



齊魯工業大學
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Electrically induced C-H bond functionalization

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**Electrically induced C-H bond
functionalization**

电 诱 导 C-H 键 的 官 能 团 化

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CONTENTS

Abstract in English.....	1
Abstract in Chinese.....	1
Chapter 1 Introduction.....	2
1.1 Research Background.....	3
1.2 History of Organic Electrochemical Synthesis.....	3
1.3 the advantage of organic electrochemical synthesis.....	5
1.3.1 organic electrochemical synthesis is more economical Compared to noble metal organic catalysts.....	5
1.3.2 Organic Electrocatalysis is Green Chemistry.....	6
1.4 Organic electrochemical synthesis and its classification and basic methods....	6
1.4.1 Principle.....	6
1.4.2 Classification.....	7
1.5 Electrolyte Solvent Reference Electrode and Factors Affecting Reaction Rate	9
1.5.1 Electrolyte Solvent Reference Electrode.....	9
1.5.2 The factors which can affect the reaction rate.....	11
1.6 Successful case of industrialization and major progress this year.....	13
1.6.1 Electrosynthesis of adiponitrile.....	13
1.6.2 Electrosynthesis of Tetraethyl Lead.....	13
1.6.3 China's current achievements in industrial production.....	14
1.6.4 Progress have been made in recent years.....	15
Chapter 2 The Progress of Functionalization of C-H Bonds.....	17
2.1 Electrochemical cyclization.....	17
2.2 Oxidative coupling of phenol.....	18
Chapter 3 Induction of C-H Bond Functionalization Experiment.....	19
3.1 Introduction.....	19
3.2 Experimental section.....	20
3.2.1 Experimental Instruments.....	20
3.2.2 The experimental drug.....	21
3.2.3 steps of experiment.....	21
Chapter 4 Results and Discussion.....	24
4.1 Analysis of experimental results.....	24
4.2 Analysis of MS graphs.....	24
Bibliography.....	26
Acknowledgements.....	27

Abstract

In recent years, with the deepening of environmental awareness and the development of technology, organic electrochemical synthesis are becoming more and more popular in the society, organic electrochemical synthesis is the combination of electrochemical and organic synthesis, with the help of the technology of electrochemical, the transformation, the catalytic efficiency have been increased greatly. Using catalytic as a catalyst, organic electrochemical synthesis saves natural resources reduce the use of precious metal catalyst and improved the reaction efficiency compared to organic synthesis. organic electrochemical synthesis have many advantages. For example, the reaction is easily to control and it costs less than organic synthesis and so on.

This paper mainly discusses the effects of electrolytes, bases, solvent reaction time, temperature, etc. on the reaction, the progress of C-H bond functionalization at home and abroad, and focuses on the author's own experiments and related progress.

In this paper, N,N-dimethyl benzene was used as the reactant and acetonitrile (CH₃CN) as the solvent. Anhydrous sodium carbonate and lithium perchlorate were added. The reaction was carried out on an intelligent magnetic stirrer to obtain a small molecule compound. . In order to obtain better experimental results, the reaction was optimized several times, and the appropriate electrolyte, alkali, time, and temperature were determined. The product was then processed in a step-by-step manner. After detection by GC-MS instrument, the possible structure of the product was obtained, and several possible products and simulated products were ionized in the mass spectrometer by further analysis of the spectrum. Mass-to-charge ratio.

Key Words: Electrochemical; C-H Bond Functionalization; Green Chemistry

摘 要

近年来，随着绿色环保意识的深入人心和科技的发展，有机电化学越来越受到人们的推崇，有机电化学合成是电化学与有机合成的结合，具有反应以控制、成本低等诸多优点。有机电化学是对环境友好的绿色化学，反应符合高效，原子经济性等现在合成理念。

本论文主要讲了电解质，碱，溶剂反应时间，温度等对反应的影响，C-H 键官能团化国内外取得的一些进展，并着重讲述了作者本人所做的实验及相关进展。

本实验是关于如何在电化学条件下制备 N, N, N', N'-四甲基联苯胺。近年来，由于其在各种领域的适用性，制备结构多样的联苯胺衍生物的高效合成方法的开发近年来受到越来越多的关注。联苯胺基化合物的化学和物理性质使其能够用于制造偶氮化合物和在细胞生物学中作为染色试剂。本论文的实验以 N,N-二甲基苯胺为反应物，以乙腈（CH₃CN）为溶剂，加入无水碳酸钠和高氯酸锂，在智能磁力搅拌器上进行反应，得到小分子化合物。之后为了得到更好的实验产率对反应进行了数次条件优化，确定了合适的电解质，碱，时间及温度。然后通过一步步处理得到纯产物，通过 MS 图和核磁共振氢谱图进一步确定了产物确实是 N, N, N', N'-四甲基联苯胺。

关键词： 电化学； C-H 键官能团化； 绿色化学

Chapter 1 Introduction

1.1 Research Background

In the past several decades, with the development of technology of our own country, China's chemical industry has also achieved unprecedented development which surprised all the country in the world. The economics of our country and the people benefited a lot from the booming of chemical industry, people's life have changed a lot. Compared to 30 years ago, chemistry technology has the development of agriculture medicine, daily chemical products, national defense and many other fields. All of these our people have a good life standard and Increased international status of us, on the other hand, because the lack of awareness in now, blind development has also led to the emergence of various problems. For example, the acid rain that has caused people to suffer from it, the ozone hole over Antarctica, the massive death of marine organisms, the pollution of rivers and the ecological environment, and the greenhouse effect are all related to the unreasonable development of the chemical industry. Environment condition is to urgent that we have to save it immediately. Organic electrochemical have been becoming a hot topic because it is a pollution-free method^[1].

