Electrochemistry
The Electrochemical Society of Japan

Received: July 12, 2024
Accepted: August 12, 2024
Published online: August 21, 2024
Issued: October 11, 2024

J-STAGE https://doi.org/10.5796/electrochemistry.24-00079

Article

Electrochemistry, **92(10)**, 107002 (2024)

Mg Electrodes Coiled with Cu Wires Promoted Formation of Diphenylacetylene from Tetrachloroethylene and Bromobenzene: One-step Electrochemical Synthesis without Pd Catalyst†

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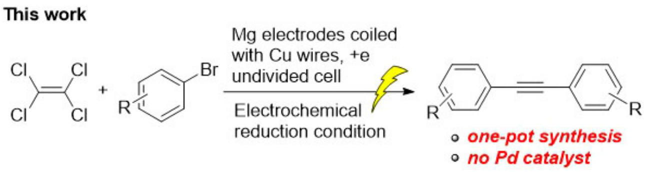
ABSTRACT

It was found that diphenylacetylene was synthesized by using electrochemical reduction with Mg electrodes, coiled with Cu wires. The electrochemical reaction of tetrachloroethylene and bromobenzene in $LiClO_4$/THF afforded diphenylacetylene in up to 38 % yield. The reaction took place in the absence of Pd catalyst. The scope and limitations, and investigation of reaction mechanism were also studied.



Keywords : Diphenylacetylene, Magnesium Electrodes, Tetrachloroethylene, Bromobenzene

1. Introduction

Diphenylacetylene and its derivatives are important compounds in organic chemistry.[1–4] In fact, they can be used in various fields. It is also useful as a synthetic platform[5] for various luminescent materials and pharmaceuticals. The basic approach for obtaining diphenylacetylene is using Sonogashira coupling reaction shown in Scheme 1a.[6–8] Because we have also been interested in the establishment of new synthetic methods for diphenylacetylene and its derivatives, we have developed the synthetic procedure, in which the reaction of tetrachloroethylene and phenylboronic acid in the presence of Pd catalyst, followed by the treatment of n-BuLi for crude product were performed based on two steps approach (Scheme 1b).[9] Recently, our method has successfully opened the synthesis of the unsymmetrical donor-acceptor diarylacetylenes, in which dechlorinations were modified by using the metal of Mg (Scheme 1c).[10]

All of the above synthetic methods use and depend on the expensive Pd catalysts. We have envisioned that the electrochemistry might overcome the use of Pd catalysts for the preparation of diphenylacetylene from tetrachloroethylene.[11,12] Electro-organic chemistry has attracted the significant attention in recent years, in the view point of an environment-friendly method in organic synthesis.[13–22] Herein, we have found that Mg electrodes coiled with Cu wires[23,24] promoted the formation of diphenylacetylene from tetrachloroethylene and bromobenzene in the absence of Pd catalyst (Scheme 1d).[25]

2. Experimental

2.1 General remarks

Varian MERCURY 300 (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz) and JEOL JNM-ECS 400 (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) were used for ^{1}H NMR and ^{13}C NMR measurements, in which $CDCl_3$ was used for NMR. The chemical shift of ^{1}H NMR was based on 0.00 ppm of tetramethylsilane (Me_4Si) of $CDCl_3$. The chemical shift of ^{13}C NMR was based on 77.0 ppm of $CDCl_3$. Thermo Fisher Scientific Exactive Plus was used for HRMS analysis. Shimadzu GC-2014 equipped with capillary column was used for GC analysis, in which FID method was conducted. GC-MS analysis was carried out by using an Agilent 7890A Mass Selective Detector, equipped with an Agilent 5975C inert XL MSD with Triple-Axis Detector. Japan Analitical Industry LC-9201, LC-9110 NEXT and LC-9210 NEXT equipped with JAIGEL-1H and JAIGEL-2H were used for preparative GPC separation and purification, in which $CHCl_3$ was used for eluent. TLC analysis was carried out by using Merck pre-coated silica gel F_{254} plates (thickness 0.25 mm). A silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 µm) was used. DC power supply of KIKUSUI PMC350-0.2A or PMX350-0.2A was used for the electrochemical reaction. Carbon felt was activated for 9 hours at 1 mmHg and 250 °C, and then used. All reactions were performed under a N_2 atmosphere. In electro-synthesis, the electrode condition was as follows. Two sets of a 1.2 mm thick Cu wire were roped around two sets of Mg rods for anode and cathode. The each Cu wire in solution was approximately 16 cm for anode and cathode.

