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The preparation of 1, 1'tetramethylene ferrocene

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THE PREPARATION OF 1,1' TETRAMETHYLENE FERROCENE

by

Arthur Frederick Grand

UC 1963

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

JUNE, 1963



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THE PREPARATION OF 1,1' TETRAMETHYLENE PERROCENE

by

Arthur Frederick Grand

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science with a Major in Chemistry.

By Arthur F. Grand

Approved by William B. Martin Jr.

(Date) 7 June, 1963

ACKNOWLEDGMENTS

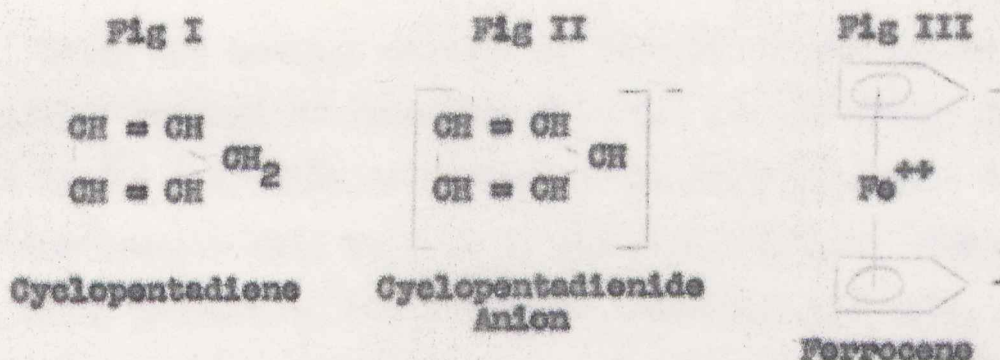
Grateful acknowledgment is made to Professor William B. Martin, Jr. for his assistance in this project. Samples of ferrocene used in this research were donated by Ethyl Corporation, New York, N. Y., and E. I. duPont de Nemours and Co., Inc., Wilmington, Delaware.


TABLE OF CONTENTS

Introduction	1
Experimental Results	9
Discussion	13
Conclusions	18
Summary	19
Tables:	
I. Summary of Reaction Products	20
II. Infra-red Data	21 22
III. Ultra-violet Data	23
IV. Solvents for Recrystallization	23
Ferrocene Spectra:	
Infra-red	24
Ultra-violet	25
Bibliography	26

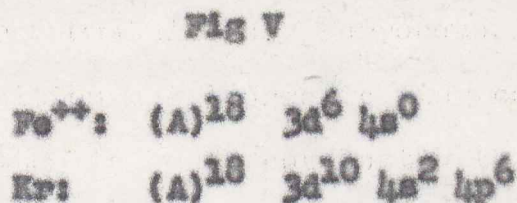
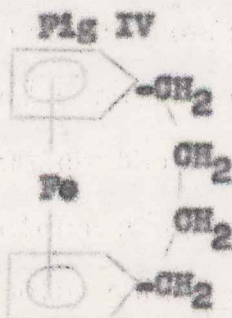
INTRODUCTION

The discovery of ferrocene, bis-cyclopentadienyl iron, in 1951 stimulated further research into a relatively new field of Organic Chemistry, organometallics. Ferrocene is the first of a series of transition metal-organic ring compounds in which the metallic atom is bound covalently to two cyclopentadiene rings (Fig III). The rings are superimposed over one another with the single atom inbetween; thus, they are often referred to as "sandwich compounds."



Ferrocene undergoes many chemical reactions in a manner similar to aromatic compounds, and very readily undergoes electrophilic substitution (8). The cyclopentadienide anion (Fig II) is a cyclic system of six pi electrons and might therefore be expected to exhibit aromaticity. The concept of resonance has been shown to be valid for this system (because of this the ring is represented as  rather than with conjugate double bonds). The noted similarity of ferrocene to benzene and its derivatives offers an excellent oppor-

tunity to give direction to the extended study of ferrocene derivatives. The particular compound of interest in this paper is 1,1' tetramethylene ferrocene (Fig IV).



