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Reaction of iodide ferroceenyl-methyle trimethyl ammonium with acetohydrazide and the electrochemical study

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GENERAL INTRODUCTION

The chemistry of organometallic compounds has found broad application possibilities in various industrial branches in recent years. A representative of these compounds is ferrocene.

The subject of this work is to do an electrochemical study by cyclic voltammetry to a hydrazide's ferrocene synthesized.

Our study have two important parts, the First is theoretic contain tow chaptre the once is a general information about ferrocene and its derived the second one is about electrochemical study and the last part is the third and fourth chaptre where we have our experiences, resultants and its discussion.

IST PART

THEORETIC STUDY

CHAPTER 1

CHEMICAL PROPRETY OF FERROCENE

CHAPTER 2

ELECTROCHEMICAL PROPRETY OF FERROCENE

I.I. Ferrocene

I.1.1. The discovered of ferrocene

Ferrocene was discovered for the first time unexpectedly by T. J. Kealy and P. L. Pauson in the early 1950[1], when they were trying to synthesize fulvene from cyclopentadienyl magnesium bromide and iron (III) chloride . The mechanism is that Fe^{+3} is firstly reduced by Grignard reagent and then reacts with C_5H_5MgBr to give ferrocene[2]. Almost at the same time, Miller and co-workers have also obtained ferrocene through reactions of Fe with cyclopentadiene under high or normal atmosphere[1]. In 1952, Wilkinson and Woodward have elucidated from measurements of IR, magnetic susceptibility and dipole moment the structure of ferrocene[3], which was confirmed by X-ray crystallography afterward. The special structure, bonding and aromaticity of ferrocene defied conventional bonding descriptions[4], thus stirred up the imagination of chemists consumedly.

The discovery and characterization of the structure of ferrocene opened up a new area of chemistry, leading to an explosion of interest in d-block metal carbon bonds and bringing about development and the now flourishing study of organometallic chemistry.

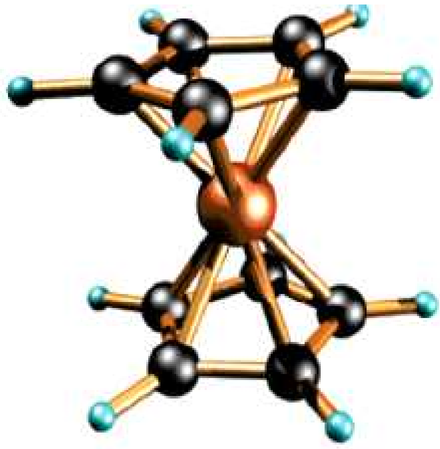


FIGURE.1

The structure of ferrocene

I.1.2. Electronic Structure of Ferrocene

Ferrocene can be considered as consisting of an Fe^{2+} ion (six d-electrons) bonded to two cyclopentadienyl anions (six π-electrons each)[5], and thus it can be seen that ferrocene obeys the 18-electron rule – all valence electrons are located in bonding or non-bonding orbitals. The anti-bonding orbitals are left unpopulated[6], and hence the compound is stable.

A more informative picture of the bonding within ferrocene is provided by a molecular orbital diagram (Figure.2), which shows the molecular orbitals which result from the interactions of the ligand and metal orbitals[4]. Symmetry considerations, the relative energies, and overlap integrals of the ligand π-orbitals and the 3d, 4s and 4p orbitals of the central iron can be used to predict which molecular orbitals will be formed[7].

The lowest-energy orbitals are ligand-based (a_{1g}, a_{2u}), as the metal orbitals with appropriate symmetry requirements (3dz^2/4s, and 4pz respectively) are so much higher in energy. The e_{2g} orbitals remain essentially metal-based ($d_{x2-\ y2}$, d_{xy}), as their δ-overlap with the ligand e_{2g} orbitals is poor. The stability of the ferrocene molecule is largely due to the overlap of the ligand e_{1g} orbitals with the d_{xz} and d_{yz} orbitals of the iron atom, which results in the formation of two strong π-bonds[4].

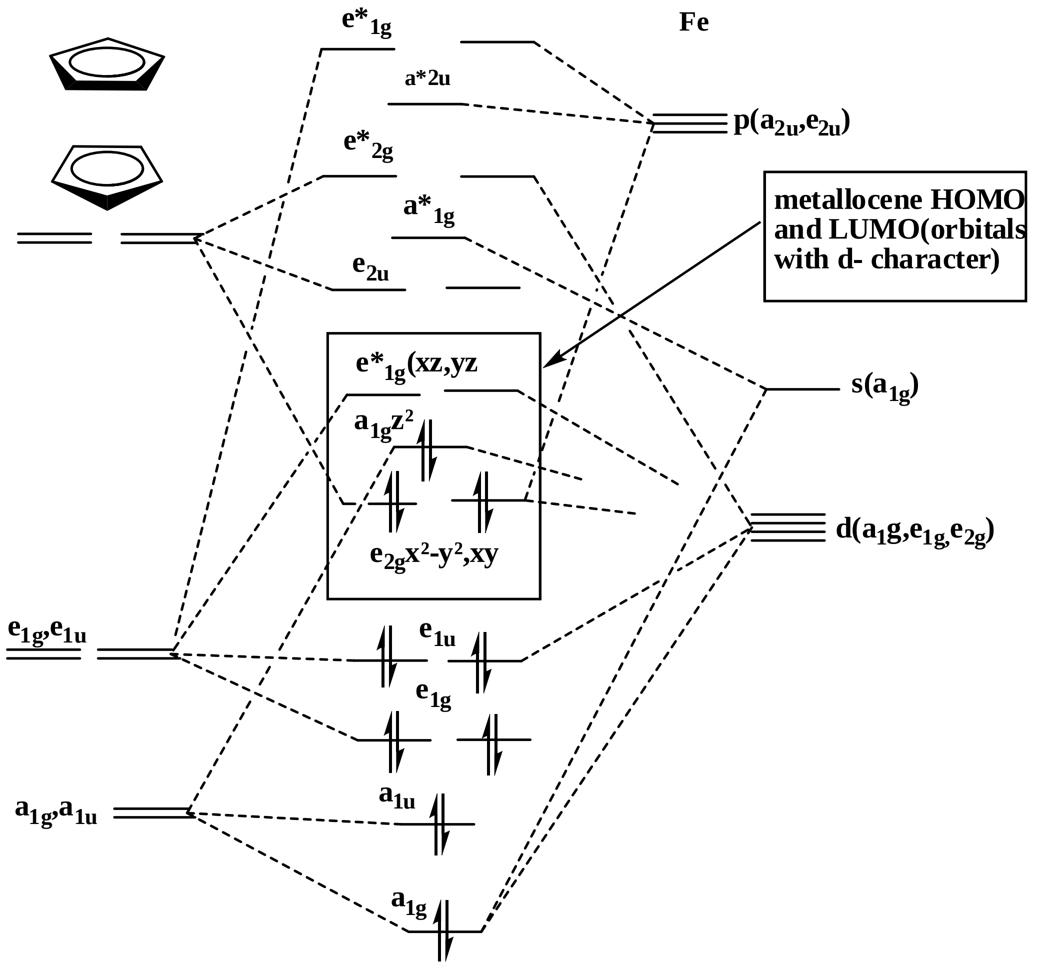


FIGURE .2

A qualitative molecular orbital diagram for the ferrocene molecule.

I.1.3. The Chemistry of Ferrocene

Ferrocene (as well as other metallocenes) are usually prepared by one of three different synthetic routes. The first of these involves the cracking of di cyclopentadiene (a retro Diels-Alder reaction), followed by deprotonation of the weakly acidic cyclopentadiene with an alkali metal. Treatment with iron (II) chloride then affords ferrocene[8]:

$$FeCl_2 + 2NaC_5H_5 \rightarrow [(\eta^5 - C_5H_5)_2Fe] + 2NaCl$$

The second method is known as metal vapour synthesis; the reactants are heated to high temperatures, and then brought together on a cold surface:

$$Fe + 2C_5H_6 \rightarrow [(\eta^5 - C_5H_5)_2Fe] + H_2$$

Finally, ferrocene can also be prepared via the use of an auxiliary base, which generates the cyclopentadienyl anion in situ:

$$FeCl_2 + 2C_5H_6 + 2C_5H_5NH \rightarrow [(\eta^5 - C_5H_5)_2Fe] + 2[C_5H_5NH_3]Cl$$

I.1.4. The proprieties of ferrocene

Ferrocene the orange crystalline compound has a molecular weight of 186.04 g.mol$^-$[9] it is 30.02% iron by weight[10]. Insoluble in water(0,1mg/mol) [9] and soluble in organic solvent (solubility ranged from a high of 5.59% Fe for benzene to 0.09% for 1-Butanol. Xylene isomers had relative high solubility’s in the 3.5 to 4.0% range. Aliphatic solvents dropped off to the 1.0 to 1.5% ranges. Chlorinated hydrocarbons were high as well as carbon disulfide and pyridine) [10], and had a melting point of 173°C[4]. Ferrocene exhibits the properties of a typical aromatic molecule. It is stable to more than 500 °C. It does not react readily with acids or bases; however, it is sensitive toward oxidizing agents. Ferrocene does not undergo addition reactions typical of cyclopentadiene, but readily undergoes electrophilic aromatic substitution[11].

temperatur (T)	Valeure (°C)
Fusion	173-174
Boiling	249
Degradation	470

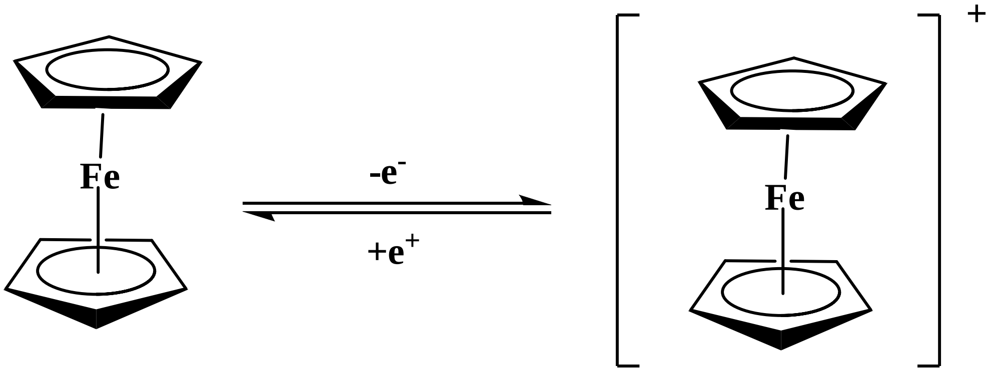
Bonds	Distance
C−C	1,40 Å
Fe−C	2,04 Å

The IR characteristic[9]:

Bonds	Forms	$\Lambda(cm^{-1})$
$C-H_{aromatic}$	Elongation	3075
C−H	Vibration	811−1002
CP	Vibration	1108
C−C	Vibration	1411

I.1.5. Basic electrochemical behaviors

A number of the ferrocene derivatives have been synthesized and used as electronic and optical materials because the cyclopentadienyl (Cp) ligand of ferrocene is readily functionalized by nucleophilic organic reagents and because electrochemical properties of the Fe(II)Cp2 fragment can be tuned by selecting the substituents introduced on the Cp ligand. The oxidation between the neutral Fe(II) state and cationic Fe(III) state, involving fast and reversible electron transfer, is the important property of the ferrocene derivatives. Introduction of electrochemically active organic groups on the ligand of ferrocene leads to molecules containing both organometallic and organic redox-active centers, which can be used as electrochemical materials in various applications[12].