1.2 History of Organic Electrochemical Synthesis

Organic electrochemical synthesis is a Interdisciplinary discipline of organic synthesis and electrochemical. Compared to conventional organic synthesis, there is no waste produced during the synthesis. It is good for ecology, and environmentally. it react via the electron transfer. Many reaction can be taken at room temperature and the condition of the reaction is easy to achieve. the history of electrochemical can date to eighteenth century, around 1790s, a famous anatomist in Italia called Gagny find the “bioelectricity” phenomenon through dissect frogs. in 1800, Volta created a battery

which can be used in daily life and opened the electrochemical century. More than a century later, The development of electrochemical technology has made remarkable achievements. Whether it is practical application or research on electrochemical theory, people have benefited a lot. Electrochemical research not only promotes the use of electricity, but also promotes the related scientific fields. the use of electricity have increased the produce efficiency and the use of machine, as a result, electrochemical have made great contribution to the development of social economy.

In 1824, the German chemist Weiler first artificially synthesized organic matter from inorganic substances, urea。 This opened the history of organic synthesis. In the 19th century, many simple organic compounds have been synthesized and made fairy well results. British chemists synthesized tropinone in the 20th century and received the Nobel Prize in Chemistry in 1947. The American chemist R.B. Woodward received the Nobel Prize in Chemistry in 1965 and is known as the father of modern organic chemistry due to his outstanding achievements. Chinese scientist Wang Hao is synthesizing artificial insulin in 1965, which is a major breakthrough in organic chemical synthesis in China^[2]

Organic electrochemical synthesis are called “green chemistry”. Organic electrochemical synthesis can date back to 19th century, at the beginning of 19th century, Petrov carried out electrolysis experiments on acids and oils and fats , in 1804,England chemists Groggs got blue indigo during the experiment of electrolysis acetic acid. in the 1940s,at the same time, he discovered the Faraday's laws (of the lectrolysis). In the 19th century, Kolbe taken electrolytic reaction on many kinds of carboxylic acid. He get Octane Number through electrolysis acetic acid. This is the Famous Collibal Electrolysis. This opened up on, organic electrochemical developed rapidly until the beginninig of 20th century. However, because organic chemistry catalysis in the 1930s is in the leadership position and thermodynamically occupied the main position and the electrochemical study itself is too impractical. The outside and inside reason makes the temporary trouble of organic electrochemical. However, since the 1960s, the introduction of Quantum Mechanics and the development in optical technology and the rapid advancement in the design, manufacture, and

application of integrated circuits in microelectronics have led to the emergence of organic electrochemical catalysis. Organic electrochemical synthesis welcomes his second spring. In 1964, Nalco built a organic electrochemical synthesis which can produce 18000t/a tetraethyl lead. In 1965, Mansanto built a organic electrochemical synthesis factory which can produce 15000t/a dinitrile. From 1980, because the rising of raw material prices and people have been raised the awareness of protecting the environment, organic electrochemical synthesis becoming the hot topic among people again.,many countries and companies put money in the study and research^[3].

1.3 the advantage of organic electrochemical synthesis

1.3.1 Organic electrochemical synthesis is more economical Compared to noble metal organic catalysts

Organic electrochemical synthesis is cheaper and more environmentally compared to noble metal organic catalyst. Organic catalyst often use platinum catalysts, ruthenium catalysts, palladium catalysts, noble metal catalysts is very expensive. However, nobel metal is used universally because it has unique catalytic activity and selectivity. metal catalyst is at the very high status in the food production, drug manufacturing, chemical product manufacturing, environment protection and many other fields. In addition to that, organic reactions are widely used in many reactions in petroleum and chemical industry too. However, organic catalyst cost a lot, and it does harm to the environment and it produces a lot of waste water and exhausted air. There are some comparative experiment about the cost of organic electrochemical synthesis and organic electrolysis. In this experiment, the author and his groups use perilla lactone as the substrate, and describe the experiment from the point of economic suitability. the experiment uses the inexpensive reticulated vitreous carbon(RVC) as anode material and the stainless stain as the cathode. They put the reaction vessel, the beaker in the air and 50g scale perilla lactone as substrate to conduct oxidation reaction.(Figure2A , illustration).finally, the yield is 47%, the selectivity is (5.6:1), which is similar to the mmol scale experiment, the remains are

the recovered start material.(26%). The results further proved how mild the condition of the reaction. The total cost of the reagent and solvent(include the MeCN quinuclidine, HFIP, Me₄NBF₄) and the electricity is about \$2517. On the other hand, the similar experiment which use TFDO or iron as catalyst lonely with the same scale cost \$9120 and \$37229^[4].

1.3.2 Organic Electrocatalysis is Green Chemistry

The so-called “green chemistry” is a kind of chemistry that does not harm to human body and there is no pollutants produced during the process. The organic electrochemistry is to use electricity technology and methods to replace those compounds that my existing technology can replace and that are polluted by the environment. However, what we have to mentioned is that organic electrochemical synthesis is different from the reaction that only reduce the amount of the pollutants. The reactions which reduce the amount of pollutants does not solve the problems fundamentally, it is just a improved method. However, Organic electrochemical synthesis is free from the pollution sources, there is no exhausted air or other things from beginning to the end. So there is less cost during the process. In addition to that, what is most important is that it reduces the pollution to the environment.

1.4 Organic electrochemical synthesis and its classification and basic methods

1.4.1 Principle

Organic electrochemical synthesis synthetic compounds are uses electricity as catalyst to replace the nobel metal catalyst. Organic electrochemical synthesis is conducted through the electron transfer to complete the redox reaction.

(a) Electrode, which can provide continuous and steady electrons

Power supply, which can provide constant current that help electrons to transfer continuously.

(b) Mediator, the medium that allow a variety of compounds to exist in the same phase.