2.2 Materials

Dry THF (tetrahydrofuran), dry DMF (N,N-dimethylformamide), and dry MeCN (acetonitrile) were purchased, and used without further purification. $LiClO_4$ (lithium perchlorate), n-Bu_4NClO_4 (tetrabutylammonium perchlorate), and n-Bu_4NPF_6 (tetrabutylammonium hexafluorophosphate) were purchased, and used without

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† A part of this paper has been presented in the 48th symposium on Organic Electron Transfer Chemistry in June/2024 (Poster presentation, P56) and in the 44th Synthetic Organic Seminar for Young Chemists in August/2024 (Poster presentation, P-28). In addition, this work has already been submitted to Japan Patent Office. (K. Matsumoto, M. Kobayashi, Shin Yoneyama, and P. Xu, Japanese Patent Application No. 2023-197997), shown in Ref. 25.

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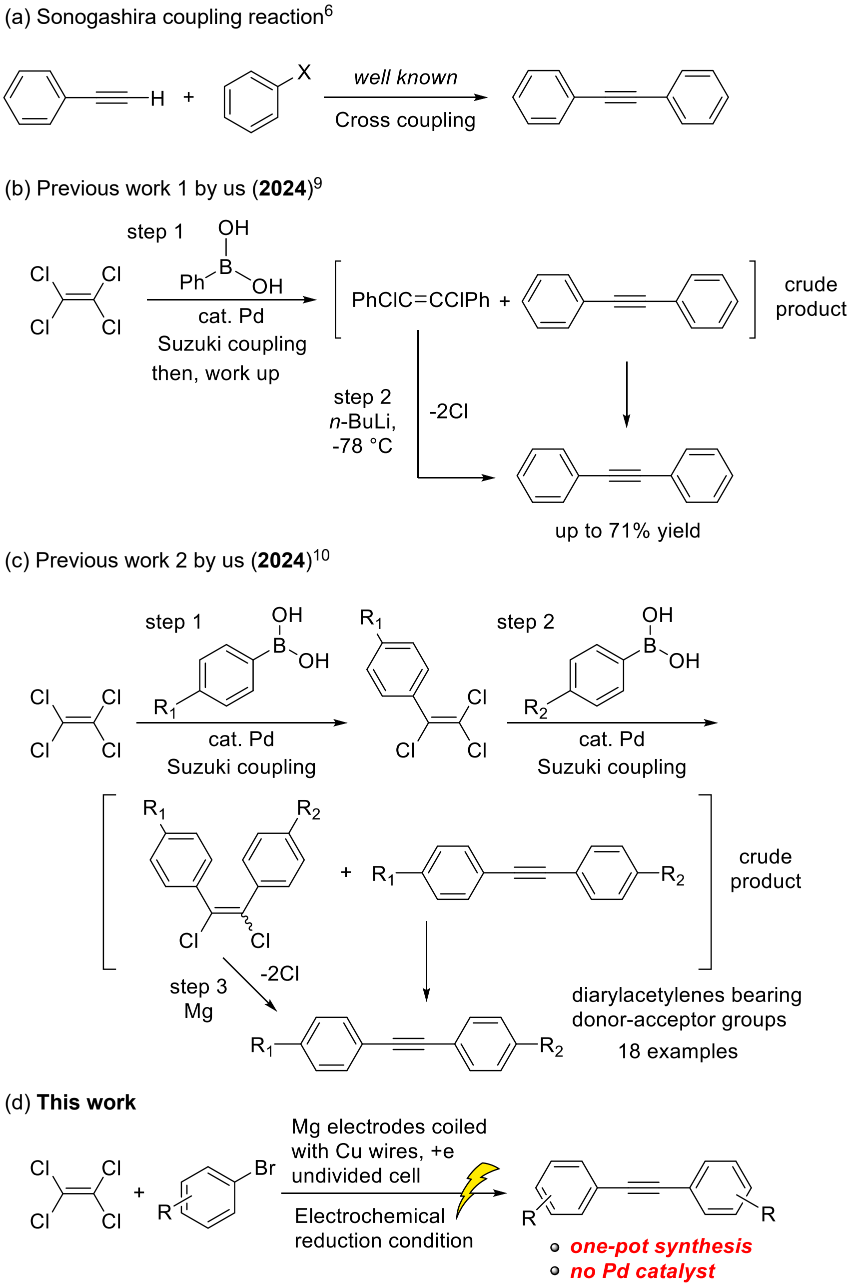


