedstock, and efficient source of acetylene for *in situ* chemical transformations.[8]

Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, is a byproduct of the coal chemical industry and commercially available on a ton scale. It is also used in the food industry for metal precipitation. In addition, it has been described as an antiagglutinating auxiliary for table salt (NaCl). Recently, $K_4[Fe(CN)_6]$ has been used as an eco-friendly cyanide source for some organic reactions to synthesize important compounds bearing cyano groups.[9]

Our recent research interests focused on the use of CaC_2 and $K_4[Fe(CN)_6]$ in the organic synthesis, respectively, and reported the synthesis of 1,3,5-triaroylcyclohexanes[10] and *N*-propargylation of secondary amines[11] directly using CaC_2 as an acetylene source, and the cyanation of unsaturated compounds including C=O, C=N and/or C=C bonds by nucleophilic addition reactions using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source.[12]

In this work, we report an efficient method for the simultaneous use of CaC_2 as a concise acetylene source and $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source in one reaction to synthesize triarylacrylonitriles from various aryl iodides by one-pot multi-component procedure. To the best our knowledge, this is the first example to utilize both CaC_2 and $K_4[Fe(CN)_6]$ in one organic reaction.

Results and Discussion

In the initial research, the reaction of iodobenzene, CaC_2 and $K_4[Fe(CN)_6]$ was selected as a model reaction to examine the feasibility for the synthesis of 2,3,3-triphenylacrylonitrile (**1**). Different catalysts, bases and solvents were screened for the model reaction (Table 1). It was found that Pd(II) catalysts, such as $Pd(OAc)_2$, $PdCl_2$ and $Pd(PPh_3)_2Cl_2$, could catalyze the reaction to give **1** in medium to good yield (Table1, entries 1−3). Pd(0) complex, for example $Pd(PPh_3)_4$, did not exhibit catalytic effect on the reaction (Table 1, entry 4). In comparison, $Pd(PPh_3)_2Cl_2$ as a catalyst could give better yield (Table 1, entry 3).

Bases played a prominent role in the reaction. Some organic bases, such as Et_3N, DBU, DMAP and DABCO, and some inorganic bases, such as NaOH, KOH, Na_2CO_3 and K_2CO_3, were tested (Table 1, entries 5−12). Most of them exhibited low activities. Especially only low yield of the desired product **1** were obtained when Et_3N and Na_2CO_3 alone were used as bases (Table 1, entries 5, 11). However, the later research showed that the combination of Et_3N/Na_2CO_3 as bases was observed to give high yield (Table 1, entry 3). In addition, the molar ratio of Et_3N over Na_2CO_3 could also influence the product yield (Table 1, entries 17−19). The highest yield was obtained by using 2:1 of Et_3N over Na_2CO_3 (Table 1, entry 17).

Solvents also had certain effect on the yield of **1**. The reaction in DMSO, PhMe, and 1,4-dioxane almost could not give product **1** (Table 1, entries 13−15). DMAc was selectable solvent

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[a] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, People's Republic of China.
E-mail: lizheng@nwnu.edu.cn

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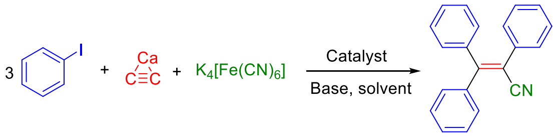
(Table 1, entry 16). In contrast, DMF could afford the highest yield (Table 1, entry 17).

Table 1. The effect of reaction conditions on the yield of **1**[a]