1,1' tetramethylene ferrocene

There are several schools of thought on the intra-molecular bonding of ferrocene (7, 8). If one thinks of the iron in the + 2 oxidation state in the molecule, then each cyclopentadiene ring must be in the - 1 oxidation state. The iron, therefore, has 6 valence electrons remaining and each ring has 6. If the iron were to accept 6 pi electrons from each ring it would assume the "rare gas configuration" of krypton (Fig V). The added stability of this type of configuration would help explain ferrocene's unusual thermal stability. The second hypothesis is similar to the first. This theory proposes 8 bonding molecular orbitals and 1 non-bonding molecular orbital formed from the 18 valence electrons in the system. This is essentially a delocalized covalent bond and, in a broad sense, the iron has taken on the krypton configuration. The third theory, and the one preferred by the author, imagines a single covalent bond

between iron and each ring formed by overlap of one d-pi and one p-pi electron. This leaves 5 delocalized electrons in each ring to circulate as if in the molecular orbital of the ring only. This hypothesis would partly account for the noted aromaticity and strong negative center for electrophilic attack.

Ferrocene is thermally stable up to about 400°C. It is resistant to alkali and acid with the exception of strong oxidizers. It is easily oxidized to the ferricinium cation (iron in the + 3 oxidation state creates the ion $(C_5H_5)_2Fe^+$) and is therefore a good reducing agent and anti-oxidant (8).

Although the procedure outlined herein uses ferrocene as an initial reagent, one of the more recent preparations of ferrocene should be noted. Little, Koestler, and Eisenthal (as reported by Peters (8)) note a 90 % yield in the reaction of cyclopentadiene, ferrous chloride, and sodium ethoxide in ethanol:



The compound under investigation in this paper, 1,1'-tetramethylene ferrocene, has no known unusual properties. It has, in fact, been prepared only once by Lüttringhaus and Kullick (6) who reported an experimental yield of 0.053 %. Their procedure consisted of the steam distillation of α, -di-cyclopentadienyl alkanes formed by the reaction of sodium cyclopentadiene and α, dibromo alkanes (Br - (CH₂)_n - Br).