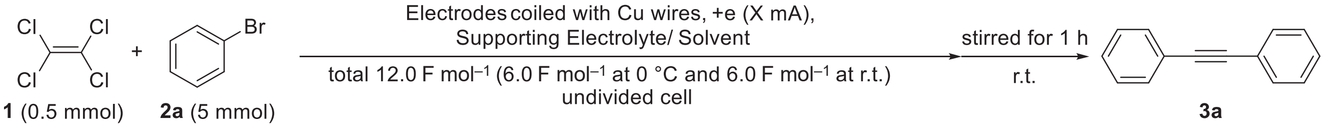
Scheme 1. Previous works of (a)–(c) and this work of (d).

further purification. Tetrachloroethylene (**1**) was obtained from KANTO DENKA KOGYO CO., LTD. and used without further purification. Bromobenzene (**2a**), 1-bromo-4-methylbenzene (**2b**), 1-bromo-2-methylbenzene (**2c**), 1-bromo-3-methylbenzene (**2d**), 1-bromo-4-ethylbenzene (**2e**), 1-bromo-4-*n*-propylbenzene (**2f**), 1-bromo-4-isopropylbenzene (**2g**), 1-bromo-4-methoxybenzene (**2h**), iodobenzene (**2i**), and chlorobenzene (**2j**) were purchased, and used without further purification. The synthesized compounds were identified by comparing their spectra with those of reported literatures.[26–28]

2.3 Typical procedure (Table 1, Entry 1)

Mg electrodes were pre-activated by 1 mol L^{-1} HCl aq and dried, in order to remove MgO of the surface of Mg. The electrochemical reaction was performed by using a 50 mL three-necked flask, equipped with two Mg electrodes (2 × 1 × 0.5 cm), which were coiled with Cu wires. The three-necked flask was dried up by heating gun under reduced pressure, and placed under a N_2 atmosphere. $LiClO_4$ (639.4 mg, 6.0 mmol) and THF (20.0 mL) were added and the solution was stirred at room temperature. Then, tetrachloroethylene (**1**, 83.7 mg, 0.50 mmol) was added and the solution was cooled to 0 °C. Bromobenzene (**2a**, 0.5 mL, $d = 1.50$ g/mL, approximately 750.0 mg, 4.78 mmol, ca. 5 mmol) was added, and the electrochemical reduction at 0 °C was started. 6.0 F mol^{-1} based on **1** was passed using 100 mA. After then, the reaction temperature was increased to room temperature. Under room temperature, additional electrolysis of 6.0 F mol^{-1} using 100 mA was conducted. After stopping electrolysis, TLC analysis was carried out for the confirmation of the product. After the solution was stirred for 1 h at same temperature, the reaction was quenched by 1 mol L^{-1} HCl aq (10 mL) at 0 °C. To the mixture, Et_2O (30 mL) was added and separated. The aqueous phase was extracted by Et_2O (30 mL × 2). The combined organic phase was washed by brine (30 mL) and dried over Na_2SO_4. After filtration and concentration under reduced pressure, short column of silica-gel by hexane (100 mL) was conducted and the solution was

Table 1. Reaction optimization for **3a**.[a]



Entry	Electrodes	Supporting Electrolyte	Solvent	Electric Current (X mA)	% Yield[b]
1	Mg (+) | Mg (−)	$LiClO_4$	THF	100	38
2	Mg (+) | Mg (−)	*n*-Bu_4NClO_4	THF	100	trace
3	Mg (+) | Mg (−)	*n*-Bu_4NPF_6	THF	100	trace
4	Mg (+) | Mg (−)	$LiClO_4$	MeCN	100	n.d.
5	Mg (+) | Mg (−)	$LiClO_4$	DMF	100	trace
6	C felt (+) | Mg (−)	$LiClO_4$	THF	100	trace
7	Mg (+) | C felt (−)	$LiClO_4$	THF	100	26
8	Mg (+) | Mg (−)	$LiClO_4$	THF	50	<32[c]
9	Mg (+) | Mg (−)	$LiClO_4$	THF	150	30