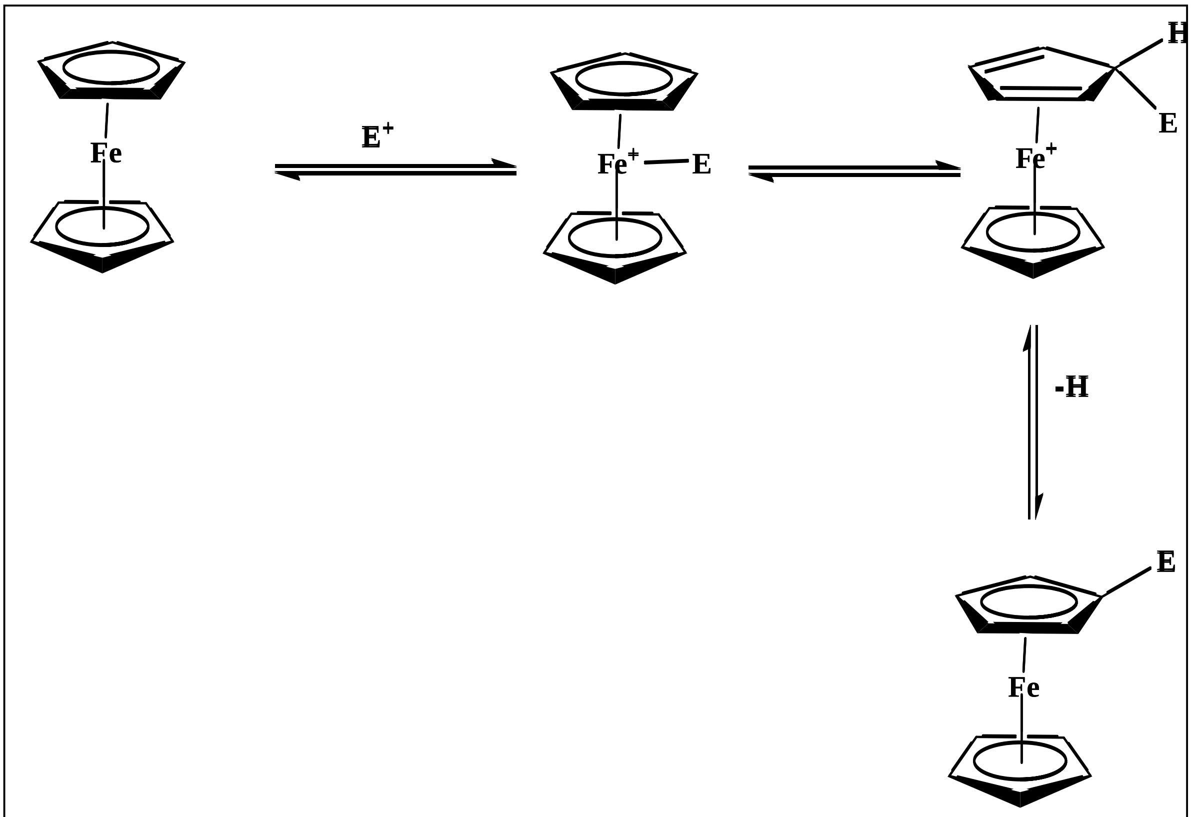


SCHEME.1 Reversible mono electronic oxidation of ferrocene

I.1.6.The main reaction of ferrocene

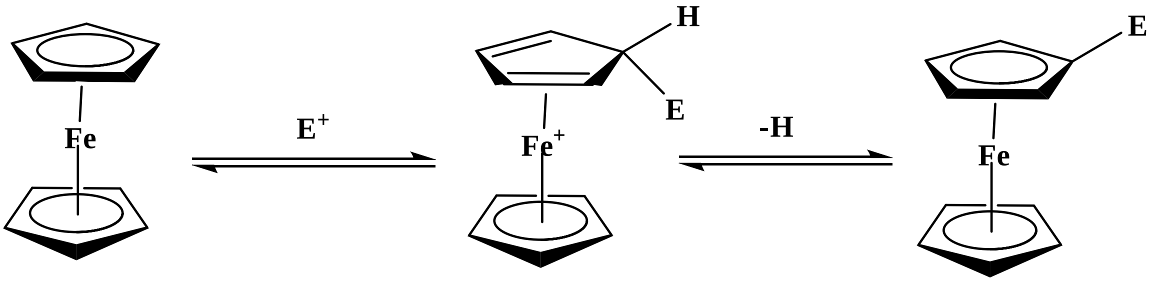
Because of its stability[13], the ferrocene moiety can survive relatively harsh reaction conditions, making a wide range of organic transformations possible. Ferrocene, having six π-electrons delocalized over five atoms, is much more prone to electrophilic substitution than benzene[8].The ferrocenyl group is also one of the strongest known electron-releasing groups (aminoferrocene is twenty times more basic than aniline) [7]. Two main mechanistic routes have been proposed for the electrophilic substitution of ferrocene[8]

In the first of these, the electrophile interacts with the central iron atom, before being transferred to the aromatic ring with subsequent deprotonation.



SCHEME. 2.The mechanism of the first route in the electrophilic substitution of ferrocene

In the second, electrophilic attack takes place directly at the exo face of the ring, with no direct metal participation.

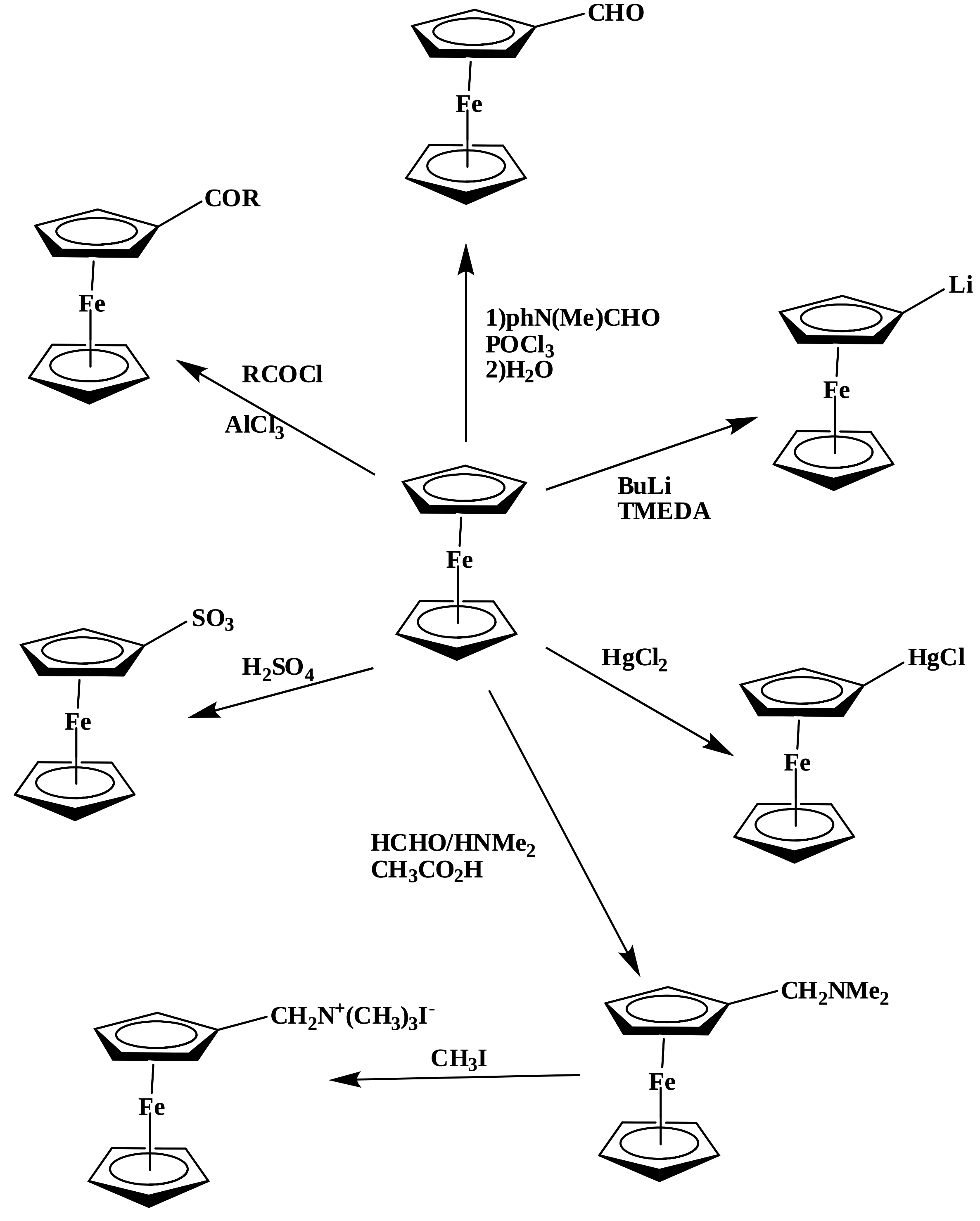


SCHEME. 3.The mechanism of the second route in the electrophilic substitution of ferrocene

Friedel-Crafts acylation of ferrocene occurs readily, yielding both mono and 1, 1’-disubstituted products. Once acylation has occurred on one ring, the unsubstituted ring is deactivated towards further substitution by a factor of 2 x104, illustrating the electronic effects that are passed from one ring to another via the iron centre. The Friedel-Crafts alkylation of ferrocene is not a useful synthetic method because of poor yields, and the resultant mixture of poly-alkylated products results[8].

Lithiation of ferrocene also occurs readily, with t-BuLi or n-BuLi the preferred reagents. As the protons of the aromatic rings of ferrocene are weakly acidic, it can be deprotonated by the hydrocarbon portion of the reagent, and the extent of lithiation can be controlled by choice of reaction conditions. The mono-lithiated intermediate can be formed exclusively via treatment of ferrocene with a stoichiometric amount of t-BuLi or i-BuLi, whereas the 1, 1’-disubstituted product is formed when n-BuLi is used in conjunction with N,N,N',N', tetramethylethylenediamine (TMEDA). No such selectivity is possible with either sodium or potassium reagents.

Unlike benzene, ferrocene can undergo the Mannich reaction with formaldehyde and an amine, and thus is more akin to thiophene than benzene in its reactivity. Another important difference between benzene and ferrocene is the behaviour of the latter in the presence of oxidizing agents (*e.g.* NO_2^+, H_2SO_4). The iron centre is quite easily oxidized to the ferricenium ion, and so direct nitration, sulphonation, or halogenation cannot be carried out in a similar manner to benzene .