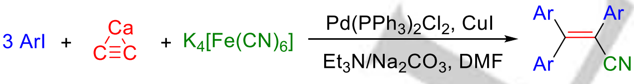


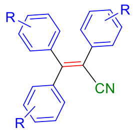
1

Entry	Catalyst	Solvent	Base	Yield (%)[b]
1[c]	Pd(OAc)$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	62
2[c]	PdCl$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	43
3[c]	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	69
4[c]	Pd(PPh$_3$)$_4$	DMF	Et$_3$N/Na$_2$CO$_3$	0
5	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Et$_3$N	25
6	Pd(PPh$_3$)$_2$Cl$_2$	DMF	DBU	Trace
7	Pd(PPh$_3$)$_2$Cl$_2$	DMF	DMAP	Trace
8	Pd(PPh$_3$)$_2$Cl$_2$	DMF	DABCO	Trace
9	Pd(PPh$_3$)$_2$Cl$_2$	DMF	NaOH	0
10	Pd(PPh$_3$)$_2$Cl$_2$	DMF	KOH	0
11	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Na$_2$CO$_3$	16
12	Pd(PPh$_3$)$_2$Cl$_2$	DMF	K$_2$CO$_3$	Trace
13[c]	Pd(PPh$_3$)$_2$Cl$_2$	DMSO	Et$_3$N/Na$_2$CO$_3$	Trace
14[c]	Pd(PPh$_3$)$_2$Cl$_2$	PhMe	Et$_3$N/Na$_2$CO$_3$	0
15[c]	Pd(PPh$_3$)$_2$Cl$_2$	1,4-Dioxane	Et$_3$N/Na$_2$CO$_3$	Trace
16[c]	Pd(PPh$_3$)$_2$Cl$_2$	DMAc	Et$_3$N/Na$_2$CO$_3$	56
17[d]	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	77
18[e]	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	71
19[f]	Pd(PPh$_3$)$_2$Cl$_2$	DMF	Et$_3$N/Na$_2$CO$_3$	53

[a] Reaction condition: Iodobenzene (1.5 mmol), K$_4$[Fe(CN)$_6$] (0.1 mmol), CaC$_2$ (1.0 mmol), H$_2$O (0.5 mmol), base (0.5 mmol), palladium catalyst (0.01 mmol) and CuI (0.1 mmol) in 3 mL of solvent under nitrogen atmosphere stirred first at room temperature for 8 h, then at 110 °C for 4 h. [b] Isolated yield. [c] Et$_3$N/Na$_2$CO$_3$ (0.5 mmol/0.5 mmol). [d] Et$_3$N/Na$_2$CO$_3$ (1 mmol/0.5 mmol). [e] Et$_3$N/Na$_2$CO$_3$ (1 mmol/1 mmol). [f] Et$_3$N/Na$_2$CO$_3$ (1.5 mmol/0.5 mmol).

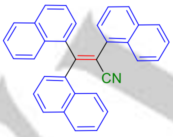
Table 2. One-pot one-step synthesis of 2,3,3-triarylacrylonitriles using single aryl iodide for one reaction[a]



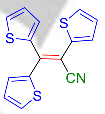


1-11

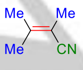
1: R= H 77%
2: R= *o*-CH$_3$ 73%
3: R= *m*-CH$_3$ 71%
4: R= *p*-CH$_3$ 74%
5: R= *m*-OCH$_3$ 38%
6: R= *p*-OCH$_3$ 33%
7: R= *p*-F 43%
8: R= *p*-CF$_3$ 36%
9: R= *o*-Cl 69%
10: R= *m*-Cl 72%
11: R= *o*-Br 68%



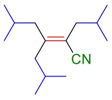
12 78%



13 47%



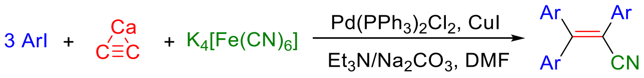
0 %

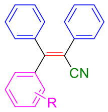


0 %

[a] Reaction condition: ArI (1.5 mmol), K$_4$[Fe(CN)$_6$] (0.1 mmol), CaC$_2$ (1.0 mmol), Et$_3$N (1.0 mmol), Na$_2$CO$_3$ (0.5 mmol), H$_2$O (0.5 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.01 mmol) and CuI (0.1 mmol) in 3 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 8 h, then at 110 °C for 4 h.

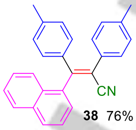
Table 3. One-pot two-step synthesis of 2,3,3-triarylacrylonitriles using two aryl iodides for one reaction[a]



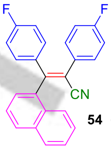


14 - 26

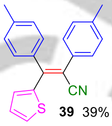
14: R= *o*-CH$_3$ 73%
15: R= *m*-CH$_3$ 69%
16: R= *p*-CH$_3$ 76%
17: R= *o*-OCH$_3$ 65%
18: R= *m*-OCH$_3$ 59%
19: R= *p*-OCH$_3$ 57%
20: R= *p*-F 47%
21: R= *o*-Cl 72%
22: R= *m*-Cl 67%
23: R= *p*-Cl 73%
24: R= *o*-Br 66%
25: R= *p*-Br 64%
26: R= *p*-NO$_2$ 37%