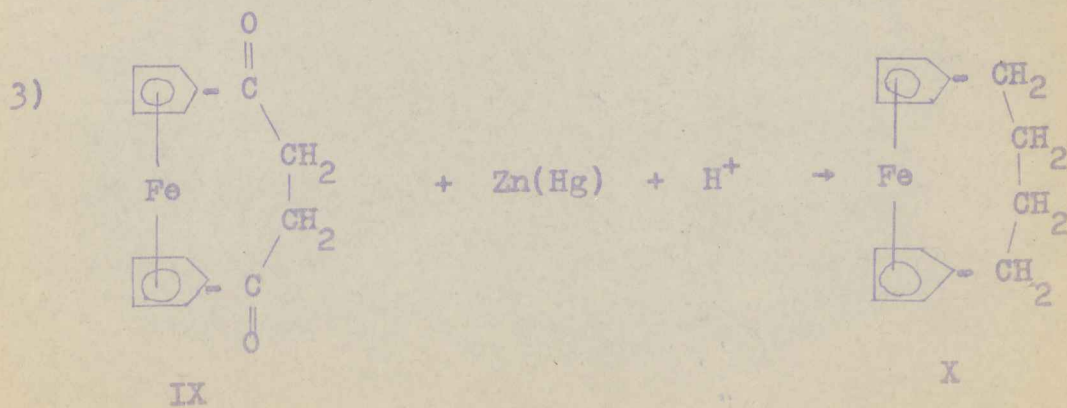
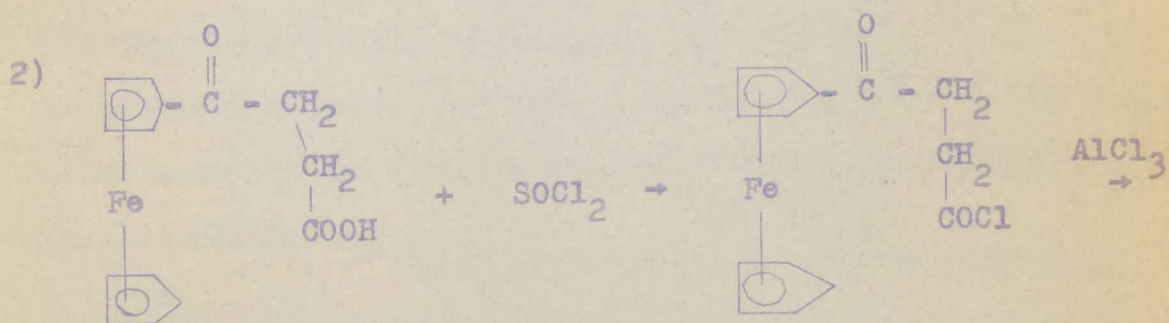
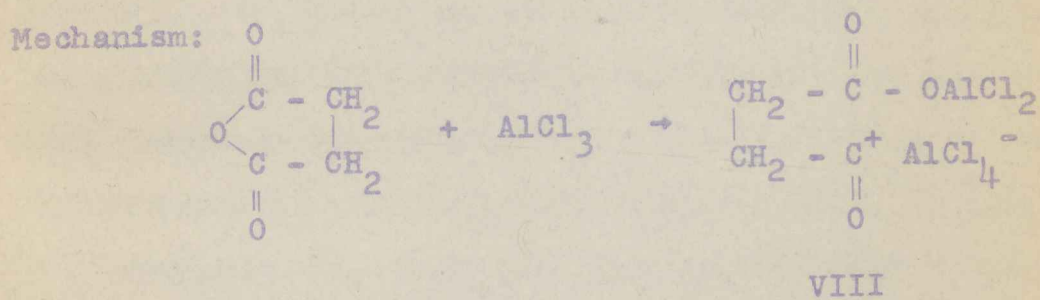
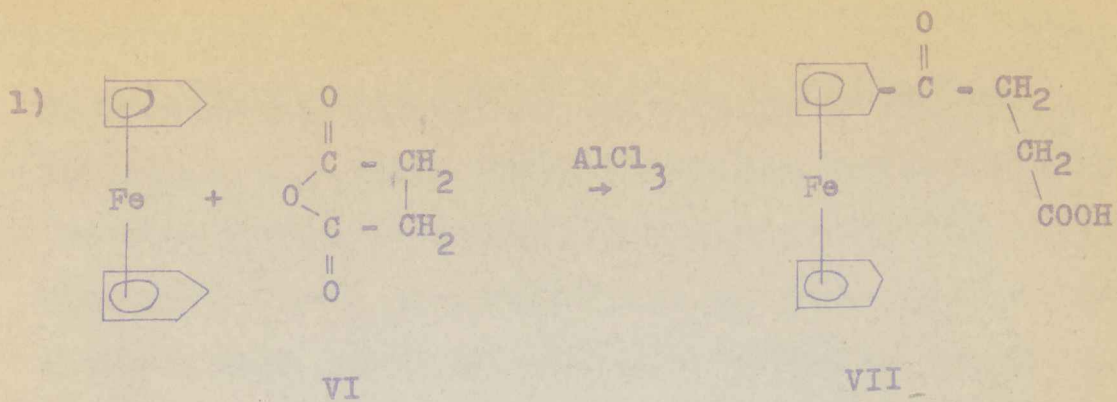
They did not report any properties of the cyclic product.