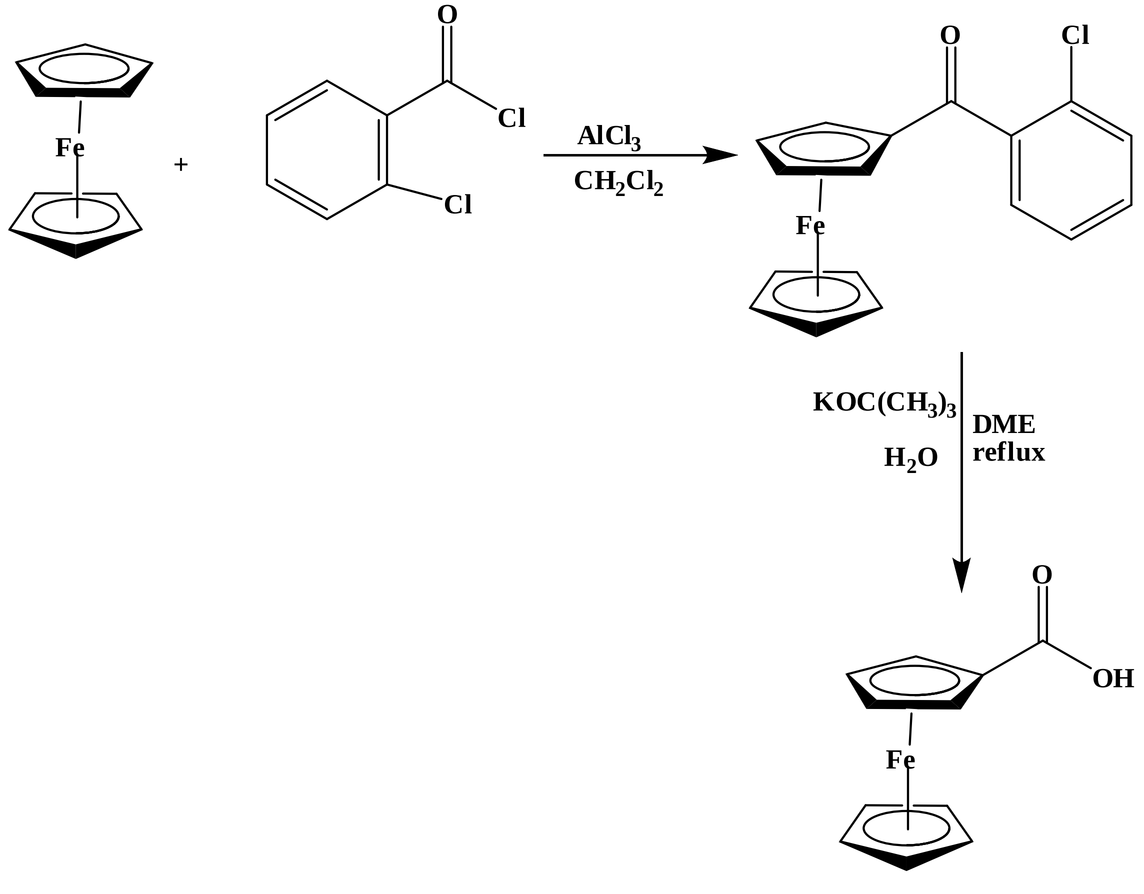


SCHEME.4. The main reaction of ferrocene

I.1. 7. The synthesis of ferrocene derivate

I.1. 7.1. Synthesis of Ferrocene Carboxylic Acid

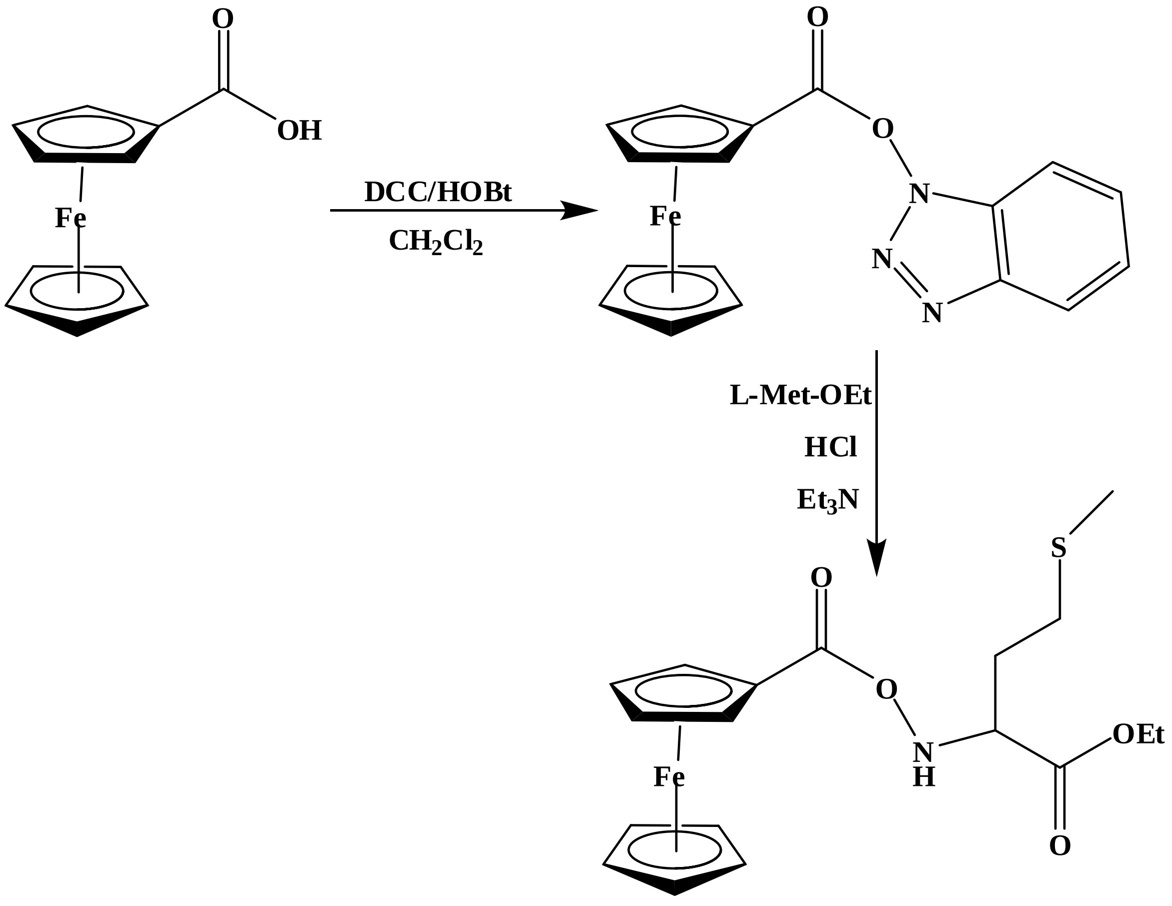
Ferrocene carboxylic acid was prepared using the method of Reeves *et al.* [14], affording the acid as a fine yellow/brown powder in very good yield (70-80%). However, instead of drying the product under vacuum, removal of residual water was accomplished by drying the acid for 6 hours at 80°C.



SCHEME.5. Synthesis of Ferrocene Carboxylic Acid

I.1.7.2. Synthesis of N-Ferrocenoyl Amino Acid Derivatives

Several routes were employed during the preparation of the *N*-ferrocenoyl amino acid derivatives, in order to optimize the conditions best suited to their synthesis. As the project evolved, consistent yields of over 80% were achieved using synthetic route 1. Several of these compounds were selected to undergo subsequent peptide chain elongation to afford *N*-ferrocenoyl dipeptide derivativessz.



SCHEME.6. Synthesis of N-Ferrocenoyl Amino Acid Derivatives

I.1. 8. Applications of Ferrocene

Because of the well defined electrochemical and spectroscopic behaviour, chemical stability and low toxicity of ferrocene[15], it has found applications in areas such as anion sensing, asymmetric catalysis, as a mediator between redox enzymes and electrodes, as liquid crystalline materials, and in materials with high second harmonic generation efficiencies for non-linear optics. The incorporation of a ferrocene moiety into biomolecules is currently an area of intense research activity. Owing to the ease with which electrophilic aromatic substitution can occur on the cyclopentadienyl rings, a vast array of ferrocene derivatives have been reported in the literature since[16]. it was first discovered over fifty years ago.

I.1.8.1. Ferrocene and Asymmetric Catalysis

During the last twenty years, there has been an increasing use of ferrocene derivatives as chiral auxiliaries in homogenous asymmetric catalysis, both in research and on an industrial scale. The ferrocene moiety offers many advantages in this respect. A chiral, redox-active ligand is, in theory, capable of acting as a chiral auxiliary in an organic transformation, with subsequent decomplexation of the ligand upon electrochemical oxidation, thus facilitating the catalytic cycle. Due to its bulkiness, a ferrocene nucleus adjacent to a stereogenic centre can improve stereo selectivity via steric hindrance, and nucleophilic substitution reactions at positions vicinal to the ferrocene group are highly favoured, and take place with retention of configuration.

I.1.8.2. Anionic Sensors Incorporating Ferrocene Units

The design of ferrocene-based anion receptors is another area of current intense research. In biological processes, the majority of enzyme substrates are negatively charged. Therefore, an understanding of the interactions which bind the guest and host molecule together, has potential application in the design of drugs capable of mimicking those interactions. Alzheimer’s disease has been linked to anion-binding enzymes, and cystic fibrosis is known to be caused by a misregulation of chloride channels. From an environmental point of view, pollutants such as phosphate and nitrate anions need to be continually monitored [17].

The first metallocene-based anion receptors reported in the literature were based on the cobaltocenium cation, which were capable of binding anions such as halides, via favorable electrostatic interactions. Electrochemically, the Cp_2Co/Cp_2Co^+ redox couple showed significant cathodic shifts upon anion complexation, with the complexed anion stabilizing the positively charged cobalt centre, thus making it harder to reduce.

Neutral, ferrocene containing secondary amides have no inherent electrostatic interaction with guest anionic species, and their complexed forms have lower stability than their cobaltocenium analogues. However, the anion-receptor interactions can be modulated via oxidation to the ferricenium cation, at which point electrostatic interactions can be 'switched on'. The oxidation of ferrocene in the vicinity of the amide group increases the acidity of the amide proton, making hydrogen-bonding stronger, and thus there is a synergy between ion-paring and H-bonding interactions .

I.1.8.3. Ferrocene Containing Molecules for Second Order Non-Linear Optics

The interest in materials with large second-order optical non-linearities stems from their potential application in telecommunications, optical computing, and optical information processing. In such materials, there is no linear relationship between the induced dipole moment, and the applied electric field, providing the field is of high enough intensity (as is the case with lasers). The induced dipole moment is given by the equation:

$$\mu^{*} = \alpha\varepsilon + 1/2\beta\varepsilon^{2}$$

Where μ^{*} is the induced dipole moment, α is the polarizability of the molecule, ε is the electric field strength, and β is the first hyperpolarizability. Large hyperpolarizabilities are associated with molecules that have large differences between the ground state and excited state dipole moments, and a small energy gap between the ground and excited state [18]. Organic chromophores which fulfil these criteria, the so-called ‘push-pull’ systems, have donor-acceptor moieties separated by conjugated bridges, for example (E)-4-(methoxy)-4’-nitrostilbene [19].

In the last ten years, there has been a substantial amount of work devoted to molecules incorporating a ferrocene group with potential NLO responses. Ferrocene derivatives are particularly suitable to function as a donor in these materials, owing to the presence of metal to ligand charge transfer bands (MLCT) in the visible region, the relatively low redox potential, and the enhanced electron delocalisation in π-substituted systems.

I.2. Electrochemical study

Electrochemical study of organic compounds and in particular cyclic voltammetry is an efficient and convenient approach for the characterization of mass transfer of probe molecules it has been used to evaluate the diffusion of redox-active reagents in many systems [20].

I.2. 1. Voltammetry

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms[21]. There are numerous forms of voltammetry[22].

- Potential Step.
- Linear sweep.
- Cyclic Voltammetry.

I.2. 2. How it works

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode. In general, an electrode provides the interface across which a charge can be transferred or its effects felt. Because the working electrode is where the reaction or transfer of interest is taking place, whenever we refer to the electrode, we always mean the working electrode. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory. Here we summarize some of the electrochemical theory or laws common to all of the voltammetric techniques[22].

I.2. 3.Cyclic voltammetry

(CV) has become an important and widely used electro analytical technique in many areas of chemistry. It is rarely used for quantitative determinations, but it is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products[23].

This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed(figure.4)[24].

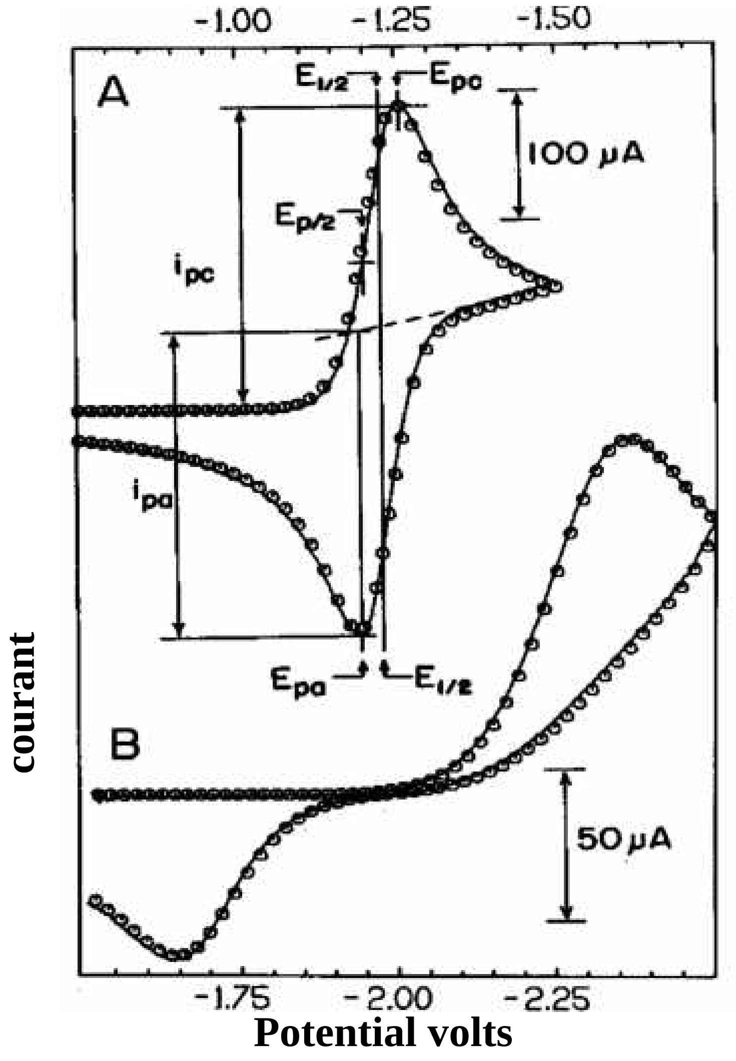


FIGURE.3. general form an characteristic of cyclic voltammetry

I.2.3.1. Basic principles

In a typical cyclovoltammetric experiment a stationary working electrode is used which is dipped into an electrolyte solution. In order to minimize the ohmic resistance a three-electrode arrangement is preferable(figure.4).