Electrodes are the most indispensable part of the organic electrochemical synthesis. Electrons cannot transfer without the current provided by the electron. Organic electrochemical is composed of three stages. They are electrochemical stage, chemical stage and physical stage. The reaction cannot be carried out under the condition that the three phases are not enough. There are six parts during the process electrochemical process. What is most important in the process is the electrode. Electrode is the place where the electron transfer performed. The electrosynthesis reaction is a combination of electrochemical processes, chemical processes, and physical processes. The typical electrosynthesis process is as follows:

- (1) The reactant (R) in the electrolyte reaches the electrode surface (physical process) by diffusion;
- (2) R is converted into an intermediate (I) (chemical process) by a chemical reaction such as desolvation and dissociation in the electric double layer or the charge transfer layer, and the solvent-free and non-associative phenomenon does not pass through this process;
- (3) Adsorption of I on the electrode forms an adsorption intermediate (Iad1) (adsorption activation process);
- (4) Iad1 discharges on the electrode and undergoes electron transfer to form a new adsorption intermediate (Iad2) (electrochemical gain and loss electrochemical process);
- (5) Iad2 reacts on the surface of the electrode and becomes a product (Pad) adsorbed on the surface of the electrode;

1.4.2 Classification

Organic electrochemical catalysis is an interdisciplinary discipline that covers organic chemistry and electrochemistry, and it is generally divided into two directions.

- (1) Divided by the types of organic reactions that occur on the surface: It can be called anodic oxidation and cathodic reduction reaction, The anodic oxidation processes include many kinds of reactions, such as electrochemical epoxidation,

electrochemical halogenation, oxidation of benzene rings and side chain groups on the benzene ring. Reduction reaction, anodizing reaction of heterocyclic compounds, anodizing reaction of nitrogen-containing sulfide, Reduction reaction also include many kinds of reactions, such as anodizing reaction of heterocyclic compounds, anodizing reaction of nitrogen-containing sulfide, anode reduction process including cathode dimerization and cross-linking reaction, electroreduction of organic halides, electroreduction reaction of carbonyl compounds, nitro-compounds Electroreduction reaction, electroreduction of nitrile-based compounds.

(2) According to the synthesis method, it can be divided into direct organic electrochemical synthesis and indirect organic electrochemical formation. Direct organic electrochemical synthesis, the reaction takes place directly on the surface of the electrode. This type of reaction occupies most of all. Which includes oxidation, reduction, cracking, coupling, condensation, halogenation, etc^[5].

Indirect organic electrochemical synthesis, redox reaction is taken place in the conventional way, but the oxidants(reducing agent) can be recycled and generated after the reaction and use it again and again. the reaction has two kinds, the first one is proceed in the groove, and the other one is proceed out of the groove. the same device in the tank The chemical synthesis reaction and the electrolytic regeneration reaction are conducted in the medium; the electrolytic regeneration of the medium is performed in the electrolytic tank in the tank type, and then the medium is transferred from the electrolytic tank to the reactor for the chemical synthesis reaction of organic substances. The basic process of organic electrochemical synthesis is the electrolysis reaction. The common reactions of organic electrochemical synthesis are constant potential electrolysis and constant current electrolysis.

Constant potential method:

The electrode potential does not only determines whether the redox reaction can take place and react continuously also determines the experiment rate and extent of the reaction. Selecting the appropriate point for electrolysis is the direction to control the electrolysis reaction and ensure that the product meets the required determinants. After prolonged, the concentration of reactants gradually decreased and the potential

of the electrodes changed, which led to the acceleration of side reactions and the decrease of the selectivity of the electrode reactions, which led to a gradual decrease in the current efficiency of the main reaction.

1.5 Electrolyte Solvent Reference Electrode and Factors Affecting Reaction Rate

1.5.1 Electrolyte Solvent Reference Electrode

Solvents can be divided into two major categories: One is protic solvents, and another is aprotic solvents. There are some requirements for electrolyte solvent. The requirements are as follows:

(1) Proton activity, when the experiment chooses protic solvents, protons have a great influence on the electrode. When the experiment chooses aprotic solvents, the anion radicals which is generated by electrode can exist a long period of time. He is more difficult to reduce than the original reactants.

(2) The potential range that can be used, the solvents that do not decompose when being energized can be used, and the wider the potential application range, the better.

(3) Dielectric constant: The tear transaction dissolves or dissociates in a solvent having a high dielectric constant.

(4) Solubility: A very small number of solvents can dissolve organic and inorganic salts at the same time.

(5) The range of temperature: The solvent is required to be in the liquid phase at a suitable temperature.

(6) Chemical stability: When the solvent is used, it cannot react with reactants, products, electrodes, and intermediate products.

(7) The solvents that be choosed should be as cheap as possible, In addition to that, it can both react with reactants, products, electrodes, and intermediate products^[6].

Electrolyte

The reaction usually chooses salts with high solubility and high decomposition voltage are used as supporting electrolytes. The electrolyte must have the two conditions at the same time, or the reaction cannot proceed smoothly. There are many

supporting electrolytes that can be used in water. For example: perchlorates, tetrafluoroborates, nitrates, carboxylates, aromatic sulfonates. non-aqueous solution.

Reference electrode

In organic systems, organic solvents are mostly used, different solvents have different redox potentials, and calomel electrodes (SCE) are widely used in non-aqueous solvents. Silver-silver chloride electrodes are also commonly used in many non-aqueous solvents.

The calomel electrode is the most common kind of reference electrode. It is composed of Hg and Hg_2Cl_2 in the saturated aqueous solution of KCL aqueous solution. There are three kinds of commonly used calomel electrodes. The saturated solution of KCL is composed of For the saturated calomel electrode, the concentration of KCl in the solution is one mole per liter. The electrode is an equivalent calomel electrode, and the KCL concentration is 0.1 moles per liter of a 0.1 mol/l calomel electrode.