The proposed procedure for this research is as follows:

- 1) A Friedel-Crafts acylation of ferrocene with succinic anhydride (VI) to yield ferrocenoyl propionic acid (VII). The solvent is to be methylene chloride with aluminum chloride, $AlCl_3$, added as a catalyst. The aluminum chloride catalysis produces an electrophile (VIII) which attacks the cyclopentadiene ring, a Lewis base.
- 2) The acid derivative is to be treated with thionyl chloride, $SOCl_2$, and aluminum chloride or with polyphosphoric acid to yield 1,1', α,α' diketo tetramethylene ferrocene (IX).
- 3) The intermediate (IX) will then be reduced by the Clemmensen Reduction (amalgamated zinc and hydrochloric acid) to yield the final product 1,1' tetramethylene ferrocene (X).

Procedure 1) has been done successfully by Rinehart (11) who obtained a yield of 87 % of the keto acid. His procedure included the reduction of the keto group adjacent to the ring and then treatment with either trifluoroacetic anhydride or polyphosphoric acid. The attempt to effect ring closure (10, 12) resulted in homoannular substitution (cyclization on the same ring), and he obtained the product 1,2 α -keto tetramethylene ferrocene (Fig XI, p. 7).

The important difference between the procedure proposed in this paper and the procedure of Rinehart is the reduction



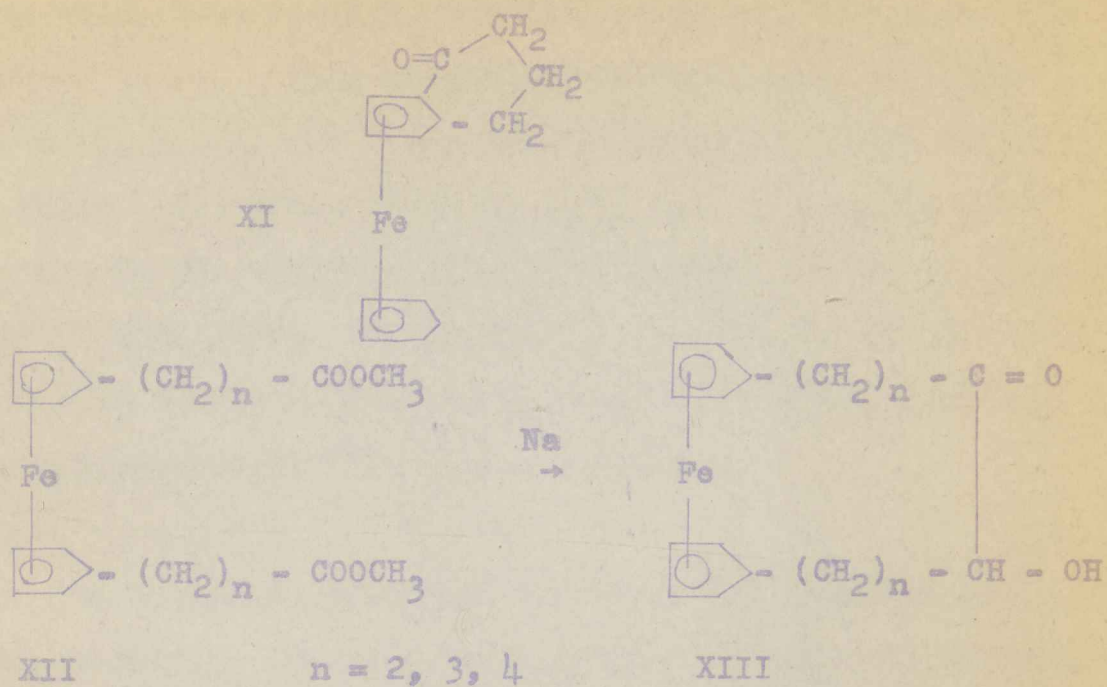
of the carbonyl adjacent to the ring in the ferrocenoyl propionic acid (VII). Alkyl groups are electron releasing and tend to make an organic ring more susceptible to electrophilic attack. α -Carbonyl groups, on the other hand, are electron withdrawing and resonance stabilized tending to deactivate the ring to electrophilic substitution. Rinehart's reduction, therefore, would tend to activate the ring and the probability of homocannular substitution is increased. Acyl groups on one ring of the molecule do tend to favor heterocannular substitution by electrophiles (9, 13).