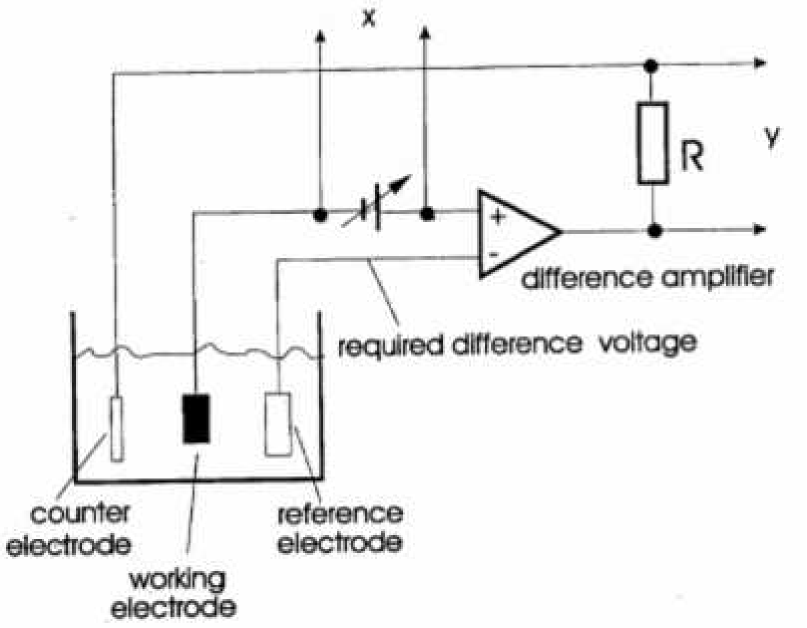


FIGURE.4. potentiostat circuit

In this arrangement the current passes between the working electrode (WE) and a counter electrode (CE). The potential of the working electrode is measured relative to a reference electrode (RE) (f. e. SCE = standard calomel electrode). In this experiment the potential of the working electrode is varied linearly with time with sweep rates between 10 mV/s and 200 mV/s. The referring current is recorded as a function of potential [25].

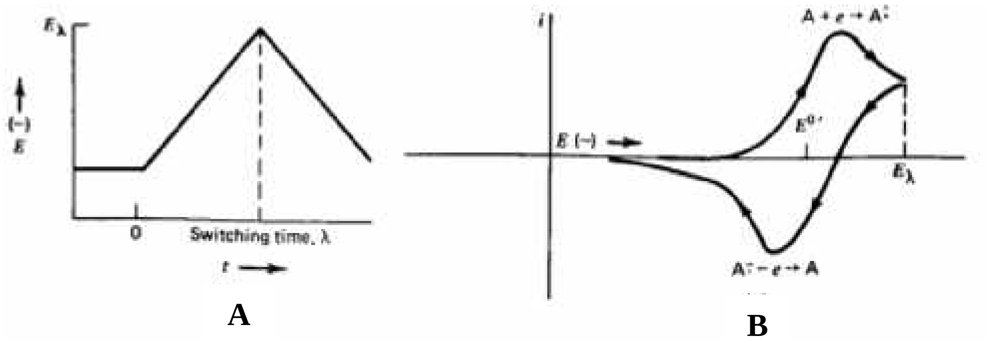


FIGURE.5

(A) cyclic potential sweep
(B) resulting cyclic voltammogram

Provided the rate of electron transfer at the electrode surface is very fast (which corresponds to an absence of an inhibition), the concentration ratio of the oxidized and reduced species at the electrode surface is dictated by Nernstian equation:

$E = E0 + (RT/nF)\ln c0(0,t)/cR(0,t)$.

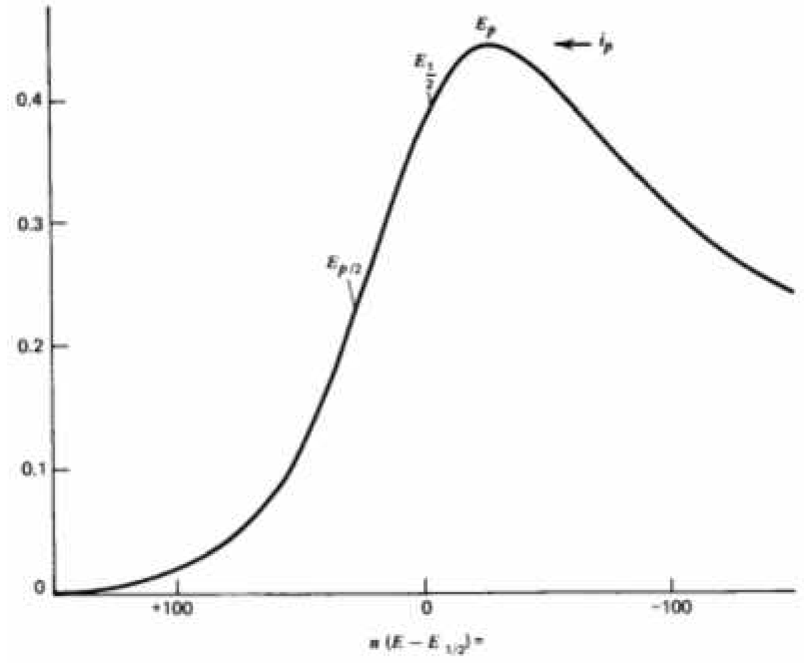


FIGURE.6. General features of a voltammogram

The CV characterized(figure.6) by several important parameters : the cathodic (Epc) and the anodic (Epa) peak potentials , the cathodic (Ipc) and the anodic (Ipa) peak current , the cathodic half-peak potential (Ep/2) and the half-wave potential.

The peak potential EP in the case of a reversible linear potential sweep is given by:

$EP = E1/2 +/- 1.109(RT/nF)$.

E1/2 is the polarographic half-wave potential, which is very close to the standard potential E0. The positive sign corresponds to an anodic (Epa) and the negative sign to a cathodic peak (Epc). For the reversible case the peak potential is independent of sweep rate and concentration. These characteristics can be used as a criterion of reversibility. Also the difference between Epa and Epc can be applied as diagnostic test of a reversible (Nernstian) reaction. Although ΔEP is slightly a function of the switching potential Eλ (figure 1) in general it can be assumed that:

$\Delta EP = | Epa - Epc |= 2.3(RT/nF) = 59/n$ mV (at 25 °C).

For repeated cycling the cathodic peak current decreases and the anodic one increases until a steady-state pattern is attained where ΔEP = 58/n mV (at 25 °C). Also the current during the first cycle is quite different from that in the second cycle. After 5-10 cycles the system has settled down and the voltammogram is independent of time.

Usually the peak in the voltammogram is rather broad, so that the peak potential may be difficult to determine. That is why it is sometimes more convenient to report the potential at 0.5 iP, called the half-peak potential EP/2, which is:

$EP/2= E1/2+1.09RT/nf$.

The difference between EP and EP/2 is: $| EP - EP/2 | = 2.2 RT/nF = 56.5/n$ mV (at 25°C),

The peak current iP for a reversible linear potential sweep is given by the Randles-Ševčik equation:

$iP = k\ n3/2\ A\ D1/2\ \ C\ V1/2$.

A – area.

D – diffusion constant.

C- concentration.

n – number of exchanged electrons.

V – sweep rate.

k - Randles-Ševčik-constant (2.69*105 As/V1/2 mol).

With the fast system :

Current peak Ip =2,69.105.An3/2.D1/2.C.V1/2. (mA)

Potential peak Ep = Ep/2 + 0,029/n. (mV)

The difference between Epa and Epc.

Epa –Epc = 0,059/n. (V)

And Ipa/Ipc =1.

With half fast system .

Ip = 2,99.105.A.n3/2.D1/2 .C.Ks.V1/2.

With the irreversible system .

Ip = 2,99.105.A.n.(αn)1/2 .D1/2 C.KS.V1/2.

I.2.4. The general electrochemical study of ferrocene

This study was performed by doctor T Lanez and we will tack it as a reference in our experience .

I. 2.4.1. Electrochemical measurement on a fixed electrode

Cyclic voltammograms of ferrocene at glassy carbon electrode were performed at concentration of 10^{-3} M of ferrocene in deoxygenated dichloromethane and in aqueous ethanol solutions with respectively 10^{-1} M of Bu4NBF4 and H2SO4 as supporting electrolyte, each solution was scanned at scan rate equal to 0.05, 0.10, 0.30 and 0.50 $V.s^{-1}$.The resultant CV curves and the electrochemical parameters are shown respectively in (figure 7) and table 3.The peak potential spacing (ΔEp), at scan rate equal to 0.05 $V.s^{-1}$ is 0.123 V for the ferrocene in CH_2Cl_2 and 0.064 V for the ferrocene in ethanol/water. A fast, reversible, one-electron transfer would ideally have a ΔEp = 0.059 V at 298 K [8].The discrepancy from this ideal value is attributed to slow electron transfers and solution resistance. The anodic and the cathodic peak heights as function of the square root of the scanning rate for platinum and glassy carbon electrodes ,electrode are shown in (figure 8). The obtained linear relationship indicates clear diffusion character. As it can be seen from (figures 8), the ratio of the anodic and cathodic current peak heights is close to one for both solutions; this indicates the reversible character of the oxidation of ferrocene in both studied medium[26].

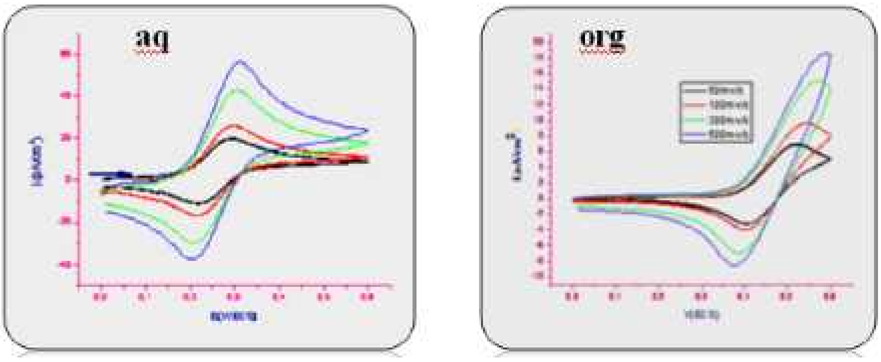


FIGURE.7
cyclic voltammetry of ferrocene 1 mM and 100 mM Bu4NBF4 in CH2Cl2 (left) and 1 mM of ferrocene in ethanol/aq.H2SO4 (right) at 2 mm diameter glassy carbon working electrode, Pt counter electrode, and CSE reference electrode at (0.05, 0.10, 0.30, 0.50 V.s-1).

I.2.4.2. Diffusion of ferrocene and ferricenium

In general, the peak current of diffusion controlled reversible or quasi-reversible electrochemical reaction follows Randles-Ševčik equation.

$$Ip = 0{,}4463nF\sqrt{\frac{nFD}{RT}}AC\sqrt{v}.$$

where Ip: the peak current, n: the number of electrons,

F: Faraday constant .

T: the temperature in Kelvin.

R: the gas constant.

A: the surface area of the working electrode.

D: the diffusion coefficient of the electro active species.

C: the bulk concentration of the electro active species and.

v: the scan rate of voltammograms.

Thus, the diffusion coefficients for ferrocene and ferricenium at 298K are calculated from the slope of the plot of Ip versus.

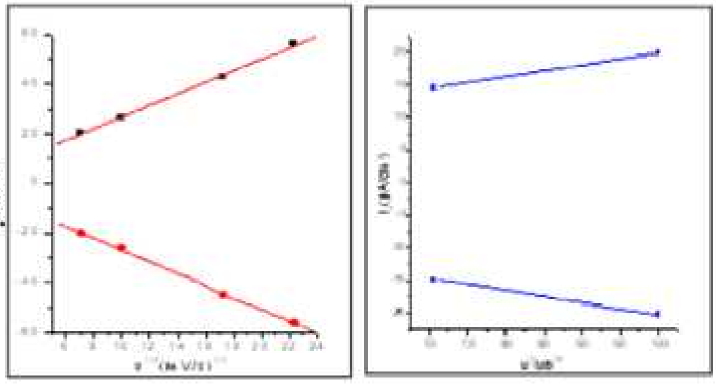


FIGURE.8
The anodic and the cathodic peak heights as function of the square root of the scanning rate for platinum electrode in CH2Cl2 (bleu) and in ethanol/H2SO4 (red) at 2 mm diameter Pt working electrode

I.2.4.3. Electrochemical measurement on rotating disk electrode

The diffusion coefficients of ferrocene organic and aqueous medium were also measured on a rotating disk electrode using the same conditions as used for voltammetry cyclic. The calculations were based on the Randles-Ševčik equation. That means the anodic peak height of ferrocene oxidation (obtained from voltammetry cyclic measurements) was

measured in quiescent solutions on both electrodes and in both medium. The obtained polarogramme are showed in(figure 9).