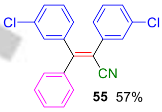
38 76%



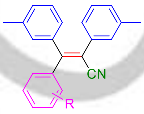
54 62%



39 39%

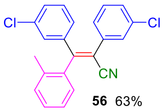


55 57%

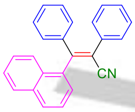


40 - 46

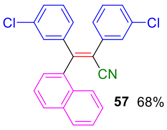
40: R= H 70%
41: R= *o*-CH$_3$ 68%
42: R= *o*-Cl 65%
43: R= *m*-Cl 71%
44: R= *p*-Cl 74%
45: R= *o*-Br 61%
46: R= *p*-Br 55%



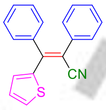
56 63%



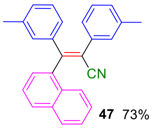
27 76%



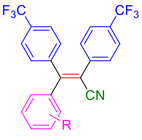
57 68%



28 43%

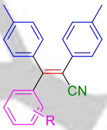


47 73%



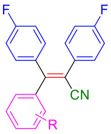
58 - 61

58: R= H 49%
59: R= *o*-CH$_3$ 61%
60: R= *p*-Cl 44%
61: R= *o*-Br 49%



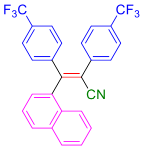
29 - 37

29: R= H 71%
30: R= *o*-CH$_3$ 73%
31: R= *m*-OCH$_3$ 42%
32: R= *p*-OCH$_3$ 32%
33: R= *o*-Cl 63%
34: R=*m*-Cl 65%
35: R= *p*-Cl 69%
36: R= *o*-Br 67%
37: R= *p*-Br 59%

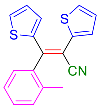


48 - 53

48: R= H 56%
49: R= *o*-CH$_3$ 49%
50: R= *m*-OCH$_3$ 32%
51: R= *p*-OCH$_3$ 39%
52: R= *p*-Cl 57%
53: R= *o*-Br 55%



62 66%



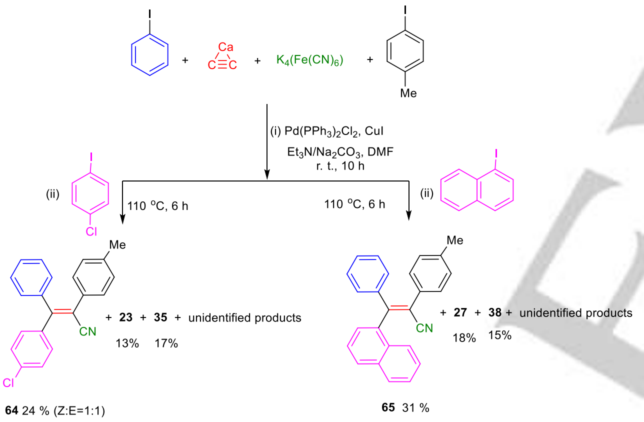
63 57%

[a] Reaction condition: Ar^{1}I (1.0 mmol), K$_4$[Fe(CN)$_6$] (0.1 mmol), CaC$_2$ (1.0 mmol), Et$_3$N (1.0 mmol), Na$_2$CO$_3$ (0.5 mmol), H$_2$O (0.5 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.01 mmol) and CuI (0.1 mmol) in 3 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 10 h, then Ar^{2}I (0.55 mmol) was added and the system was stirred at 110 °C for 4 h.

Having the optimized conditions in hand, the substrate scope using single aryl iodide for one reaction through one-pot one-step procedure to synthesize 2,3,3-triarylacrylonitriles was examined, and the results summarized in Table 2. The reactions could tolerate a wide range of functional groups on aromatic rings, and produce the corresponding products in satisfactory yield. The substituents on the *ortho*-, *meta*- and *para*- positions of aromatic rings of aryl iodides had no obvious effect on the yield of products. The substrates bearing Me, Br and Cl groups on the aromatic rings could afford good yield (**1−4**, **9−11**). In contrast, the substrates bearing methoxy group gave the corresponding products in slightly lower yield (**5−6**) possibly because of the resonance donation of electrons from oxygen. The similar situations were observed for substrates bearing F and CF$_3$ groups (**7−8**) possibly due to the strong electron-withdrawing effect. The aryl iodide bearing fused ring (naphthyl) could also give good yield (**12**). In addition, the aryl iodides including heteroaromatic ring (thienyl) was also effective for the reaction (**13**). Unfortunately, the attempts for reactions of aliphatic iodides, such as methyl iodide and isobutyl iodide, were not successful.