Since the potential of an individual electrode cannot be measured, the relative electromotive force value of the electrode is often determined by using a standard hydrogen electrode as a reference electrode. However, although the standard hydrogen electrode is stable, it is inconvenient to use, so a calomel electrode with good reproducibility and stability is commonly used as a reference electrode. The calomel electrode is a reference electrode composed of mercury and calomel with different concentrations of KCl solution, and its electrode potential can be accurately measured with a standard hydrogen electrode to form a battery. Therefore, this electrode is also called a secondary standard electrode.

The silver chloride electrode is an electrode formed by depositing silver chloride on the silver surface of the silver chloride in a solution containing chloride ions, and the AgCL electrode is represented by $\text{Ag}/\text{AgCl}/\text{CL}^-$.

The potential of the AgCL electrode is constant and its reproducibility is good. It is a very common reference electrode. His standard electrode potential is +0.2224V (25 degrees). The feature is that it is more stable than other electrodes when the temperature rises. There are often three types. When this electrode is used for

CL-containing solutions, it is affected by the amount of trace oxygen, and N₂ protection can be added during precise activity. When the solution contains nitric acid or chloride ions, bromide ions, ammonium ions, and cyanide ions, it cannot be used. In addition, it can also be used as an internal reference electrode for other electrodes such as glass electrodes and ion selective electrodes.

1.5.2 The factors which can affect the reaction rate

Electrodes, mediators, electrolytes, and solvents, as well as the size of the current, have a very important influence on the reaction. An experimental group has conducted experiments specifically for this and has published papers.

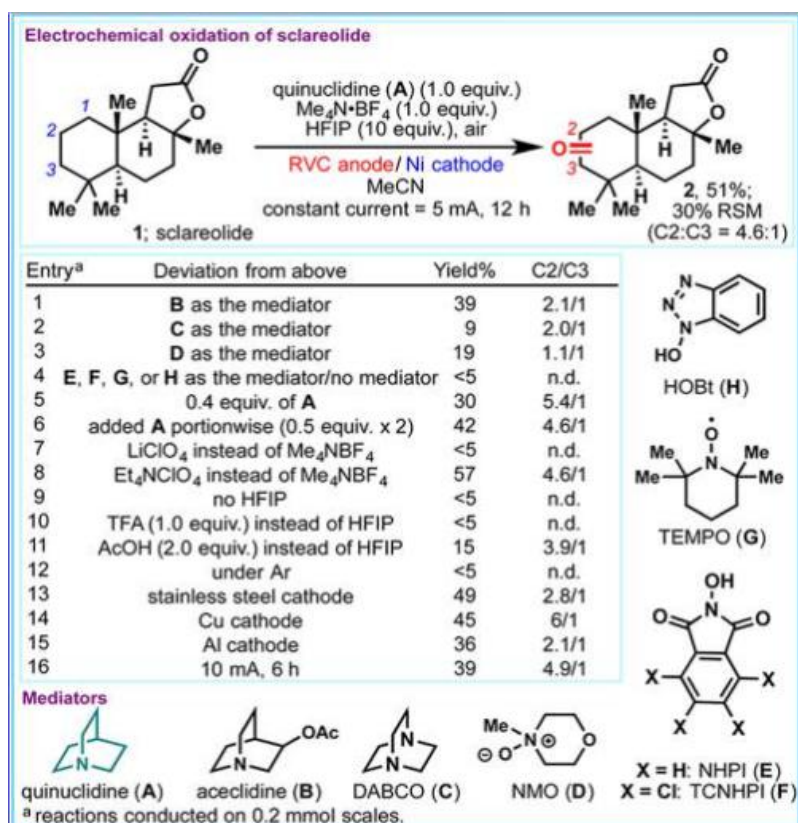


Figure.1

Because as mentioned earlier in this article. We should use the solvents as cheap as possible. as a matter of fact, we should not only use cheap solvent as much as possible, but also should use the cheap electrode, cheap electrolyte, cheap materials as much as possible, because the money is limited, the experiment is unlimited, the cheaper the cost, the more experiments we can take place.

As shown in the figure, basilolide and quinoline were reacted to give a product. The use of quinuclidine (A) as a medium allowed the experiment to generate methylene oxidation at 1.8 V (compared with the Ag/AgCl reference electrode). However, we cannot get a good yield like the reaction described before when we use the compounds which have the similar structure with Perilla lactone such as aceclidine (B) and DABCO (C). In fact, the TCNHPI (F), which is a highly effective medium for vinyl groups cannot produce enough ketone 2 yield. Both NMO (D) and TEMPO (G) and HOBT (H) are all proved to be ineffective materials. So it is not surprising that the oxidation product is less than 5% in the absence of media in entry 4. The choice of dielectric has a great influence on the result. The attempts to decrease the amount of Quinine ring leads to the decrease of oxidation product (entry 5). At the same time, increasing the amount of quinuclidine (A) in batches had little effect on the yield and selectivity of the reaction. The use of lithium perchlorate almost has no effect on the reaction. According to the reaction principle, maybe the lithium cation has chelated with the quinuclidine (A) (entry 7). However, Et₄N.ClO₄ and Me₄N.BF₄ are almost equally effective. (entry eight). The latter one was chosen because it is very safe and the price is very low. In another word, It is more economical and security. Hexafluoroisopropanol was considered as a necessary additive after the completion of the extension test; The experiment has also made other attempts to improve the reaction. For example, attempts to use other Bronsted acids such as acetic acid and trifluoroacetic acid also failed. (entries 9-11). Oxygen on the surface acts as an oxidant at the end of the reaction. And it works very well. On the other hand, there is no product produced under the atmosphere of Ar.