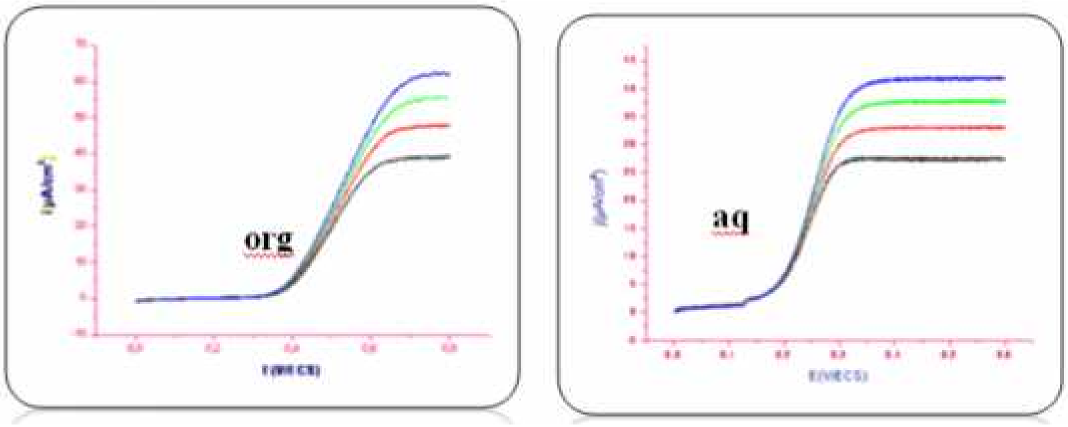


FIGURE.9
Polarogramme of ferrocene 1 mM and 100 mM Bu4NBF4 in CH2Cl2 (left) and 1 mM of ferrocene in ethanol/H2SO4 (right) at 2 mm diameter glassy carbon working electrode, Pt counter electrode, and CSE reference electrode at 0.50 V.s-1. (Rotating rate 400, 600, 800, 1000 rpm)

The anodic peak heights as function of the square root of the rotating disk electrode rate for platinum and glassy carbon electrodes are shown in(figure 10). The coefficient diffusion for ferrocene is calculated from (figure 10) as follows: The Levich equation predicts the current observed at a rotating disk electrode and shows that the current is proportional to the square root of rotation speed. The equation is:

$$\delta = 0{,}654D1/3\gamma1/2\omega(-1)/2.$$

Table 3: Electrochemical parameters obtained from voltammograms of (figure 7).

V(mV/s)	Epa(mV)		Epc(mV)		Ipa(µA/cm2)		Ipc(µA/cm2)		ΔEp(mV)		E1/2(mV)	
	org	aqu	org	aqu	org	aqu	org	aqu	org	aqu	org	aqu
50	540	293.5	14.58	20.15	377.5	219.5	-14.87	-20.46	162.5	74	416.7	256.5
100	–	295	19.86	26.21	363	212	-20.26	-26.32	–	83	–	253.5
200	–	306	–	42.90	336	213	–	-44.49	–	93	–	259.5
300	–	310	–	56.12	320	200	–	-56.3	–	110	–	255

Table4: Diffusion coefficients of ferrocene calculated from polarogramme of (figure 10).

Electrode/medium	P	D.10^{-6}(Cm²/s)	δ(nm)
GC/CH_2Cl_2	1.95	77.16	1962.62
GC/aqu-ethanol	1.34	32.82	2609

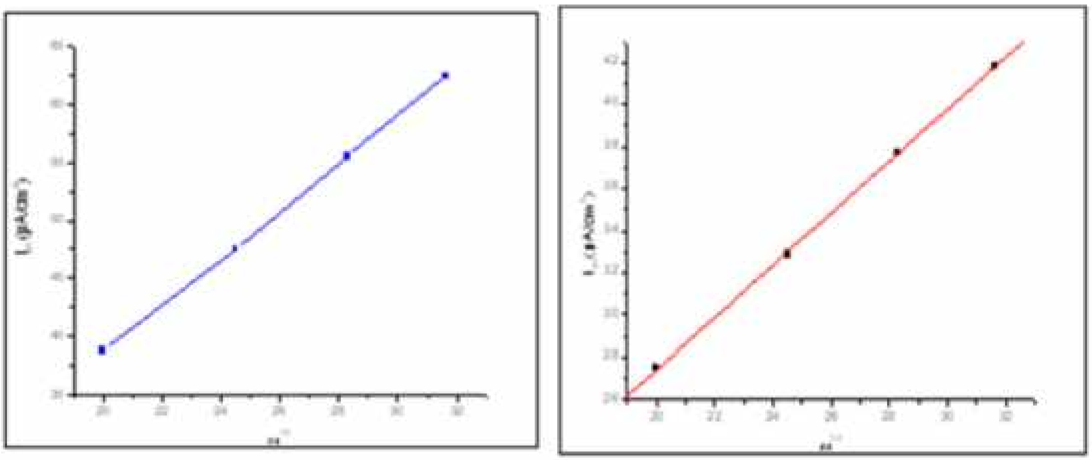


FIGURE.10
The diffusion current as function of the square root of the rotating rate for glassy carbon electrode in CH_2Cl_2 (bleu) and in ethanol/H_2SO_4 (red)

From Figure 10 the slope of the line gives:

$P= \frac{i}{\sqrt{w}}$.

On another hand the limited current is given by:

$i = \frac{nFADC}{\delta}$.

Where is:

n, number of electrons.

F: is the Faraday (9.65.104 C/mol).

A: is the area of the working electrode (cm^2).

D: is the coefficient diffusion ($cm^2.s^{-1}$).

C: is the concentration (mol/cm^3), in our case is equal to10^{-3} mol/l

D2/3 =(P1,6γ1/6)/(nFAC√2)

For a rotating rate of the working electrode equal to 400 t/min., the coefficient diffusion of ferrocene in dichloromethane is:

$D = 77,16.10^{-6}Cm^2.s^{-1}$.

The coefficient diffusion of ferrocene in aqueous ethanol is calculated as above. Table 2 summarize the obtained values.

IInd PART

EXPERIMENTAL STUDY

II.1. General condition of experimental study

II.1.1. Techniques of synthesis

II.1.1.1. General terms of work:

Drying of organic solvents

- Toluene and ether diethylic (Et2O) on sodium and benzophenone.
- The dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) on P_2O_5.
- The amines (trimethylamine, pyridine .....) on KOH.
- The solvents were distilled under atmosphere of nitrogen before use.

Atmosphere of reaction:

All the operations of synthesis utilizing ferrocenyl are carried out under an atmosphere of nitrogen.

Evaporation of solvents

The rota-steamer used for the evaporation of solvents is of mark Janke and Kankel RV 05-ST.

II.1.1.2. Techniques of analysis and equipment:

Chromatography

Thin layer chromatography (TLC) is carried out on plate Whatman an aluminum covered by a thin layer of silica gel. The development of the spots carried out with (a solution permanganate of potassium-KOH, iodizes, UV…) as revelator.

The chromatography on silica gel were carried out with micro silica “Merck” 230-400 mesh.

IR Spectrophotometry

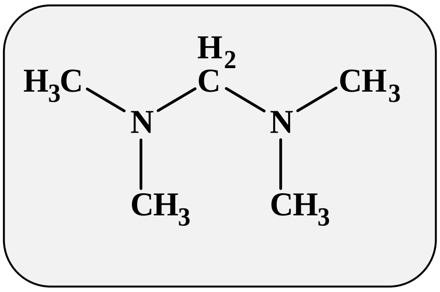
The infra-red spectra are recorded by an apparatus to transform of Fourier FTIR 830 marks SHIMADZU. The solid products are analyzed in the form of pastilles of KBr, whereas oils are analyzed in the form of a film .

Spectrometry NMR

The spectra NMR of ^1H and ^{13}C were recorded on apparatuses Bruker AC 300. The spectra were carried out with 20°C and the chemical shifts are given partly per million (ppm, $\delta 10^{-6}$). The reference interns taken for CDCl3 is of 7.26 ppm for the ^1H and 77.16 ppm for the ^{13}C .

II.2. Exprimental processes

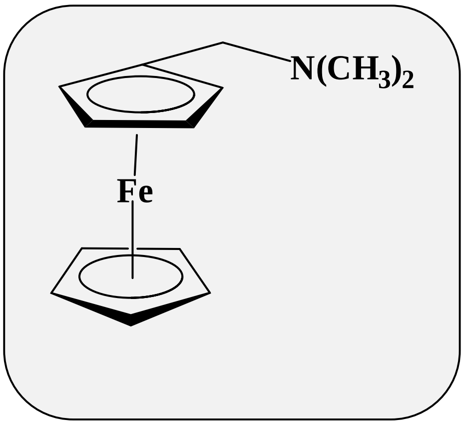
The synthese of maniche reagent



In a 500 ml erlenmeyer at temperature about 15°C we add drop by drop solution of dimethyl amine at the rate 40% (165g ; 1.5mol) to formaldehyde solution at the rate 37% (60.7g ; 0.75 mol) with magnetic agitation for 60 minute then we add slowly a quantity of KOH to have tow phase , we separate the organic phase (the higher phase) and we dry it by the addition of potassium hydroxide for 24houre.

Finally we filtrate the solution (by filtration) and purify (by distillation) to have at the end a 61.85g of methylene dimethyl amine as transparent liquid its output is 81% and its boiling point is 84°C.

The synthese of dimethyl aminomethyle ferrocene



In three necked flask (1000 mL) provide with condenser and magnetic stirring at the presence of direct current of nitrogen (N_2) we put (46.4 g ;0.25mol) of ferrocene ,(43.2g ; 0.422mol) of methylene dimethyl amine ,(43.2g ; 0.45mol) of ortho-phosphoric acid and 400ml of acetic acid.

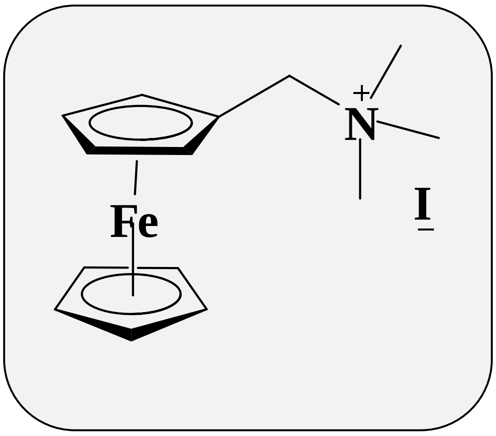
We heat the mixture on wetter-bathe for 5houres to have a brown solution we diluted it by 550ml of distilled wetter.

We extract the rest ferrocene with ether(325ml X 3) ,than we cooling the aquatic phase obtained in ice-bath it transformed quickly to base after addition of KOH disks.

The black oleic (tree-ferrocenic amine) appear on the surface of the basic solution , the first one dissolution again by wetter and extract with ether (500ml X 3).

The organic solution washed by wetter then dry by $NaSO_4$ finally we vapor the ether to get reed viscous solution (dimethyl amino methyl ferrocene) its mass 54.70g with 90% as output.

The synthese of tri-methyl ammonium –methyl ferrocenyl iodide



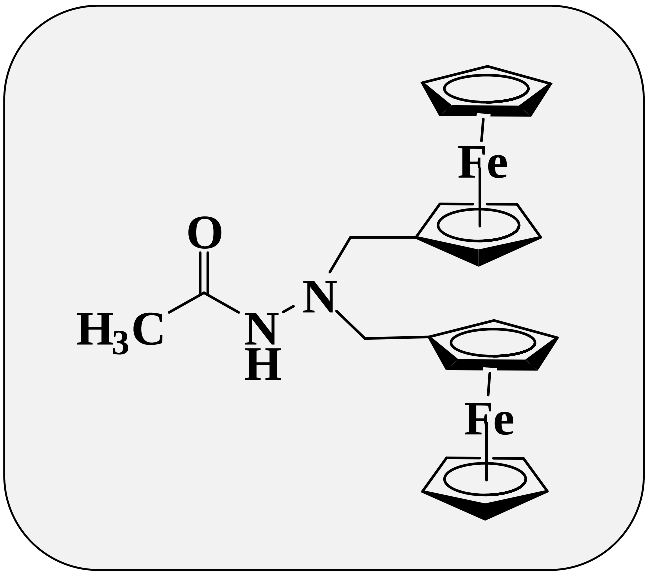
A quantity about (74.70g , 0.225mol)of dimethyl amino methyl ferrocene dissolved in 60ml of methanol and heat in wetter-bath for 5minutes.

We add to the mixture a 54ml (123g , 0.87mol) of methyl iodide (the addition be by steps cause the reaction is exo-thermic).

The iodide salt of methyl ferrocenyl – tree methyl ammonium cooled to the ambient temperature ,then we pour it in a beaker (1000ml) it will be solid after addition of ether (800ml) . the solid product was filtrated and washed by ether then dried at 25°C.

The yellow precipitate is the iodide salt with mass (81.43g , 0.211mol) and 94% as output and melting point at 218°C.

The synthese of N',N'- di ferrocenyl methyl- N- acetohydrazide



In three necked flask (250 mL) provide with condenser and magnetic stirring at the presence of direct current of nitrogen (N_2) we have :

- 5g(12mlmol) of iodine salt of ferrocenyl methyl tri-methyl ammonium.
- 0.88 g(12mlmol) of acetohydrazide.
- 80ml of toluene as a solvent.

all this under temperature about 120°C for 5hour.

after cooling we removal the solvent by the rota-steamer to get a brown solid powdery compound.

It is a mixture of reagents with tow organic compound we separate them with chromatographic column.