[a] Standard condition was as follows. **1** (82.9 mg, 0.5 mmol), **2a** (0.5 mL, 5 mmol), 0.3 mol L^{-1} supporting electrolyte/solvent (20.0 mL), undivided cell, and 100 mA were used. 6.0 F mol^{-1} at 0 °C using ice bath was used, and 6.0 F mol^{-1} at room temperature was used, which mean total 12.0 F mol^{-1} was consumed. [b] Isolated yields using the preparative GPC separation of the crude products for the purification. [c] Determined by GC.

concentrated under reduced pressure to give the crude product. The crude product was purified and isolated by using the preparative GPC separation to give diphenylacetylene (**3a**, 34.6 mg, 0.19 mmol, 38 % yield).[26]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.37 (m, 6H), 7.50–7.56 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.3, 123.2, 128.2, 128.3, 131.6 ppm; HRMS (ESI) calculated for $C_{14}H_{11}$ ($[M+H]^+$): 179.0855, found 179.0855.

2.4 Typical procedure (Table 2, Entry 1)

Mg electrodes were pre-activated by 1 mol L^{-1} HCl aq and dried, in order to remove MgO of the surface of Mg. The electrochemical reaction was performed by using a 50 mL three-necked flask, equipped with two Mg electrodes (2 × 1 × 0.5 cm), which were coiled with Cu wires. The three-necked flask was dried up by heating gun under reduced pressure, and placed under a N_2 atmosphere. $LiClO_4$ (639.1 mg, 6.0 mmol) and THF (20.0 mL) were added and the solution was stirred at room temperature. Then, tetrachloroethylene (**1**, 82.8 mg, 0.50 mmol) was added and the solution was cooled to 0 °C. 1-Bromo-4-methylbenzene (**2b**, 861.2 mg, 5.04 mmol, ca. 5 mmol) was added, and the electrochemical reduction at 0 °C was started. 6.0 F mol^{-1} based on **1** was passed using 100 mA. After then, the reaction temperature was increased to room temperature. Under room temperature, additional electrolysis of 6.0 F mol^{-1} using 100 mA was conducted. After stopping electrolysis, TLC analysis was carried out for the confirmation of the product. After the solution was stirred for 1 h at same temperature, the reaction was quenched by 1 mol L^{-1} HCl aq (10 mL) at 0 °C. To the mixture, Et_2O (30 mL) was added and separated. The aqueous phase was extracted by Et_2O (30 mL × 2). The combined organic phase was washed by brine (30 mL) and dried over Na_2SO_4. After filtration and concentration under reduced pressure, short column of silica-gel by hexane (100 mL) was conducted and the solution was concentrated under reduced pressure to give the crude product. The crude product was purified and isolated by using the preparative GPC separation to give 1,2-di-*p*-tolylethyne (**3b**, 25.9 mg, 0.13 mmol, 26 % yield).[26–28]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 6H), 7.14 (d, $J = 8.0$ Hz, 4H), 7.41 (d, $J = 8.0$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 88.8, 120.4, 129.1, 131.4, 138.1 ppm; HRMS (ESI) calculated for $C_{16}H_{14}Na$ ($[M+Na]^+$): 229.0988, found 229.0984.

1,2-Di-*o*-tolylethyne (3c) (Table 2, Entry 2).[26] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 6H), 7.14–7.28 (m, 6H), 7.51 (d, $J = 7.2$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 92.3, 123.3, 125.6, 128.2, 129.5, 131.9, 139.9 ppm; HRMS (ESI) calculated for $C_{16}H_{15}$ ($[M+H]^+$): 207.1168, found 207.1166.

1,2-Di-*m*-tolylethyne (3d) (Table 2, Entry 3).[26,27] The purity of **3d** was 90 % by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 6H), 7.13 (d, $J = 7.6$ Hz, 2H), 7.22 (d, $J = 7.6$ Hz, 2H), 7.30–7.41 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 89.2, 123.1, 128.2, 128.6, 129.1, 132.2, 138.0 ppm; HRMS (ESI) calculated for $C_{16}H_{15}$ ($[M+H]^+$): 207.1168, found 207.1165.