Rinehart also attempted ring closure with three- and five-carbon atom chains (10). He succeeded in preparing the heterocannular product 1,1' trimethylene ferrocene, but got homocannular cyclization with the five-atom chain. This indicates that bond distances and angles are such that "ideal" conditions are met with a three-atom chain, essentially a six-member hetero-ring

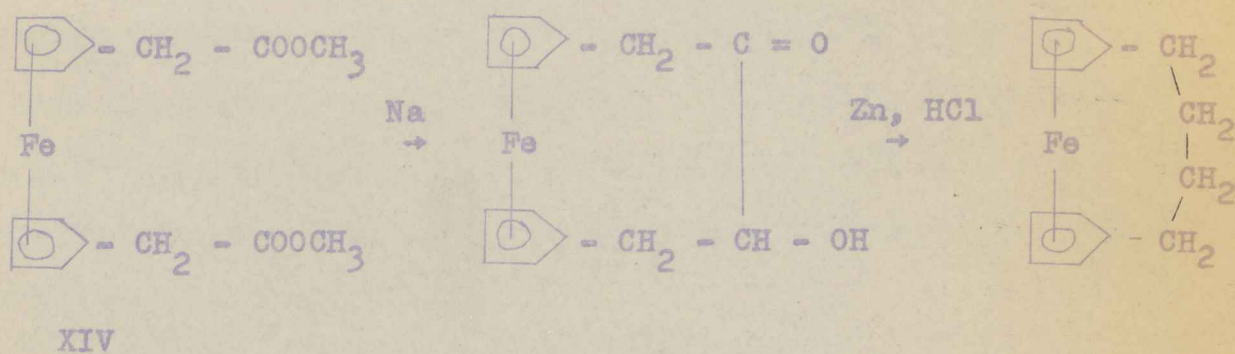
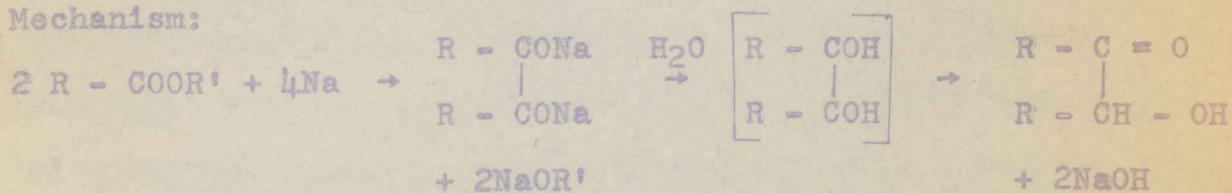
$$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}_2 \\ | \qquad \qquad | \\ (\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C} - \text{Fe} - \text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}) \end{array}$$

Apparently, even four atoms overshoots the mark. However, in the keto acid the carbons of the group $-\text{CO}-\text{CH}_2-$ must be co-planar with the ring (this is not true with the group $-\text{CH}_2-\text{CH}_2-$). The remaining two atoms in the keto acid chain must span the distance between the rings. This may be slightly strained, but there is less danger of overshooting the mark.

Another possible method of preparation of the final product is via the Acyloin Condensation. The methyl ester of a heterocannular di-substituted acid derivative of ferro-



Mechanism:



cene (XII) is treated with sodium metal to yield a cyclic product (XIII). This reaction has been carried out with $n = 2, 3, 4$ (9). No attempted reduction of the product was reported. For this method to yield 1,1' tetramethylene ferrocene, the methyl ester of ferrocene 1,1' diacetic acid must be used (XIV). This reaction ($n = 1$) has not been reported in chemical literature. Reduction could again be accomplished by the Clemmensen reaction.