One of them is yellow 1.7g and output about 54% and melting point 191°C and the other is reed its mass 0.9g ,its output 15% and its melting point is 193°C.

II.3. Resultats and discussion

The trimethylamine groups of ferrocenyl methyltrimethylamonium, as the figure.11 indicates it, confers a high reactivity with electrophilic substitution.

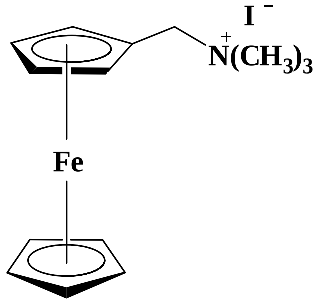


FIGURE.11

Ferrocenyl methyltrimethylamonium

This property made it possible to prepare hydrazide by the action of the acetohydrazide (figure12) which carries an active site on no amidic nitrogen, with ferrocenyl methyltrimethylamonium.

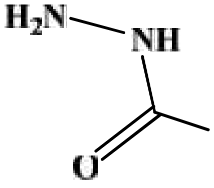
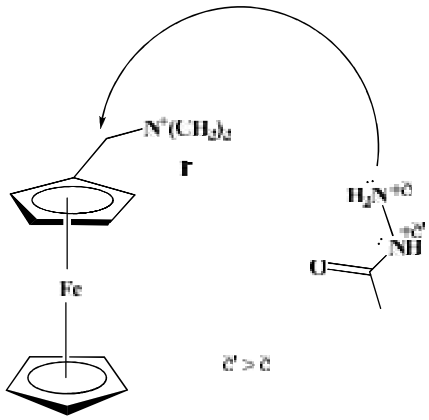


FIGURE.12

acetohydrazide

The nucleophilic effect of the amidic nitrogen atom is very weak if it compared with that of the aminic nitrogen atom.

The way of synthesis chosen, thus consists in preparing the quaternary salt of iodide ferrocenyl methyltrimethylamonium in the first time, and to make it react with the acetohydrazide in the second time, according to the scheme.7.

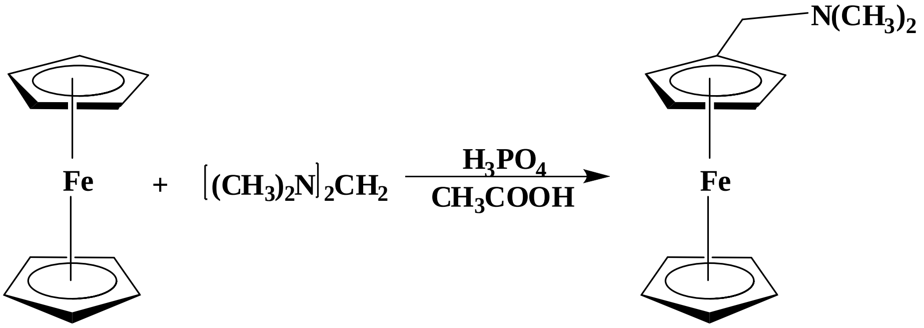


SCHEME.7

Ferrocenyl methyltrimethylamonium is prepared according to the method of Lindsay and Hauser [71]. This preparation is carried out in two stages:

In the first, the attack of the reagent of Mannich on ferrocene is catalyzed by the phosphoric acid by using the acetic acid as solvent as the schéma.8 shows it.

The reagent of Mannich reacts only with one of the two cycles by giving the monosubstituted compound easily separable and with an appreciable output.

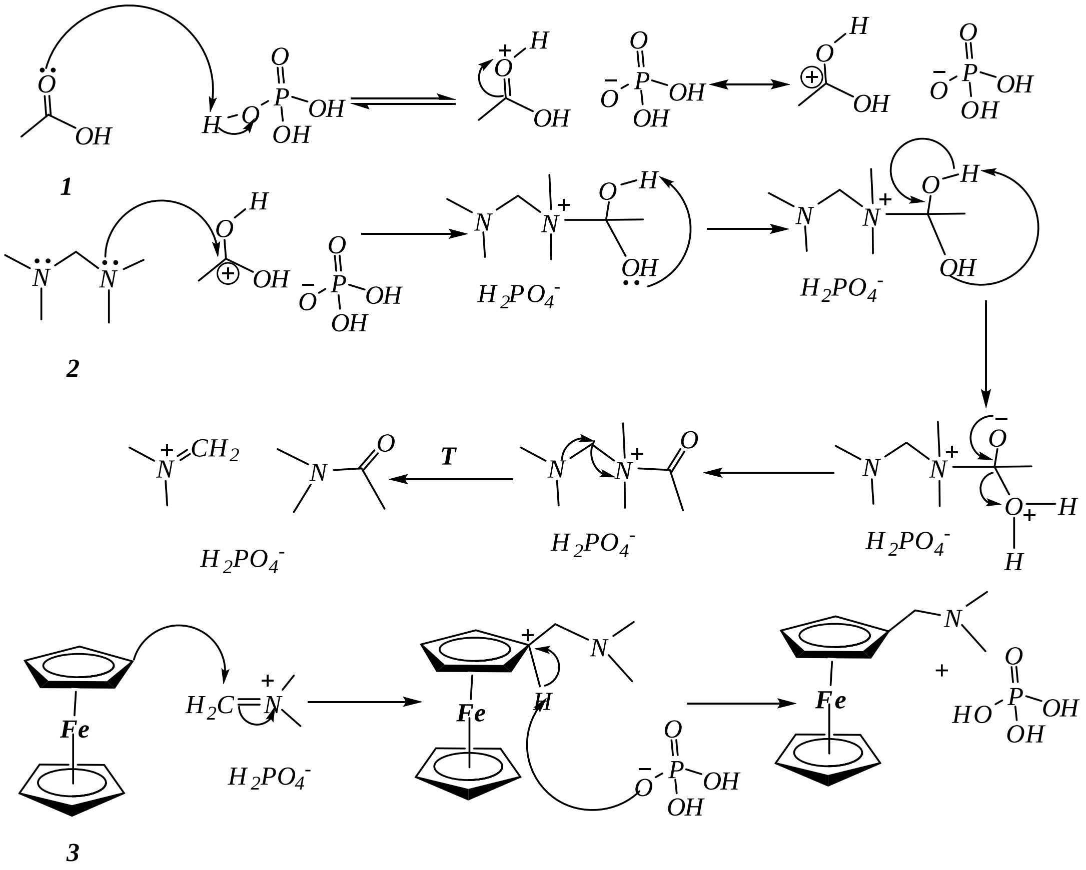


SCHEME.8

In the second phase, one makes react the compound with the iodide methane to give iodide of the ferrocenyl methyltrimethylamonium thermodynamically stable and sufficiently pure for the use in other reactions .

These above mentioned properties give to made up great importance in organic synthesis.

The mechanism of reaction:



SCHEME.9. the mechanism detailed of reaction

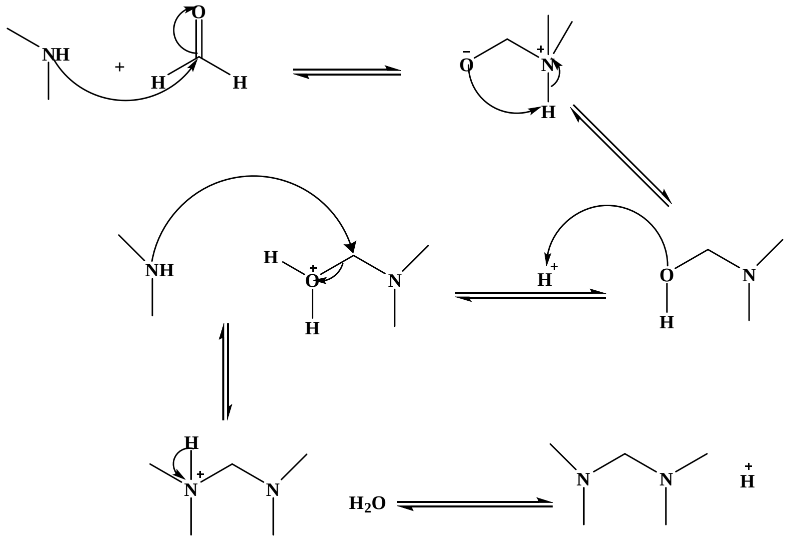
II.III. 1. Synthesis of the reagent of Mannich (methylene dimethyl amine)

The reagent of Mannich is synthesized by the dimethylamine condensation with the formaldehyde, at a temperature lower than 15°C (scheme.10).

$$HCHO + 2\,(CH_3)_2NH \longrightarrow [(CH_3)_2N]_2CH_2 + H_2O$$

SCHEME.10

The relational mechanism of methylene dimethyl amine synthese



SCHEME.11. **the mechanism detailed of reaction**

The infra-red spectrum of the reagent of Mannich (methylene dimethyl amine) is characterized by the bands of adsorptions specific to the groups: CH2, N-CH3, and CN, successively to 750,1045.3,1020 and 1259 cm^{-1}.

Spectrum ^{1}H NMR is characterized by two peaks with 2.20 ppm relative to the twelve protons of four methyl groups and a peak with 2.70 ppm relative to the two protons of the methylene group.

Spectrum ^{13}C NMR watch clearly a signal with 42.66 ppm relating to the methyl groups, and another peak with 83.33 ppm corresponding to the methylene group.

II.III.2. Synthesis of the amine ferrocenyl methyldimethylamine

The tertiary amine (amine ferrocenyl methyldimethylamine) is prepared by the reaction between the reagent of Mannich (methylene dimethyl amine) and the ferrocene in a mixture of crystalline acetic acid and the phosphoric acid.

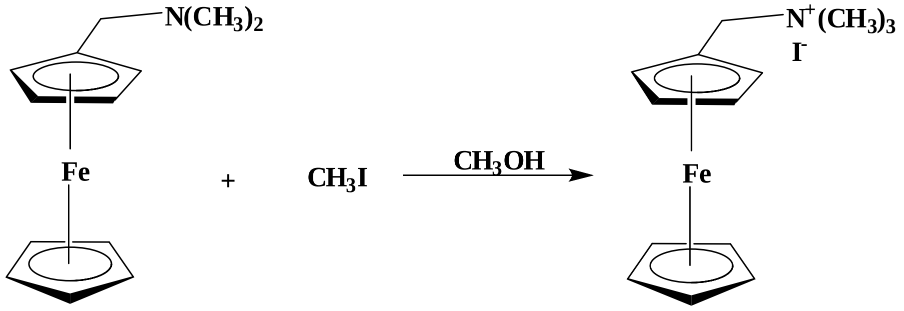
The structure of the amine ferrocenyl methyldimethylamine is confirmed by the following spectral methods:

Spectrum ^{1}H NMR shows four signals with 2.14,3.24,4.07,4.14 ppm, corresponding successively to six hydrogen of two methyl groups, with two hydrogen of the methylene groups, five hydrogen of the unsubstituted cyclopentadienyl and for four hydrogen of the amino methyl cyclopentadienyl.

Spectrum ^{13}C NMR presents two signals to 44.76 and 59.14, corresponding successively to carbons of two methyl groups and the carbon of the methylene group. Four other signals with 83.15,70.04,67.97 and 68.43 ppm characterize carbons of ferrocenyl.

II.3. 3. Synthesis of iodide ferrocenyl methyltrimethylamonium

The iodide of the ferrocenyl methyltrimethylamonium is prepared by the addition of an excess of iodide methane to a solution of the tertiary amine (amine ferrocenyl methyldimethylamine)in methanol, according to the scheme.12.



SCHEME.12

Spectrum ^{1}H NMR of quaternary salt presents five characteristic signals: the first with 3.26 ppm represents the new protons of the methyl groups, the second with 4.26 ppm relative to the five protons of unsubstituted cyclopentadienyl, the third and the fourth with 4.29,4.56 ppm correspond to the four protons of monosubstituted cyclopentadienyl, and a signal relative to the two protons of the methylene group at 4.87 ppm.

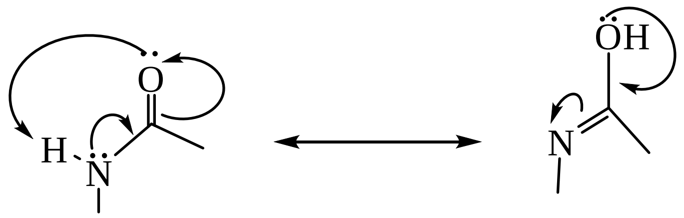
Spectrum ^{13}C NMR show five signals, the first with 52.68 ppm equivalent with nine carbons of methyl, the second with 67.16 relating to the carbon of the methylene group, and ten signals with 69.63,70.71 and 72.29 ppm relative to nine ferrocene ’s carbons.