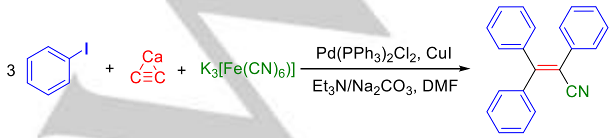
To our great delight, 2,3,3-triarylacrylonitriles bearing two different aryls could be readily obtained by one-pot two-step method using two aryl iodides for one reaction (Table 3, **14−63**). The similar substituent effect was also observed for these reactions.

In addition, the reactions using three different aryl iodides for one reaction were also attempted by one-pot two-step procedure. However, the reaction system was complex and many products were observed for one system. For example, the reaction system using iodobenzene, 4-iodotoluene and 1-chloro-4-iodobenzene could produce 2,3,3-triarylacrylonitrile bearing three different aryls **64**, 2,3,3-triarylacrylonitriles bearing two different aryls **23** and **35**, and other unidentified products in low yield (Scheme 1). Similarly, the reaction system using iodobenzene, 4-iodotoluene and 1-iodonaphthalene could obtain 2,3,3-triarylacrylonitrile bearing three different aryls **65**, 2,3,3-triarylacrylonitriles bearing two different aryls **27** and **38**, and other unidentified products in low yield (Scheme 1)



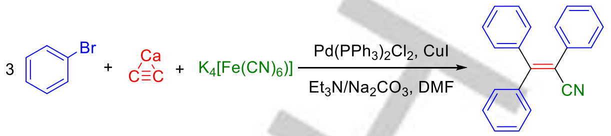
Scheme 1. One-pot two-step synthesis of 2,3,3-triarylacrylonitriles using three aryl iodides for one reaction. Conditions: Iodobenzene (0.5 mmol), $K_4[Fe(CN)_6]$ (0.1 mmol), CaC_2 (1.0 mmol), 1-iodo-4-methylbenzene (0.5 mmol), Et_3N (1.0 mmol), Na_2CO_3 (0.5 mmol), H_2O (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.01 mmol) and CuI (0.1 mmol) in 3 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 10 h, then 1-chloro-4-iodobenzene or 1-iodonaphthalene (0.55 mmol) was added and the system was stirred at 110 °C for 6 h.

It is noteworthy to mention that reaction substrates and reagents could also be extended. When $K_3[Fe(CN)_6]$ was used to replace $K_4[Fe(CN)_6]$ in the reaction, the product **1** could also be obtained in 49% yield (Scheme 2). When bromobenzene was used to replace iodobenzene in the reaction, the product **1** could be obtained in 12% yield (Scheme 3).



1 49%

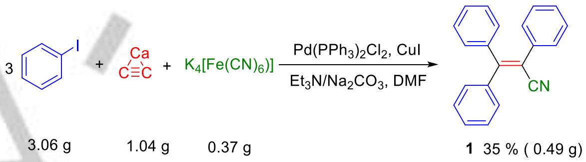
Scheme 2. Synthesis of **1** using $K_3[Fe(CN)_6]$ instead of $K_4[Fe(CN)_6]$. Conditions: Iodobenzene (1.5 mmol), $K_3[Fe(CN)_6]$ (0.1 mmol), CaC_2 (1.0 mmol), Et_3N (1.0 mmol), Na_2CO_3 (0.5 mmol), H_2O (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.01 mmol) and CuI (0.1 mmol) in 3 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 8 h, then at 110 °C for 4 h.



1 12%

Scheme 3. Synthesis of **1** using bromobenzene instead of iodobenzene. Conditions: Bromobenzene (1.5 mmol), $K_4[Fe(CN)_6]$ (0.1 mmol), CaC_2 (1.0 mmol), Et_3N (1.0 mmol), Na_2CO_3 (0.5 mmol), H_2O (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.01 mmol) and CuI (0.1 mmol) in 3 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 24 h, then at 110 °C for 6 h.

The studied reaction could also be performed on gram scale (Scheme 4). The reaction of 3.06 g of iodobenzene with 1.04 g of calcium carbide and 0.37 g of $K_4[Fe(CN)_6]$ in DMF (20 mL) was performed under the optimized condition to give **1** in 35% (0.49 g) isolated yield. The success of this gram scale reaction further showed the potency of optimized condition for the bulk processes.