The use of expensive electrode materials (such as palladium electrodes) are avoided consciously at the beginning of the reaction, The experiment uses reticulated vitreous carbon (RVC \$3 each) as anode. On the other hand, steel, copper, and even stainless steel are considered as proper cathode materials. (entries 13-15). The reaction can be taken place at room temperature and direct current conditions. The reaction does not need special temperature. The experiment can be taken place under the room temperature. It does not need a divided cell, it can be taken place in a single cell

(Figure 1) [7].

1.6 Successful case of industrialization and major progress this year

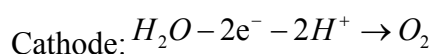
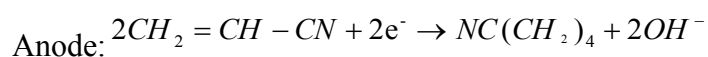
1.6.1 Electrosynthesis of adiponitrile

Baizer proposed in 1959 that hydrogenation of acrylonitrile through the cathode produces adiponitrile. In 1965, the Monsanto Company of the United States industrialized this method and built an adiponitrile production plant with a capacity of 15,000 t/a, and later expanded to 100,000 t/a. The synthesis of adiponitrile is divided into two steps:

(1) Using propylene as a raw material to be converted into acrylonitrile by ammonia

oxidation, the reaction is $2CH_2 = CH - CH_3 \xrightarrow{NH_3} 2CH_2 = CH - CN$

(2) Hydrogen dimerization to adiponitrile on the cathode surface by electrolysis:



Dinitriles are used as chromatographic fixatives; Intermediates for the production of Polyamide fiber, accelerators and rust inhibitors. Additives for detergents, spinning solvents for Acrylonitrile, Methacrylonitrile and Methyl methacrylate terpolymer, Polyvinyl chloride fiber Wet spinning and Dry spinning solvent, colorants for Polyamide, auxiliaries for fabric bleach, Acetate, Propionate, Butyrate, and Mixed ester plasticizer; and extractants for aromatic extraction, and the like. Gas chromatography fixative. For organic synthesis, used as analytical reagents, solvents. Gas chromatography fixative. Separation, analysis of amines and nitro compounds

1.6.2 Electrosynthesis of Tetraethyl Lead

The Grignard reagent and lead pellets were electrolyzed to synthesize tetraethyl lead. Chloroethane was continuously added to the solution during the reaction, and the Grignard reagent was regenerated with the Mg precipitated at the

cathode, and the byproduct $MgCl_2$ was used to produce Mg.

The reaction is: $C_2H_5Cl + Mg \longrightarrow C_2H_5MgCl$

Anode: $4C_2H_5MgCl + Pb - 4e^- \longrightarrow Pb(C_2H_5)_4 + 2MgCl_2 + 2Mg^{2+}$

Cathode: $2Mg^{2+} + 4e^- \longrightarrow 2Mg$

Tetraethyl lead has been widely used as a gasoline additive to enhance fuel

Octane can avoid engine explosions, and higher compression ratios can be used to increase the efficiency and power of automotive engines. The first to add tetraethyl lead is the United States of America. Compared with alcohol as an additive, the advantage of leaded gasoline is that its high energy content facilitates long-term storage. It has become the most widely used additive. Its greatest advantage is that tetraethyl lead can increase the amount of octane by using only a very small amount of tetraethyl lead compared to other high octane gasoline blends. The solution of tetraethyl lead can be obtained by adding it to gasoline.

In the past three decades, organic electrochemical synthesis become more and more popular among scientist and factory. Especially in the developed countries , such as the United Kingdom, the United States, Germany, and Japan and so on. Their development and application in this field is quite active. The number of patents has increased greatly. The failed that can make a lot of money are their target such as medicine manufacturing, spices produce, the production of photosensitive materials, and the produce of pesticides. Up to now, there are more than 100 types of organic electrosynthetic products that have reached industrial production, and there are more than 8 thousand products can be produced in the laboratory which is waiting for the industrial production. There is a bright future in this field. the perspective is very board.

1.6.3 China's current achievements in industrial production

Over the past years, more and more organic electrosynthesis has been used in industrial production. More than 100 organic electrosynthesis products have been

used to produce more than 80 products. Although organic synthesis in China is not too early, the progress is rapid. Several examples of organic synthesis used in industrial production, such as L-cysteine, which was originally used in large-scale production in China. He extracted cysteine from the coat of livestock and used electrolysis to generate L- Cysteine. In the last two decades, this method has been used on a large scale in many parts of the country, producing over 600 tons per year. This has become the most important method of producing L-cysteine, and it is also a leading product of China's foreign sales.

Dimethyl carbonate is also an important product of organic synthesis. It is an important chemical intermediate and is widely used in the synthesis of various compounds. It can be used as paint manufacturing, non-toxic solvent, gasoline additive, it can replace Freon, $C_2H_3F_3$, C_2HF_3 , C_6H_6 , for production, dimethyl dimethyl carbonate, green and environmental protection, has little side effects on human body and has many reaction characteristics. , No pollution in production, convenient transportation, commonly used by people.

1.6.4 Progress have been made in recent years

(1) The application of solid polymer electrolyte (SPE) in electrochemistry. Solid polymer electrolyte is a kind of polymer ion exchange contact. It has good chemical and metal stability, and excellent conductivity and so on.

(2) The latest research progress of carbon-based Sb-Pb-Pt electrocatalytic nanomaterials. Experiments show that the catalytic activity and stability of carbon-based Sb-Pb-Pt electrocatalytic nanomaterials are much higher than those of commonly used metal electrodes such as Sb and Pb. The application prospect is very good.

(3) Recent developments in the synthesis of metal organics, metal organics have special functions and it can be used as catalysts, polymeric materials, stabilizers, preservatives and pigments.

(4) The latest application of ultrasound in organic synthesis. The application of

ultrasound can solve many problems in organic electrochemical synthesis, it provides another way which is different from other solutions, especially in the best point chemical reaction conditions, and shows a good prospect of industrial use.