II.3.4. Synthesis of N' N'- diferrocenyl methyl-N' – acetohydrazide

The derivative - of N'- ferrocenyl methyl-N' – acetohydrazide is prepared by the reaction of iodide of ferrocenyl methyltrimethylamonium and the acetohydrazide in toluene or ebullient water.

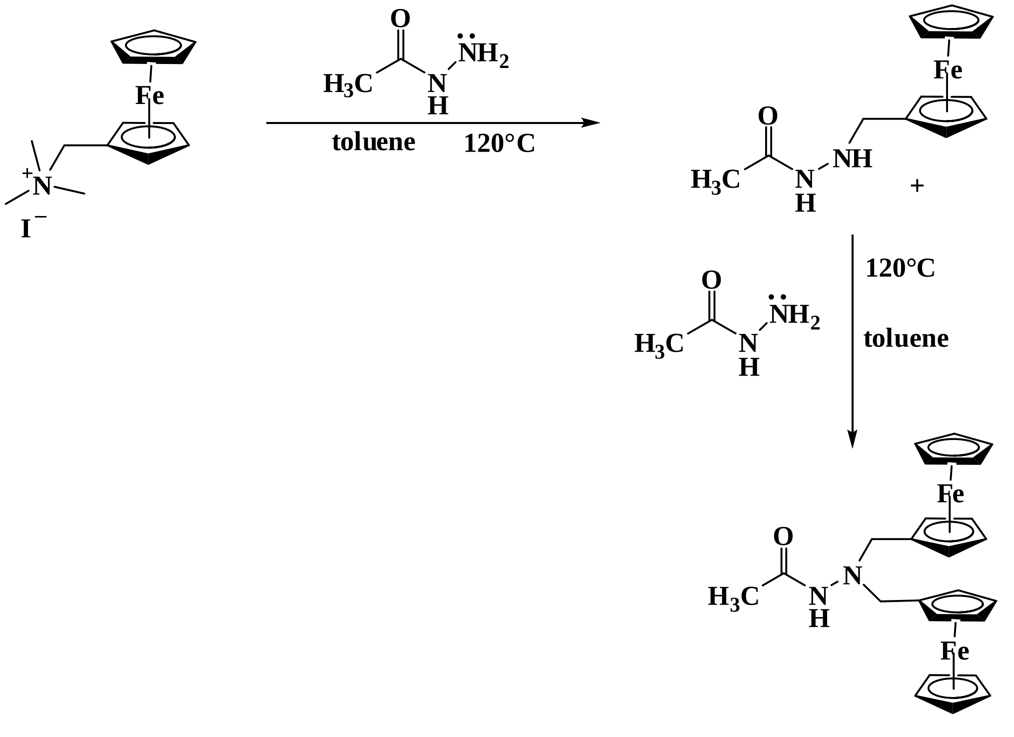
The choice of solvent is extremely important. The use of ebullient water, under a good magnetic agitation led to the complete disappearance of the reagents at the end of 20 minutes. The disadvantage of this reaction is the simultaneous formation of many products, which decreases the output and complicates obtaining the product wished in a pure state. Thus, the use of the dry toluene coldly distilled at a temperature of the engine of approximately 120°C leads to the formation of only one product with an output of 82%, in one duration of approximately 8 hours.

the ferrocenic salt have scarce solubility in toluene (no polar solvant) and the carbonyl group (–C=O) joined direct with -NH- in amid function that's make it in resonance as show:



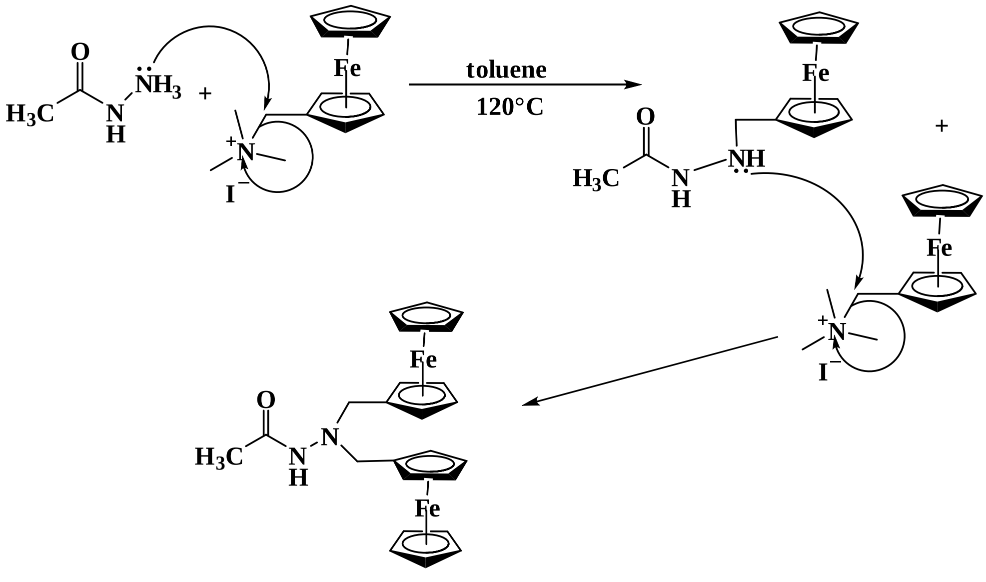
SCHEME.13

This resonance make busy the double free electrons of azote it means the electrophilic substitution on the amidic azote was very difficult (or impossible), but with primary and secondary amine the double free electrons of azote con associate in any electrophilic substitution with height reactivity.



SCHEME.14. the reaction with toluene as solvant

A mechanism of the reaction in toluene is as a show:



SCHEME.15. the mechanism detailed of reaction

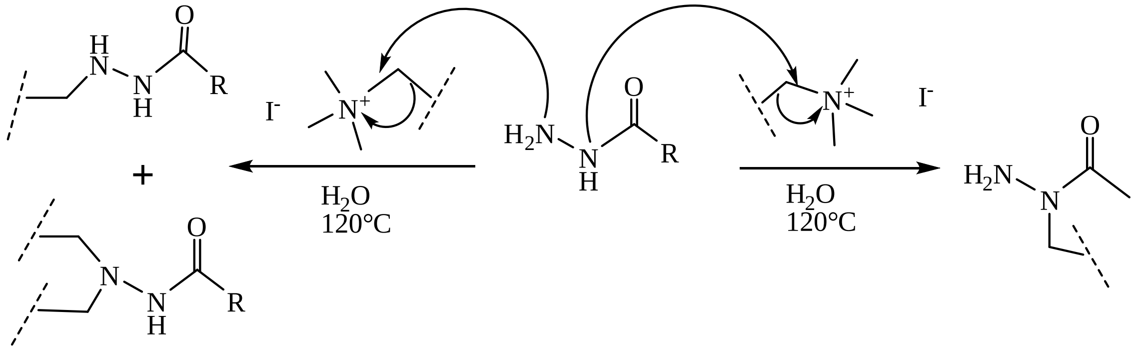
The ^{1}H-NMR spectrum show eight signals tow for the CP unsubstituteds at 4.13 and 4.15 ppm another tow at 4.19 and 4.261ppm for the monosubstituteds CP and two for the methylene groups at 3.53 and 3.70 ppm the signal of NH group at 6.02 pp; and the last one at 1.55 pp; for the methyle group.

The ^{13}C-NMR spectrum show two signals the first one at 57.40 ppm for the methylenes group it was confirmed by DEPT show a negative pick at 57.40 ppm ,and the second at 68 to 80?69 ppm for ferrocenyl group.

In the state of polar solvant and high temperature more than 100°C as ebullient water there is a weak output of electrophilic substitution with the double free electrons of amidic azote.

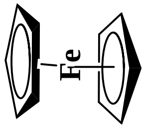
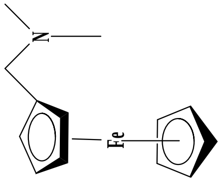
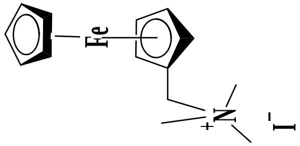
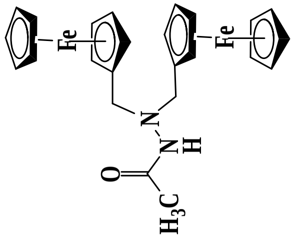
while the primary and secondary amine have a very higher nucleophility on the double free electrons of azote that is to say the possibility of attack on leaving group is great specially with the good leaving groups as in the ferrocenic salt.

in polar milieu there is competition between the double electronic free electrons of amidic azote and the double electronic of the azote of the amine because the ferrocenic salt dissolved completely in polar solvant but the higher output is to the attack of amine on the ferrocenic salt.



SCHEME.16. the reaction in polar milieu

Table.5: the resultats of IR spectroscopic analytic of the Synthesis product

Fonction (cm-1) / Compounds	FC-					$-CH_2-$	CON-H	-NHC=O	Me-C=O
	CH(Ar)	C=C	CH(vib)	C-H	Bi-Ar				
	3096.06	1407.9	1105	1001	851	---------	---------	---------	-----------
	3096.06	1456.9	1105	1020	801.7	2922.0	---------	---------	-----------
	3096.06	1470	1105	1100	880	2937.4	---------	---------	-----------
	3076.2	1458.1	1103.2	1028	817.8	2937.4	3369.4	1654.8	1716.5

II.4. The electrochemical study of the compound synthesized

II.4.1. Apparatus

For the electrochemical experiments a computer controlled potentiostat type PGZ301 Volta Lab 40 was used. Cyclic voltammetry was performed in a three-electrode voltammetry cell using a glassy carbon electrode as the working electrode, reference electrode, and a Pt wire as auxiliary electrode.

The automatic data processing carried by Volta Master 4.

The cell should be closed and joined with a source of azote to eliminate the gaseous oxygen

We must clean the working electrode before each experience by rinsing with wetter and acetone using scraper paper then dried with JOSIF paper.

II.4.2. Chemical

II.4.2.1. The solvant used in this study

The solvant used must be:

1. Inert electrochemistry in the range of the study.
2. Dissolved the salt and the product studies.
3. Dissolved the electroactif compound.
4. Little or no volatile.

We use the ethanol as solvant in this study.

To have a conductive milieu , we add a solution can prevent the oxidation of cations and the reduction of anions in the range of study.

II.4.2.2. The supporting electrolyte

The supporting electrolyte should be :

1. Good solubility in the solvant used.
2. Its concentration more 50 to 100 time than the concentration of the electroactif compound.
3. Its electroreactivty range must be large.

We use sulfuric acid H_2SO_4 10^{-1}M as supporting electrolyte.

This study was performed in chemical laboratory in university eloude (VTRS).

We studies the electrochemical behavior of the synthesized compound at the concentration 0.0047 M dissolved in ethanol 25ml and sulfuric acid (0.1M ,25ml).

We use in this experience:

- The glassy carbon electrode as working electrode.
- Standard calomel electrode(SCE) as reference electrode.

- The platinum wire as auxiliary electrode.

II.4.3. Resultats and discussion

Before the start of the study we determined the range and the speed of the scan of the supporting electrolyte.

- The range (0 to 800 mV).
- The speed 100 mV /s.

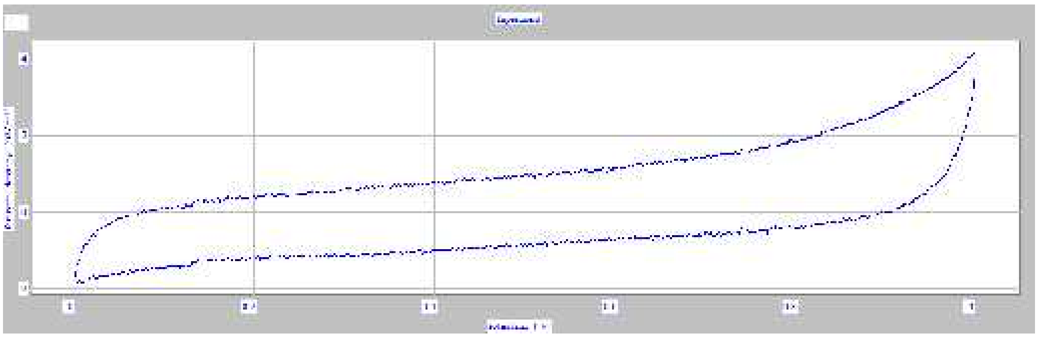


FIGURE.13. the voltammogram of solvant (MeOH 25ML/H2SO4 (0.1M,25mL)) from 0 to1000mv and with speed 100mV/s

II.4.3.1. The electrochemical behaviors of ferrocene

The voltammogram of cyclic voltammetry of ferrocene was applied in the range (0 to 800 until 1500 mV) and with different speeds (20 ,40, 50, and 100 mV /s).

We remark from the generals forms of the voltammogram.