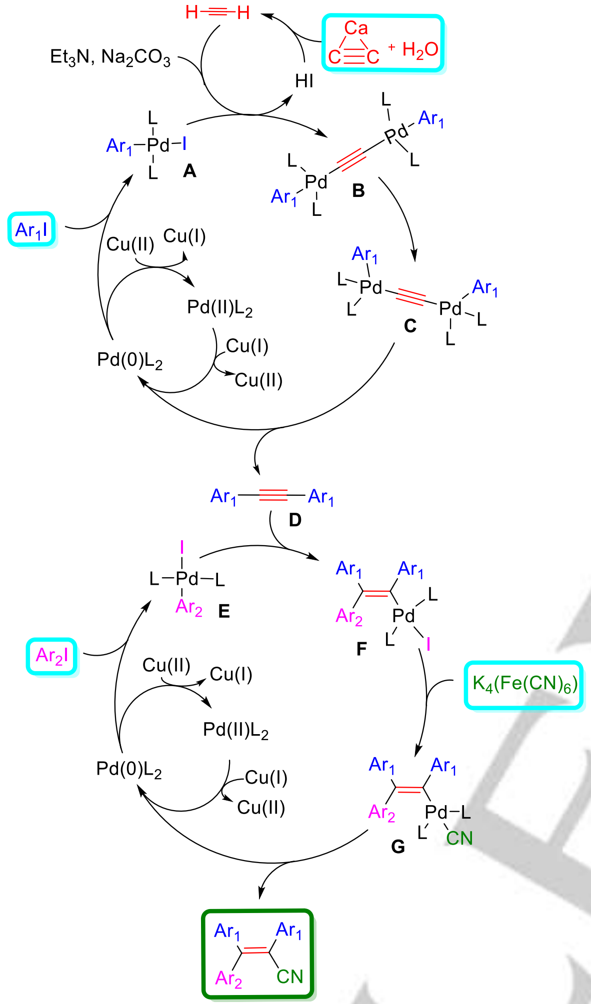


Scheme 4. Gram-scale synthesis of **1**. Conditions: Iodobenzene (15 mmol), $K_4[Fe(CN)_6]$ (1 mmol), CaC_2 (12 mmol, 1.04 g for 74% purity), Et_3N (10 mmol), Na_2CO_3 (5 mmol), H_2O (5 mmol), $Pd(PPh_3)_2Cl_2$ (0.1 mmol) and CuI (1 mmol) in 20 mL of degassed DMF under nitrogen atmosphere stirred first at room temperature for 15 h, then at 110 °C for 6 h.

A plausible mechanism is proposed for the synthesis of triarylacrylonitriles (Scheme 5). CaC_2 first reacts with water to give acetylene *in situ*. Simultaneously, $Pd(0)L_2$ from the reaction of $Pd(II)L_2$ with Cu(I) combines with Ar^1I through oxidative addition to produce arylpalladium(II) intermediate **A**. **A** exchanges ion with acetylene in the presence of Et_3N and Na_2CO_3 to give an ethynyl palladium intermediate **B** and co-product HI, which can react with calcium carbide to generate more acetylene in the reaction. The trans/cis-isomerization of **B** produces intermediate **C**. The reductive elimination of **C** gives diarylacetylene (**D**) and releases $Pd(0)L_2$ to continue the cycle. **D** reacts with another arylpalladium(II) intermediate **E** formed from Ar^2I by *cis*-addition to afford a vinylic palladium intermediate **F**. **F** exchanges ligand with cyanide ion of $K_4[Fe(CN)_6]$ to form a new intermediate **G**. **G** conducts reductive elimination to produce triarylacrylonitrile as a final product and release $Pd(0)L_2$ to continue the cycle or by Cu(II) oxidation to produce $Pd(II)L_2$ catalyst.

Conclusions

In conclusion, we have developed a novel method for the synthesis of triarylacrylonitriles from various aryl iodides using calcium carbide as a concise acetylene source and potassium hexacyanoferrate(II) as an eco-friendly cyanide source by one-pot multi-component procedure. The selective use of one, two or three kinds of aryl iodides could obtain various different aryl substituted triarylacrylonitriles. The application of safe, inexpensive and eco-friendly raw materials, mild conditions, good substrate tolerance and simple work-up procedure made this protocol a good alternative for the synthesis of many desired triarylacrylonitriles.