Chapter 2 the Progress of Functionalization of C-H Bonds

2.1 Electrochemical cyclization

The cyclization of compounds has always been a problem for chemists. In this respect, after years of efforts, US chemists have now achieved good results. Through electrochemical oxidation, they have used electron-rich groups to increase their activity and have obtained closed loops. Alkanes, (Figure 2) In China, Professor Xu Haichao has achieved remarkable results in electrochemistry after years of hard work. They used ferrocene as a medium to form activated radicals under the action of electricity and synthesized functional groups of C-H bonds.(Figure 3)

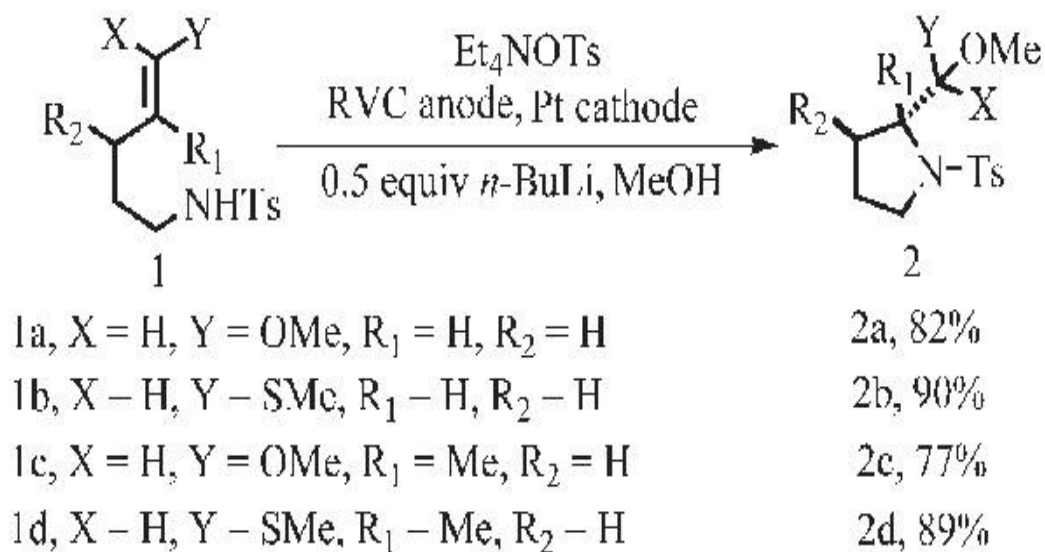


Figure.2

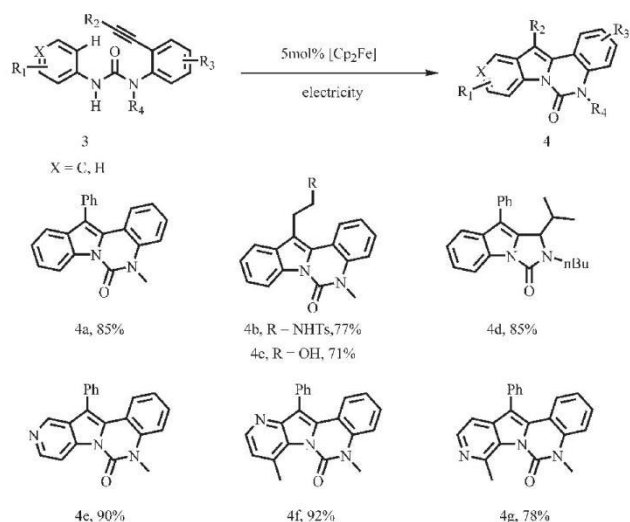


Figure.3

2.2 Oxidative coupling of phenol

Phenol compounds have special electrochemical properties, they can react under the anode to form free radicals, and then the next series of experiments in the experiment, a team of German universities teaching their team to make excellent results, they are mainly engaged in such research, they add diamonds to the anode. After oxidation, the compounds generate free radicals, followed by a coupling reaction to achieve functionalization of the C-H bond. Figure 4

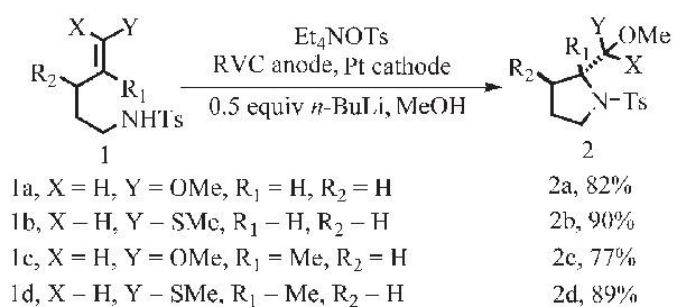


Figure.4

Chapter 3 Electric induction of C-H bond functionalization

Experiment

3.1 Introduction

Electric induction of C-H bond functionalization is use electricity as catalyst to replace the expensive noble metal catalyst to take place the reaction. this not only can reduce costs but also reduce pollution. It is a sustainable way to take place reaction from the point of both economic and environment. The ultimate goal of organic electrochemistry is to combine experiment and practice. The ultimate goal of organic electrochemical synthesis is to combine experiment and industrial production together to drive production, this can promote the development of economy and it can promote the development of technology on the other hand. The progress and economic benefits of science and technology will be promoted by science and technology, and production will be used to bring scientific research results to the ground and promote each other. Production, education and research will be combined to help each other. Now since our laboratory has just set up for several months. All members of our laboratory works very hard, starting out fresh and starting from scratch. We study from morning to the night, from Monday to Saturday. Try our best to correct the error in order to make progress little by little and get a good result. Steps to improve, read the literature, learn from existing scientific research achievements, and use this as a basis for improvement and innovation. The electrical induction of functional grouping of C-H bonds is a research direction of great research value. As mentioned above, many achievements have been made in recent years. Since our undergraduates have a poor foundation, So we conduct the experiment which have already completed by our seniors. Our experiment is the exploration of the completed experiment. The C-H bond functionalization is efficient, clean, easy to carry out, easy

to control, and very suitable for carrying out in the laboratory.