1) The general format (0to 800 mV, 100 mV /s) present an anodic pick at (488.4 mV , 34.74 µA/cm²) for the oxidation of ferrocene and another pick cathodic at (340.1mV , -19.19 µA/cm²) for the reduction of ferrocene.

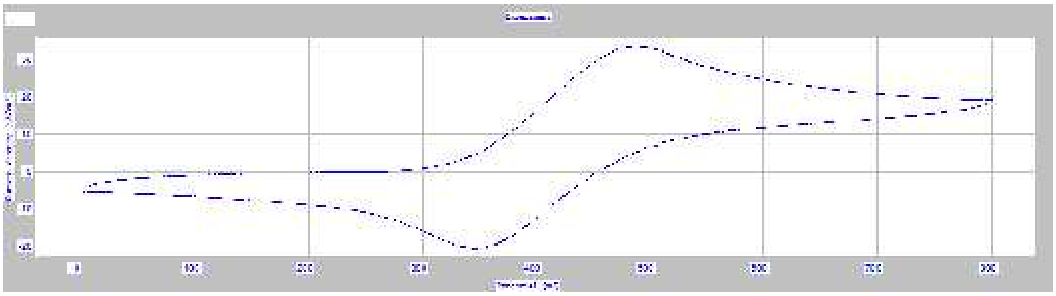


FIGURE.14. the voltammogram of ferrocene (0.002M) from 0 to800mv and with speed 100mV/s

2) preserve the same geometrical forms at deferent speeds.
3) the pick of intensity currant decrease with the degradation of the speed of scan.
4) the system is reversible.

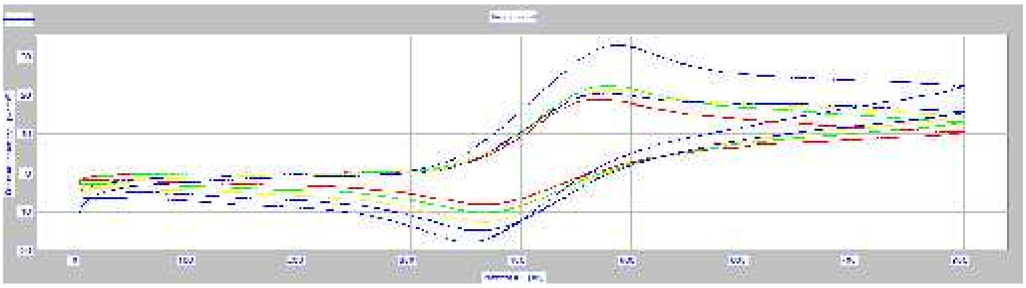


FIGURE.15. the voltammogram of ferrocene (0.002M) from 0 to800mv and with deferent speeds(20,30,40,50 and 100mV/s)

Table 6 :the electrochemical characteristic of ferrocene at deferent speeds.

Speed of scan	Epa (mV)	Epc(mV)	$V^{1/2}$(mV /s)	Ipa(µA/cm²)	Ipc(µA/cm²)
20	466.2	373.4	4.472	18.41	-7.774
30	473	366.3	5.477	21.38	-9.961
40	474.9	360.7	6.324	22.11	-12.88
50	484.4	348	7.071	28.12	-15.06
100	488.4	340.1	10	34.74	-19.19

On the basis of the previous table we trace the curve $f(V^{1/2})$ = Ipa it is as a show:

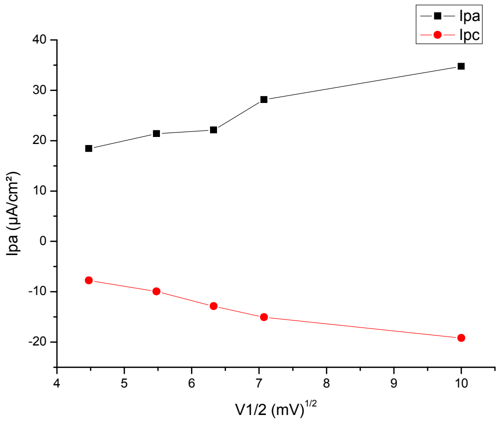


FIGURE.16. the curve of f(V1/2) = Ipa)

We remark :the curve f($V^{1/2}$) =Ipa is a right line it mean that the diffusion phenomenon is the responsible in the transfusion of charged.

II.4.3.2. The electrochemical behaviors of N',N'- di ferrocenyl methyl- N-acetohydrazide

This compound is studies in the medium of sulfuric acid H_2SO_4 (0.1M, 25ml) and ethanol 25ml and the concentration of the compound 0.002M.

The range of study 0 to 800 until 1600 mV and the speed of scan is 100 mV /s.

We remark from the generals forms of the voltammogram.

1) The general format (0to 1600 mV, 100 mV /s) present tow anodic picks the first at (529.3 mV , 17.85 µA/cm²) and the second at(1006 mV , 50.02 µA/cm²) for the oxidation of the double ferrocenyl groups and another cathodic pick at (432.6 mV, -11.06 µA/cm²) for the reduction of ferrocene.

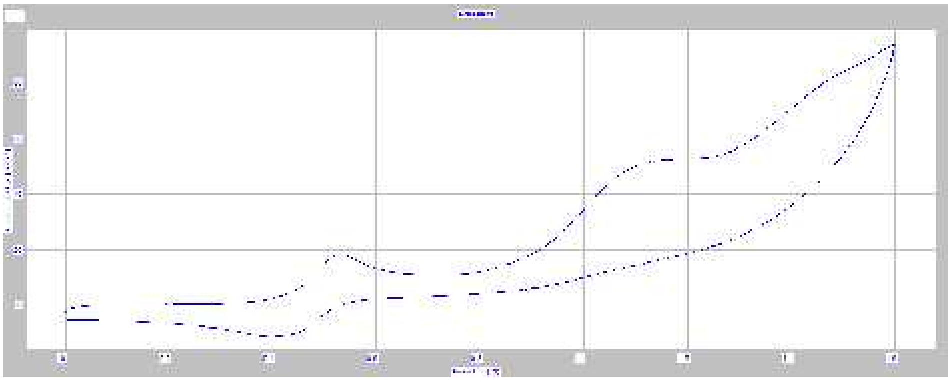


FIGURE.17. **the voltammogram of N',N'- di ferrocenyl- N- acetohydrazide (0.002M) from 0 to1600mv and with speed 100mV/s**

1) preserve the same geometrical forms at deferent speeds(30, 40,50 and 100 mv/s).
2) the pick of intensity currant decrease with the degradation of the speed of scan.

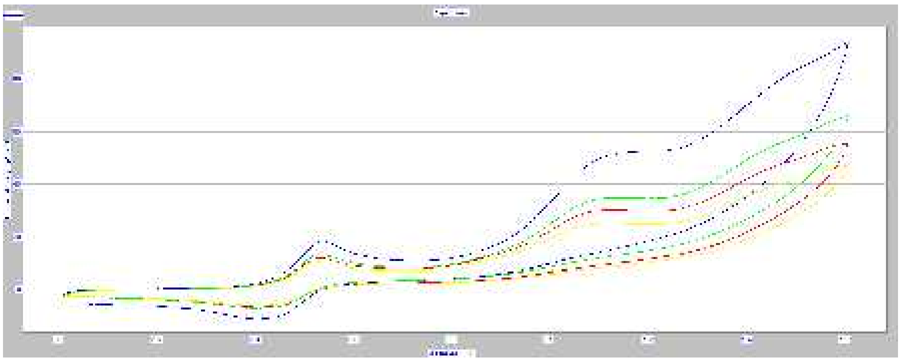
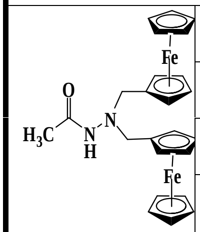
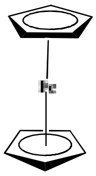


FIGURE.18. **the voltammogram of N',N'- di ferrocenyl- N- acetohydrazide (0.002M) from 0 to1600mv and with deferent speeds(30,40,50 and 100mV/s)**

Table 7: the electrochemical characteristic of N',N'- di ferrocenylmethyl- N- acetohydrazide at deferent speeds.

Speed of scan	Epa (mV)		Epc(mV)	$V^{1/2}$(mV /s)	Ipa(µA/cm²)		Ipc(µA/cm²)
	Pick1	Pick2			Pick1	Pick2	
30	518.6	1065	425.9	5.477	10.06	23.39	-6.538
40	519.9	1088	425.9	6.324	11.32	29.42	-6.538
50	524	1085	425.9	7.071	12.82	33.95	-6.538
100	529.3	1006	432.6	10	17.85	50.02	-11.06

Table 8: comparison between the electrochemical characteristic of N',N'- di ferrocenyl methyl- N- acetohydrazide and the ferrocene at deferent speeds.

Speed of scan		Epa (mV)		Epc(mV)	$V^{1/2}$(mV /s)	Ipa(µA/cm²)		Ipc(µA/cm²)
		Pick1	Pick 2			Pick1	Pick2	
	30	518.6	1065	425.9	5.477	10.06	23.39	-6.538
	40	519.9	1088	425.9	6.324	11.32	29.42	-6.538
	50	524	1085	425.9	7.071	12.82	33.95	-6.538
	100	529.3	1006	432.6	10	17.85	50.02	-11.06
	20	466.2		373.4	4.472	18.41		-7.774
	30	473		366.3	5.477	21.38		-9.961
	40	474.9		360.7	6.324	22.11		-12.88
	50	484.4		348	7.071	28.12		-15.06
	100	488.4		340.1	10	34.74		-19.19

The electrochemical study of N',N'- di ferrocenyl- N- acetohydrazide show:

It is stable electrochemically.

All the redox reactions are a fast reversible stable system.

The diffusion phenomenon is the responsible in the transfusion of charged.

GENERAL CONCLUSION

The synthese

To synthesize the ferrocenic compound (N',N'- di ferrocenyl methyl- N- acetohydrazide) we flow the next steps:

- React mol of formaldehyde with tow mol of dimethylamine to give methylene dimethylamine.
- React mol of methylene dimethylamine with mol of ferrocene in the acetic acid as solvant and phosphoric acid as catalyze to give dimethylamine methyl ferrocene.
- React mol of dimethylamine methyl ferrocene with mol of methyl iodide to give the iodide ferrocenic salt.
- React mol of the iodide ferrocenic salt with acetohydrazide to get the our product(N',N'- di ferrocenyl methyl- N- acetohydrazide).

The deferent spectral methode to indentify the structure of the synthetic compound.

The electrochemical study

The cyclic voltammetry study of this compound cried in a three-electrode cell

- The glassy carbon electrode as working electrode.
- Standard calomel electrode(SCE) as reference electrode.
- The platinum wire as auxiliary electrode.

We conclude that

The compound is sable electrochemically, it is as a fast ,reversible and stable system

APPENDIX

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Abstract : The subject of this work is the synthesis of a Hydrazide's ferrocenic compound (N',N'- di ferrocenyl- N- acetohydrazide) by the reaction between the iodide ferrocenic salt and acetohydrazide.

And the electrochemical study of this compound with the cyclic voltammetry in an aqueous ethanol as solvant and sulfuric acid as supporting electrolyte.

At the end of this study we are able to identify the structure and the natural of this product , and cheek their stability and reversibility.

Keywords : Cyclic voltammetry ,electrochemistry, organometallic chemistry, ferrocene , ferrocenic derived , Hydrazide's ferrocenic.

Résumé : le but de ce travail est la synthèse d'un hydrazide ferrocenique(N',N'- di ferrocenyl- N- acetohydrazide) par la réaction de sel ferrocenique avec l'acetohydrazide .

Notre travail consiste également a faire un étude électrochimique de ce produit avec voltamétrie cyclique dan un milieu aqueuse d' éthanol en présence de acide sulfurique.

A la fin de ce travail nous somme parvenu à identifier la structure et la nature de ce produit et à vérifier leur stabilisation et réversibilité .

Mots-clés : voltamétrie cyclique, électrochimie, chimie de organométallique, ferrocene, les dérive ferrocenyl, hydrazide ferrocenique.

الملخص: ان الهدف من هدا العمل هو تصنيع احد مشتقات الهيدرازيد الفيروسينبة ودالك بتفاعل الملح اليودي لفيروسينيل مثيل ثلاثي مثيل امونيوم مع الايسيتو هدرا زيد وكدا الدراسة الكهروكميائية لنواتج التفاعل في وسط مائي للايثانول في وجود حمض الكبريت بطريقة الفولطامبيرومتري الحلقية.

بفضل هده الدراسة تمت معرفة بنية وطبيعة المادة المصنعة ,مدى استقرارها وعكوسيتها.

الكلمات الدالة : الفولطامبيرو متري الحلقية , الكهروكيمياء , الكيمياء العضو معدنية , الفيروسان , المشتقات الفيروسينية ال , هدرازيدات الفيروسينية