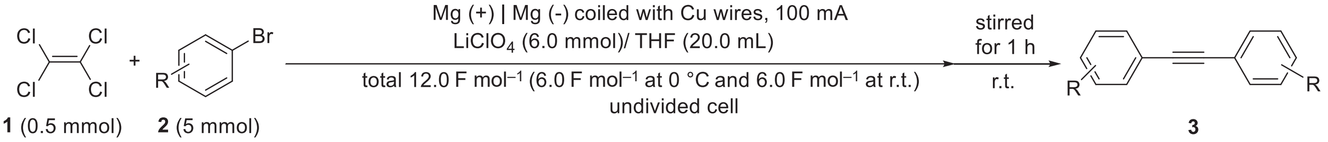
1,2-Bis(4-ethylphenyl)ethyne (3e) (Table 2, Entry 4).[27] The purity of **3e** was 89 % by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, $J = 7.4$ Hz, 6H), 2.65 (q, $J = 7.4$ Hz, 4H), 7.17 (d, $J = 8.4$ Hz, 4H), 7.44 (d, $J = 8.4$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 28.8, 88.9, 120.6, 127.9, 131.5, 144.5 ppm; HRMS (ESI) calculated for $C_{18}H_{19}$ ($[M+H]^+$): 235.1481, found 235.1478.

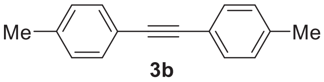
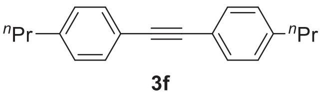
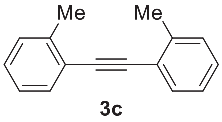
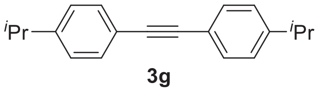
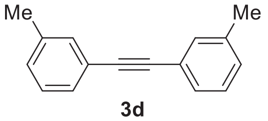
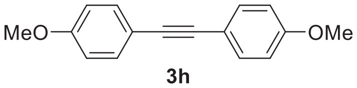
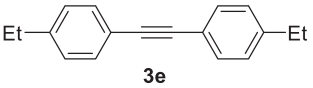
1,2-Bis(4-*n*-propylphenyl)ethyne (3f) (Table 2, Entry 5).[28] The purity of **3f** was 80 % by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, $J = 7.2$ Hz, 6H), 1.64 (sext, $J = 7.2$ Hz, 4H), 2.59 (t, $J = 7.2$ Hz, 4H), 7.14 (d, $J = 8.4$ Hz, 4H), 7.43 (d, $J = 8.4$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 24.3, 37.9, 88.9, 120.6, 128.5, 131.4, 142.9 ppm; HRMS (ESI) calculated for $C_{20}H_{23}$ ($[M+H]^+$): 263.1794, found 263.1795.

1,2-Bis(4-isopropylphenyl)ethyne (3g) (Table 2, Entry 6).[27] The purity of **3g** was 81 % by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, $J = 6.8$ Hz, 12H), 2.90 (hept, $J = 6.8$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 4H), 7.45 (d, $J = 8.4$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 34.1, 88.8, 120.8, 126.4, 131.5, 149.1 ppm; HRMS (ESI) calculated for $C_{20}H_{22}$ (M^+): 262.1722, found 262.1712.

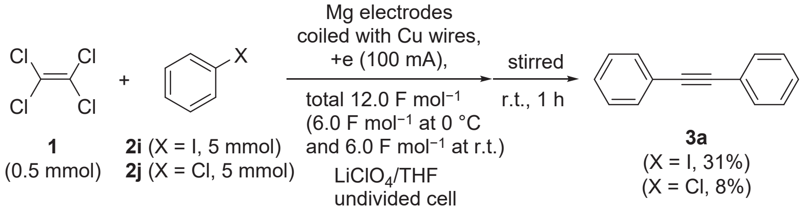
1,2-Bis(4-methoxyphenyl)ethyne (3h) (Table 2, Entry 7).[26] The purification was carried out by the silica gel column chromatography, followed by the preparative GPC separation. The purity of **3h** was 87 % by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 6H), 6.83–6.89 (m, 4H), 7.42–7.47 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 87.9, 113.9, 115.7, 132.9, 159.4 ppm; HRMS (ESI) calculated for $C_{16}H_{15}O_2$ ($[M+H]^+$): 239.1067, found 239.1067.

Table 2. Scope and limitations.[a]



Entry	Product (**3**)	% Yield[a]	Entry	Product (**3**)	% Yield[a]
1	 **3b**	26	5	 **3f**	<12[b]
2	 **3c**	6	6	 **3g**	<10[b]
3	 **3d**	<18[b]	7	 **3h**	<6
4	 **3e**	<24[b]			

[a]Isolated yields using the preparative GPC separation of the crude products for the purification. [b]Determined by GC.



Scheme 2. Some control experiments.