3.2 Experimental section

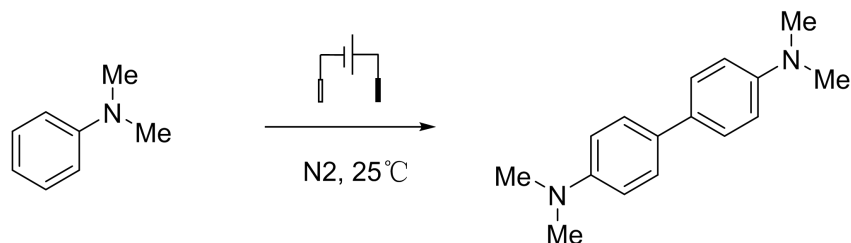


Figure 3.2.1

3.2.1 Experimental Instruments

Dark box type UV analyzer	ZF-10D	Gongyi yuhua instrument co. LTD.
The potentiostat	DJS-292B	Shanghai xinrui instrument co. LTD.
Intelligent magnetic stirrer.	ZNCL-BS	Gongyi yuhua instrument co. LTD.
Pioneer electronic balance.	Pioneer electronic balance.	Auhaus instrument (changzhou) co. LTD.
Pipetting gun ul 100-1000	YE181AG0190718	Auhaus instrument (changzhou) co. LTD.
Pipetting gun 20-200 ul	YE178AF0080763	Auhaus instrument (changzhou) co. LTD.
Rotary evaporator	YRE-2000B	Gongyi yuhua instrument co. LTD.

Low temperature cooling circulation pump.	CLA-20	Gongyi yuhua instrument co. LTD.
CNC ultrasonic cleaning device.	KQ3200DB	Kunshan ultrasonic instrument co. LTD.
Electric heating constant temperature drying oven	DHG-9020A	Gongyi yuhua instrument co. LTD
Vacuum drying oven.	DZF-6020	Gongyi yuhua instrument co. LTD

3.2.2 The experimental drug

N,N- dimethylaniline. C ₈ H ₁₁ N	Pure analysis	Tianjin da MAO chemical reagent factory.
acetonitrileCH ₃ CN	Pure analysis	Tianjin fuyu fine chemical co. LTD.
Lithium perchlorateHClO ₄	AR (99%)	Shandong western chemical co. LTD.
Anhydrous sodium carbonateNa ₂ CO ₃	Pure analysis	Tianjin beichen founder reagent factory.

3.2.3 steps of experiment

1. Take a small reaction flask, add magnets to the flask in the reaction flask, and call the medicine. 0.0636 g of anhydrous sodium carbonate and 0.0425 g of lithium perchlorate were weighed and then the liquid was weighed. Pipette was used to remove 5 ml of acetonitrile and 126.25 ul of N,N-dimethylaniline.
2. Take a rubber stopper, still in the rubber stopper still two small holes, insert the lead, deducted to the reaction flask, the lead core has not been liquid, but do not touch the

magnet, hindered the reaction, and then, to the reaction flask filled with nitrogen After filling, pay attention to seal the edge of the bottle with a sealing film and seal it several times to prevent air leakage. After everything is in place, the vial is clamped onto the clamp and placed in the oil bath of the ZNCL-BS Smart Magnetic Stirrer. The lead is set on both the black and red clamps of the DJS-292B potentiostat and the potentiostat is set. Current is 5mA, speed is 300r/min, temperature is 25 degrees Celsius.

3. After about nine hours, close the reaction and record the time and voltage at this time. Open the reaction flask.

4 After the reaction flask is opened, thin layer chromatography (dot) processing is performed next. Compared with the reactants, a new point is found, that is, a new substance is generated. If no new point is generated, no product is produced. That is, there is no reaction of the raw materials and it is necessary to conduct experiments again and filter the conditions.

5 If there is a new point, further experiments will be carried out to confirm what the new point is. The first thing that needs to be done is to perform column chromatography separation (pass the column) and filter the new point solution to a new eggplant type before passing the column. In the bottle, the excess solid particles are removed, and after filtration, about 2 ml of silica gel powder is placed in an eggplant-type bottle containing the filtrate, and then the bottle is placed on a YRE-2000B rotary evaporator and suspended. Volatilize cleanly, leaving only dry powder in the bottle.

6 Separating column chromatography of the suspended powder, collecting the liquid from the column chromatography, using tubes, and ordering them in order. Then, the liquid in the tube is again spotted and new points appear. The liquid in the test tube was collected and suspended again. Before being suspended, the bottle was weighed and the mass was recorded. Do not put silica gel powder this time, until the liquid evaporates to the end, and there are solid particles attached to the bottle wall. When there is still a little liquid in the bottle, this point plate is used to check the purity of the product.

7 Suspension was completed and dried. The bottle after the completion of the suspension was placed in a DEZ-6020 vacuum drying oven and dried. After drying, weighing was performed again. Data were also recorded to calculate the yield. After the weighing was completed, the chromatographically pure methanol was placed in a bottle and the resulting mixture was added to a 1000-fold concentration and placed in a GC-MS bottle. Conduct the test.