The following procedure is that which Rinehart (11) used to prepare the acid derivative β -ferrocenoylpropionic acid (VII). The preparation consists of adding 7.4 g. of ferrocene and 2.0 g. of succinic anhydride in 150 ml. of methylene chloride to 5.8 g. of aluminum chloride in 150 ml. of methylene chloride. The reaction was stirred for two hours at room temperature, then decanted over ice. The crude acid was extracted from methylene chloride with sodium carbonate, filtered through Celite, and reprecipitated with dilute hydrochloric acid. The orange acid was recrystallized from methanol-benzene. Results of elemental analysis for carbon, hydrogen, and iron, and infra-red data supported the proposed structure (VII).

EXPERIMENTAL RESULTS

Data for the following procedures is summarized in Table I. Infra-red data is reported in Table II.

Procedure 1

Since no methylene chloride was available at the time, tetrachloroethane (TCE) was used as the solvent. Only 300 ml. of TCE were available so 3.7 g. of ferrocene, 1.0 g. of succinic anhydride, and 2.9 g. of aluminum chloride were used. The mixture was stirred for two hours at room temperature then poured over ice. The product of extraction with sodium bicarbonate, then sodium carbonate, was filtered through Celite and acidified with hydrochloric acid to pH 2. The acid solution was then extracted with ether.

Evaporation of the ether yielded nothing. The TCE was distilled under reduced pressure in a Hickman Still. The orange-brown residue was shown to be unreacted ferrocene by infra-red analysis.

Procedure 2

It was decided that methylene chloride should be used instead of TCE for the next reaction. However, only 150 ml. were available so the proportions of reagents were again reduced proportionately to 1.85 g. of ferrocene, 0.5 g. of succinic anhydride, and 1.45 g. of aluminum chloride. The mixture was worked up as before, filtered, acidified, and

extracted with ether. A small yield was obtained from the ether. An infra-red analysis (Spectrum I) was performed.

Procedure 3

Closer examination of the amounts of reagents needed revealed that only 2.2 moles of catalyst were available for each mole of anhydride. Normally 2.4 moles are required. This third procedure used 7.4 g. of ferrocene, 2.0 g. of succinic anhydride, and 6.4 g. (revised) of aluminum chloride in a total volume of 600 ml. of methylene chloride. The reaction was run for 2 and one half hours. The deep purple solution was poured over ice, and the aqueous and organic layers separated. The orange organic layer was extracted several times with sodium carbonate solution. This red aqueous solution was filtered through Celite and acidified to pH 2 with hydrochloric acid. About 1.8 g. of orange precipitate (31 %) was collected. Attempted recrystallization from methanol-benzene was not successful. The solid obtained from the evaporation of the methanol-benzene solution melted at 170-173°C with noted blackening.

A portion of the original orange flakes that precipitated from the acidified solution was soluble in ether. The ether insoluble residue was a dull brown solid, and the ether solution yielded red-orange crystals on evaporation (elution through a column of silica gel had no effect). These crystals melted at 169-172°C with blackening. Infra-red analyses

were done on both the ether soluble (Spectrum IV) and the ether insoluble (Spectrum II).

Procedure 4

Procedure 3 was repeated exactly. About 2 g. (34 %) of orange flakes were obtained melting at 169-172°C with blackening. An infra-red analysis was performed (Spectrum III). Attempted recrystallization from benzene-ethanol was unsuccessful. Recrystallization from 1,4 dioxane and water yielded brown crystals melting at 162-163°C with no darkening (however, this method was not successful with larger quantities). The ether soluble and ether insoluble products were separated. The ether insoluble product was the same dull brown solid obtained before, and red crystals were again obtained from evaporation of the ether solution.

A neutralization equivalent determination on the original orange product was attempted. A measured amount of this crude acid was dissolved in a known amount of sodium hydroxide and titrated with hydrochloric acid. Measurement with a glass-electrode pH meter showed a very gradual decrease, but no sharp end-point was found.

When attempted recrystallizations from solvent pairs apparently failed, an unsuccessful search was made for a solvent that could cause recrystallization upon cooling after solution was effected at a higher temperature. The results of this are summarized in Table IV.