3. Results and Discussion

First, we have investigated the reaction optimization. The model reaction was described in Table 1. The electrochemical reduction was carried out using the round flask equipped with two Mg electrodes, which was undivided cell. Cu wires were coiled on the surface of Mg electrodes. The solution of 0.3 mol L^{-1} $LiClO_4$/THF containing tetrachloroethylene (**1**, 0.5 mmol) and bromobenzene (**2a**, 5 mmol) was electrolyzed at 0 °C using 100 mA and the electricity of 6.0 F mol^{-1} was passed for the solution. Then, the solution was further electrolyzed at room temperature using 100 mA and the electricity of 6.0 F mol^{-1} was passed, to give diphenylacetylene (**3a**) in 38 % yield (Entry 1). In order to improve the chemical yield, various parameters such as supporting electrolyte, solvent, and materials of electrodes were examined. The use of *n*-Bu_4NClO_4 and *n*-Bu_4NPF_6 in THF were not effective and the results gave trace of **3a** (Entries 2–3). MeCN and DMF were also not suitable for the current reaction (Entries 4–5). The materials of electrodes were also critical and the carbon felt instead of Mg for the anode decreased the yield of **3a** in trace amount (Entry 6), although the carbon felt instead of Mg for the cathode gave **3a** in 26 % yield (Entry 7). The decrease or increase of the current such as 50 mA and 150 mA was not problem for chemical yield of **3a** (Entries 8–9). Thus, we have determined the optimized condition of Entry 1 for the current reaction.[29]

Next, we have examined the scope and limitations shown in Table 2. The reaction of **1** and 1-bromo-4-methylbenzene (**2b**) gave the corresponding 1,2-di-*p*-tolylethyne (**3b**) in 26 % yield (Entry 1). The reactions using 1-bromo-2-methylbenzene (**2c**) and 1-bromo-3-methylbenzene (**2d**) afforded the **3c** in 6 % yield and **3d** in <18 % yield, respectively (Entries 2–3). In addition to Me group, other alkyl groups such as Et, *n*-Pr and *i*-Pr groups at *para* position of benzene ring were also tested and the reactions produced **3e** in <24 % yield, **3f** in <12 % yield, and **3g** in <10 % yield, respectively (Entries 4–6). 1-Bromo-4-methoxybenzene (**2h**) bearing MeO as the electron-donating group was studied and **3h** was obtained in <6 % yield (Entry 7).

As for the comparison of the reactivity of iodobenzene (**2i**) and chlorobenzene (**2j**) instead of bromobenzene, the electrochemical reactions using **2i** and **2j** were conducted under the optimized condition (Scheme 2). **2i** gave **3a** in 31 % yield and **2j** produced **3a** in 8 % yield, indicating that iodobenzen (**2i**) showed the similar reactivity, compared with bromobenzene (**2a**).

We have carried out the analysis of the electrolyzed solution by using GC-MS and HRMS, in order to clear the reaction mechanism