Scheme 5. The proposed mechanism for the synthesis of triarylacrylonitriles

Experimental Section

General Information: ^1H NMR and ^{13}C NMR spectra were obtained with Mercury–400 MB or Mercury–600 MB instrument using $CDCl_3$ as solvent and Me_4Si as the internal standard. The Elemental analyses were performed on a Vario El Elemental Analysis instrument. Melting points were observed in an electrothermal melting point apparatus. The solvents (DMF and the others) were degassed. All reagents were purchased from Energy Chemical Company (China). Calcium carbide (purity ≥ 74 %) was ground into fine powder prior to use. $K_4[Fe(CN)_6]\cdot 3H_2O$ was dehydrated at 80ºC under vacuum for 24 h and finely powdered before use.

The general procedure for the preparation of 2,3,3-triarylacrylonitriles 1−13: The mixture of ArI (1.5 mmol), $K_4[Fe(CN)_6]$ (0.1 mmol, 0.037 g), CaC_2 (1.0 mmol, 0.086 g for 74% purity), $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 0.007 g), CuI (0.1 mmol, 0.020 g), Et_3N (1 mmol, 0.101 g), Na_2CO_3 (0.5 mmol, 0.053 g) and H_2O (0.5 mmol, 0.009 g) in 3 mL of degassed DMF was stirred at room temperature under nitrogen atmosphere for 8 h. Then the system was warmed to 110 °C and continued to stir for 4 h. The resulting mixture was filtered, and the solid was washed with ethyl acetate (3×10 mL). The liquor was washed with saturated brine (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 125:1) as eluent to give pure product.

The general procedure for the preparation of 2,3,3-triarylacrylonitriles 14−63: The mixture of Ar^1I (1.0 mmol), $K_4[Fe(CN)_6]$ (0.1 mmol, 0.037 g), CaC_2 (1.0 mmol, 0.086 g for 74% purity), $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 0.007 g), CuI (0.1 mmol, 0.020 g), Et_3N (1 mmol, 0.101 g), Na_2CO_3 (0.5 mmol, 0.053 g) and H_2O (0.5 mmol, 0.009 g) in 3 mL of degassed DMF was stirred at room temperature under nitrogen atmosphere for 10 h. Then Ar^2I (0.55 mmol) was added and the system was warmed to 110 °C and continued to stir for 4 h. The resulting mixture was filtered, and the solid was washed with ethyl acetate (3×10 mL). The liquor was washed with saturated brine (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 125:1) as eluent to give pure product.

The general procedure for the preparation of 2,3,3-triarylacrylonitriles 64, 65: The mixture of Ar^1I (0.5 mmol), Ar^2I (0.5 mmol), $K_4[Fe(CN)_6]$ (0.1 mmol, 0.037 g), CaC_2 (1.0 mmol, 0.086 g for 74% purity), $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 0.007 g), CuI (0.1 mmol, 0.020 g), Et_3N (1 mmol, 0.101 g), Na_2CO_3 (0.5 mmol, 0.053 g) and H_2O (0.5 mmol, 0.009 g) in 3 mL of degassed DMF was stirred at room temperature under nitrogen atmosphere for 10 h. Then Ar^3I (0.55 mmol) was added and the system was warmed to 110 °C and continued to stir for 6 h. The resulting mixture was filtered, and the solid was washed with ethyl acetate (3×10 mL). The liquor was washed with saturated brine (3×10 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (v/v 125:1) as eluent to give pure product.

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Keywords: calcium carbide, potassium hexacyanoferrate(II), triarylacrylonitrile, one-pot reaction, multicomponent synthesis

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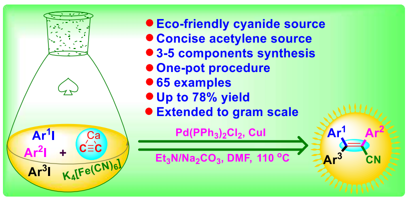
Table of Contents

FULL PAPER

An efficient method for the one-pot multicomponent synthesis of triarylacrylonitriles from various aryl iodides direct using calcium carbide as a concise acetylene source and potassium hexacyanoferrate(II) as an eco-friendly cyanide source is described.



Triarylacrylonitriles

*Geyang Song, Zheng Li**

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One-Pot Multi-Component Synthesis of Triarylacrylonitriles Direct Using CaC_2 as a Concise Acetylene Source and $K_4[Fe(CN)_6]$ as an Eco-Friendly Cyanide Source