Change the condition response as follows

Entry	Sol.(ml)	Base(mol%)	Electrolyte	Temperature	Time (h)	Yield(%)
1	CH ₃ CN	Na ₂ CO ₃	LiClO ₄	25°C	6	45
2	DMF	Na ₂ CO ₃	LiClO ₄	25°C	6	23
3	DMSO	Na ₂ CO ₃	LiClO ₄	25°C	6	34
4	CH ₂ Cl ₂	Na ₂ CO ₃	LiClO ₄	25°C	6	13
5	CH ₃ OH	Na ₂ CO ₃	LiClO ₄	25°C	6	24
6	CH ₃ CN	Na ₂ CO ₃	<i>n</i> Bu ₄ NBF ₄	25°C	6	26
7	CH ₃ CN	Na ₂ CO ₃	C ₁₆ H ₃₆ BrN	25°C	6	31
8	CH ₃ CN	<i>t</i> BuOK	LiClO ₄	25°C	6	24
9	CH ₃ CN	Et ₃ N	LiClO ₄	25°C	6	15
10	CH ₃ CN	Na ₂ CO ₃	LiClO ₄	40°C	6	30
11	CH ₃ CN	Na ₂ CO ₃	LiClO ₄	60°C	6	22
12	CH ₃ CN	Na ₂ CO ₃	LiClO ₄	25°C	5	21
13	CH ₃ CN	Na ₂ CO ₃	LiClO ₄	25°C	7	26

In order to determine the optimal reaction conditions, solvents, bases, electrolytes, temperatures, reaction times were screened, and the optimal experimental protocol (entry.1) was finally determined. Among them, the reaction time has a great influence on the reaction, and 6h is the optimal reaction time. The reaction time longer than 6h will cause the resulting product to continue to react and produce by-products, which will reduce the yield.

Chapter 4 Results and Discussion

4.1 Analysis of experimental results

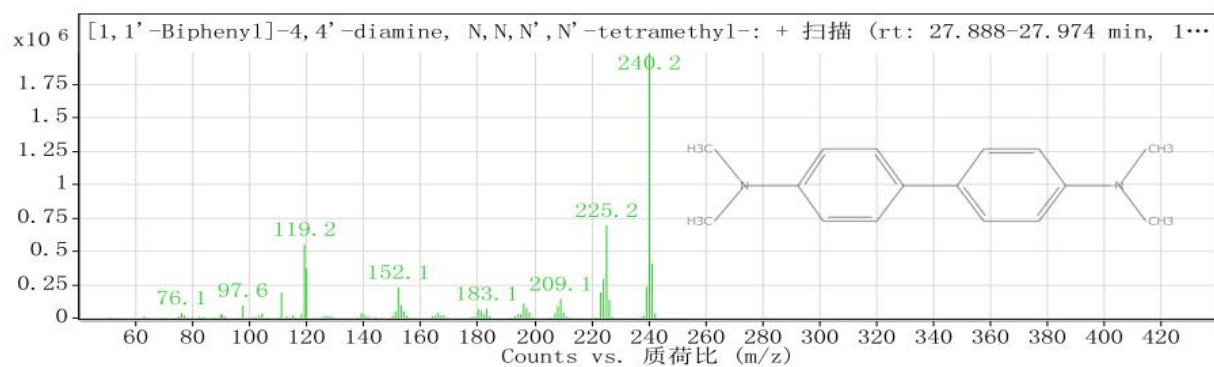


Figure 3.1.1 shows the MS after column chromatography.

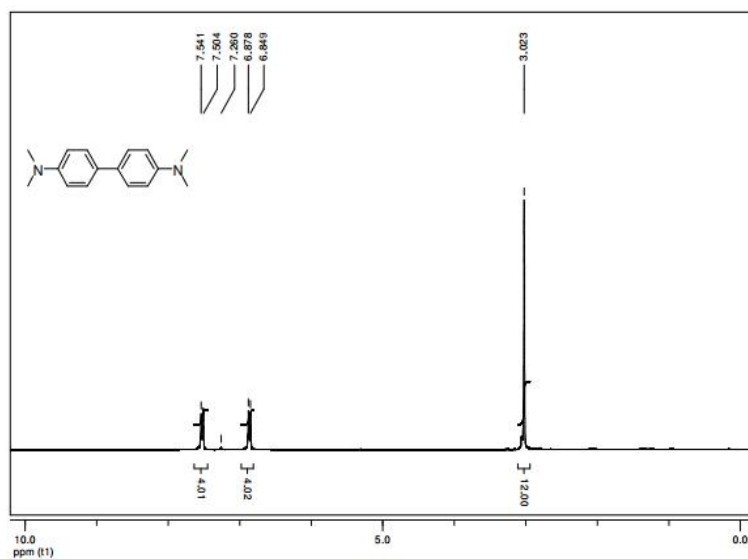


Figure 3.1.2 shows the ¹H NMR of the production

4.2 Analysis of graphs

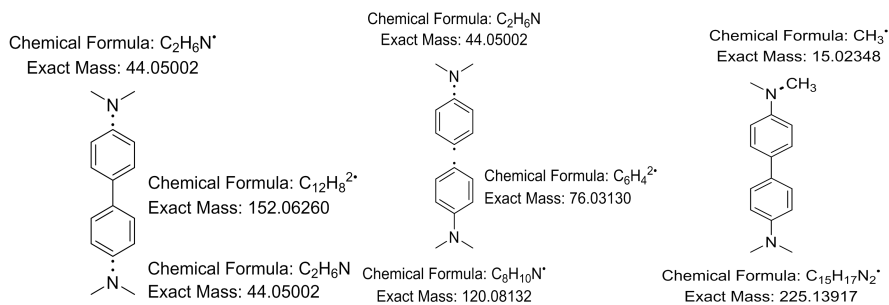


Figure3.2.1

Figure3.2.2

Figure3.2.3

The figure above shows the mass-to-charge ratios of the parts of the simulated product that are ionized in the mass spectrometer, which are consistent with the peaks in the mass spectrum and more accurately determine the structure of the product. On the other hand, it cannot react completely if less than 6 hours.

Through the chemical shift and the number of H on HNMR and MS graphs we can know the production is N,N,N',N' -tetramethylbenzidine.

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