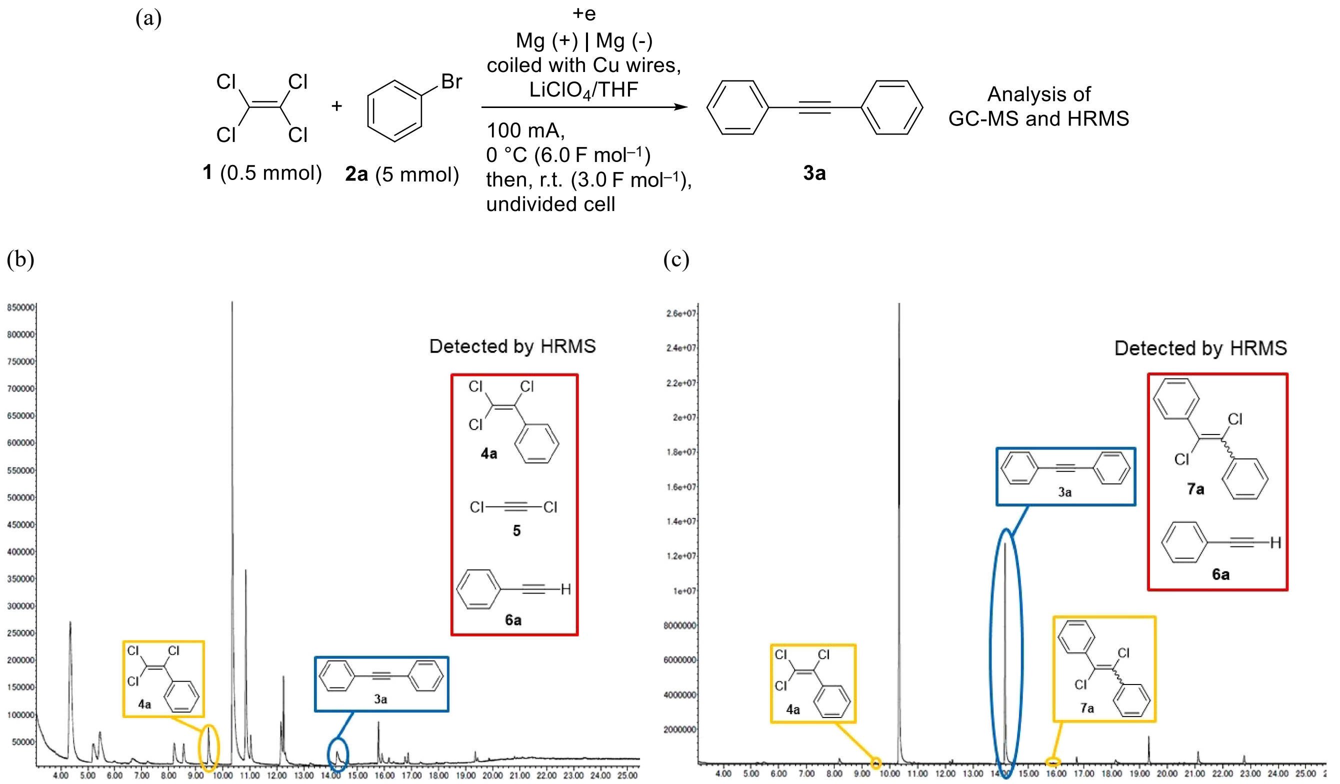


Figure 1. Analysis during electrochemical reaction. (a) Monitoring of reactions by GC-MS and HRMS at 3.0 F mol^{-1} and 9.0 F mol^{-1}, using same lot of the experiment and GC-MS monitoring after the electrolysis for (b) 24 min, 3.0 F mol^{-1} and (c) 72 min, 9.0 F mol^{-1}.

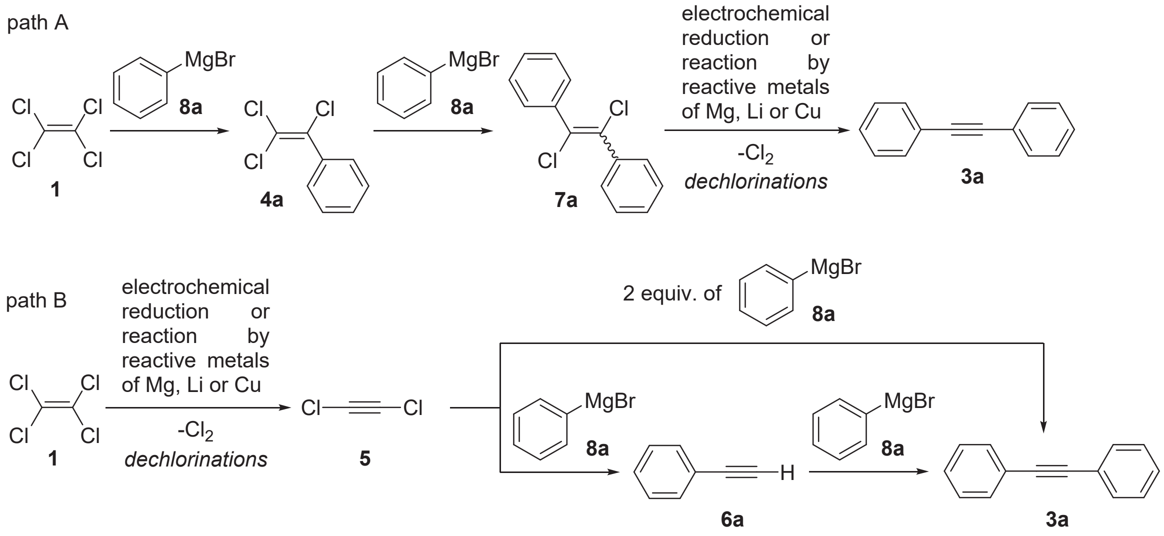


Figure 2. A plausible reaction mechanism.