An attempt was made to effect ring closure using the crystals obtained from evaporating the ether extract. The acid was refluxed with thionyl chloride for several hours. The thionyl chloride was then removed by evaporation under reduced pressure and nitrobenzene was added as a solvent for the reaction. Aluminum chloride was added and the mixture was heated to 100°C. The nitrobenzene solution was washed several times with water and with sodium carbonate solution, then dried with anhydrous sodium sulfate. The nitrobenzene was filtered and an infra-red analysis was performed on the dark, clear solution.

DISCUSSION

A number of infra-red spectra were obtained on different samples. Taking into account the poor performance of the instrument at the time, correcting for solvent absorption where needed, and reporting relative strengths of peaks within a spectrum, the data obtained is reported in Table II. Rinehart (11) reports that a carboxyl-carbonyl should absorb at about $1712-1705\text{ cm}^{-1}$ (5.85-5.94 μ); that a carbonyl adjacent to the ferrocene nucleus should absorb at $1667-1663\text{ cm}^{-1}$ (6.0 μ); and that all monosubstituted ferrocene derivatives should absorb at both 1110 and 1005 cm^{-1} (9.0 and 9.95 μ). This "9-10 rule" states that all ferrocene derivatives with one unsubstituted ring show absorptions at both 9 and 10 microns. The absence of both of these absorptions would be strong evidence of heteroannular disubstitution; however, the presence of one (either 9 or 10) is not conclusive proof of disubstitution or of monosubstitution). Ewing (3) reports carboxylic acid absorptions at 3.03-3.45, 5.75-6.0, 6.94-7.4, and 7.7-8.3 μ .

Ferrocene (Spectrum 0) has a broad absorption at 5.7-6.1 μ whereas each of the derivative samples shows two sharp peaks at about 5.85 and 6.0 μ , the latter being the stronger. The ferrocene absorption should cause added absorption in that area, but the presence of the two peaks is strong evidence of an α -keto carboxylic acid grouping. The other

evidence in support of this is inconsistent. All of the spectra except VI show absorptions around 8.0 μ ; all of the spectra except III and V show absorption in the range 6.9-7.4 μ ; and three of the six spectra show absorptions at 3.3 μ . The presence of these do support the hypothesis that the derivatives are all carboxylic acids with a keto group adjacent to the ferrocene nucleus.

The conclusions that may be drawn from the presence or absence of absorptions at 9 and 10 microns (9-10 rule) have been stated. Since the presence of a single absorption band proves nothing, the problem of analysis for degree of substitution remains present. Both bands show up strongly in only two spectra, 0 and I. The absorption at 9 μ appears in some degree in each of the others, but that at 10 μ makes almost no appearance at all. This being the only measure of the degree of substitution, no safe conclusions can be drawn. However, considering the lack of purity of the samples, the slight absorptions at both 9 and 10 μ in at least one derivative do indicate monosubstitution.

Ultra violet and visible spectra were obtained for pure ferrocene and for three stages in the product analysis. The samples were dissolved in ethanol and several dilutions were made on each sample to aid in locating all absorptions. The data from the spectra are summarized in Table III. No data was found in the literature on the acid derivative so

no direct comparisons could be made. However, Rinehart (8) reports ultra-violet wave-length maxima at 226 and 270 millimicrons for his product 1,2 a keto-tetramethylene ferrocene (XI). In another paper (13) he reports ferrocenyl ketone absorptions in the ultra-violet near 230 and 270 μ . Since these maxima do not appear in the ferrocene sample and do appear in the other three, we can safely conclude that they are a result of a carbonyl group, probably adjacent to the ferrocene nucleus.

Comparison of melting-point data gives a better basis for conclusions concerning degree of substitution. Rinehart (11) reports a melting point of 166.5-167.5°C for the keto acid β -ferrocenoyl propionic acid, after recrystallization from methanol-benzene. All of the products from the experimental procedures outlined in this report melt in the range 169-173°C with the exception of that recrystallized from dioxane and water which melted at 162-163°C. The nearness of these melting points to that reported in the literature strongly suggests a monosubstituted product; however, there was an indication of decomposition in these products by blackening at the melting point without return to the orange color on cooling.