and to obtain deeper insight. Figure 1a shows the outline of the current analysis. At the stage of 3.0 F mol^{-1} and 9.0 F mol^{-1}, a small amount of solution was taken and subjected to analysis, after desalinization. Figure 1b is the result of GC-MS monitoring at 24 min (3.0 F mol^{-1}) and the result of the detection of HRMS, indicating the detection of **3a**, **4a**, **5** and **6a**. In the case of Fig. 1c, which is derived from 72 min (9.0 F mol^{-1}), the result of the detection of GC-MS and HRMS demonstrated that there were **3a**, **4a**, **6a** and **7a** in the solution phase. These detections support the reaction mechanism (vide infra). Also, through various experiments, GC-MS analysis indicated that when the yield of diphenylacetylene (**3a**) was high, the formation of the byproduct of biphenyl also tended to be high yield.

Based on the above results, plausible reaction mechanism has been described in Fig. 2. In the one of the pathways, the reaction of **1** and **8a** might give **4a** as the intermediate. **4a** was also allowed to react with **8a** produced **7a**, which underwent dechlorinations by the electrochemical reduction or reaction by highly reactive metals in the solution phase (path A).[30] In fact, this reaction pathway is one of the candidates, because the solution contains the metal ions of Mg^{2+}, Li^{+}, and Cu^{2+}, which might be reduced on the surface of the cathode (Fig. 3). Actually, our recent report cleared that metal of Mg could serve as an effective reagent for dechlorinations of derivatives of **7a**.[10] Another possibility to be considered as the path B is the formation of **5**, followed by the cross coupling reaction with **8a** under the presence of the metals or metal ions to give **3a**. There is

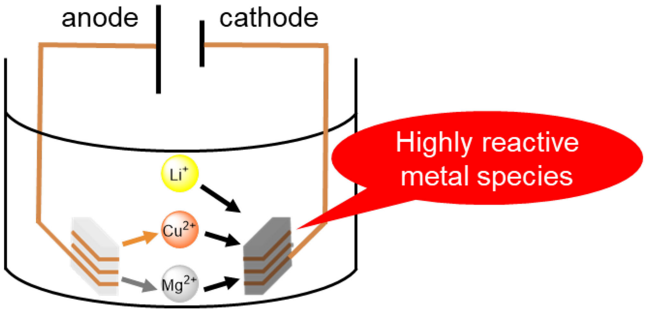


Figure 3. Schematic diagram of Mg electrodes, coiled with Cu wires. Under the electrolysis, leaching of metals of Mg and Cu on the anodes, and deposition of Li, Cu and Mg as highly reactive metal species by electrochemical reduction on the cathode, were expected.

possibility that **3a** is formed directly from the reaction of **5** with 2 equivalents of **8a**. Another possibility to be considered is a stepwise reaction via **6a** or its equivalent with **8a**. In the path B, **5** might be generated from **1** by the electrochemical reduction or reaction by highly reactive Mg, Li, or Cu. Although the detail is not cleared present, it may be a mixture of both pathways such as path A and path B.

4. Conclusions

We have developed the Mg electrodes coiled with Cu wires were found to be effective for the formation of diphenylacetylene from tetrachloroethylene and bromobenzene under the electrochemical reduction. This method does not use the expensive catalysts such as Pd and is environmentally friendly synthetic tool, although the product yields were not high at present.[25] Further synthetic application using this method has been studied in our laboratory.

Acknowledgments

This work was financially supported in part by JSPS KAKENHI (JP24K08506) (Grant-in-Aid for Scientific Research [C]). This work was also partially supported by 2021 Kindai University Research Enhancement Grants (KD2106 and KD2104). We appreciate Dr. Masafumi Kobayashi and Ms. Akiko Kuwabara of KANTO DENKA KOGYO CO., LTD. for discussion and various supports of this paper. We thank the reviewers for their careful review and helpful comments.

CRediT Authorship Contribution Statement

Kengo Hamasaki: Conceptualization (Equal), Data curation (Equal), Writing – original draft (Equal)
Ryoichi Tomiyama: Data curation (Supporting)
Shin Yoneyama: Conceptualization (Equal), Methodology (Equal), Supervision (Equal)
Pengyu Xu: Conceptualization (Equal), Project administration (Equal), Supervision (Equal)
Kouichi Matsumoto: Conceptualization (Equal), Project administration (Equal), Supervision (Equal), Writing – original draft (Equal)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

Funding

JSPS: JP24K08506
Kindai University: KD2106
Kindai University: KD2104

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