There are a number of problems that have not yet been solved and several points that have been left without discussion. The reason in that only bare hypotheses can be made with the data available, and no conclusions can be drawn without further organized study. Comparison of the

many spectra both infra-red and ultra-violet show definite similarities among samples of essentially two distinct physical forms - dull brown powder and red-orange crystals. These both have acidic properties as evidenced by their extraction with base and reprecipitation with acid, but differ in their solubility in ether. They have comparable melting points. The chief difference between the ether soluble and ether insoluble product is very possibly due to differences in the oxidation state of the iron. In ferrocene and its derivatives the iron is in the +2 oxidation state, but it can be oxidized to +3 giving the entire molecule a charge of +1. The ether soluble product is probably the neutral molecule whereas the zwitterion would be insoluble in ether. Both products would be insoluble in ether. Both products would have acidic properties; both would have nearly identical infra-red and ultra-violet spectra; they would have comparable melting points; but they would have different physical appearances.

The oxidation of iron to +3 could partly explain the gradual curve obtained in titration. This reaction is particularly unusual for carboxylic acids which show sharp end points. The fact that some acid precipitated at higher pH's is again unusual. However, if the iron is in the +3 oxidation state, it has an effective charge of +1. In basic solution the carboxylic acid exists as the -COO^- anion. It is possible that the acid anion has chelated with the +1 iron complex and caused precipitation earlier than expected.

The small yields (31 and 34%) of acid derivative compared to Rinehart's (84%) is also a puzzle. The only explanation is that more efficient stirring, longer period of reaction, or higher temperature must be used.

The two problems that remain unsolved and offer no outlet for speculation are the apparent decomposition (blackening) of the samples at the melting point and the recrystallization from 1, 4 dioxane and water. The solvent pair dioxane-water effectively recrystallized a small sample of the derivative, but later attempts could not even effect solution with dioxane. Perhaps again air oxidation of the iron in the molecules creates the difference.

CONCLUSIONS

Taking into account the spectra obtained, the melting point data, and other experimental observations it can be safely concluded that the product of the initial procedures was ferrocenoyl propionic acid (Fig. VII). The product was impure, probably mixed with unreacted succinic acid and any number of side-products involving ferrocene, succinic acid, and methylene chloride. Separation of these products was not accomplished because suitable solvents for recrystallization could not be found.

The final procedure and attempt at ring closure was never analyzed due to extremely poor response of the infrared spectrophotometer.

SUMMARY

Using the noted aromaticity of ferrocene, the study of this compound has been extended to include a Friedel-Crafts acylation with succinic anhydride and attempt at ring closure. The method of Rinehart (11) has been the basis for preparation of the α -keto acid derivative ferrocenoyl propionic acid. This procedure was done several times. Recrystallization from several solvents and solvent pairs was unsuccessful. Infra-red and ultra-violet analyses were performed on the crude acid.

The conclusion was that the yield was the acid derivative sought after but that there was a distinct possibility of the iron existing in more than one oxidation state. Separation of the ether soluble and other insoluble products was effective.

The final procedure was that of attempting ring closure. Results were inconclusive due to extremely poor functioning of the infra-red spectrophotometer.

TABLE I

Summary of Reaction Products

Procedure No.	1	2	3	4
Solvent	300 ml. $C_2H_2Cl_4$	150 ml. CH_2Cl_2	600 ml. CH_2Cl_2	600 ml. CH_2Cl_2
Ferrocene	3.7 g.	1.85 g.	7.4 g.	7.4 g.
Anhydride	1.0 g.	0.50 g.	2.0 g.	2.0 g.
$AlCl_3$	2.9 g.	1.45 g.	6.4 g.	6.4 g.
Products	<p>none negligible a) about 1.8 g. (from aqueous a) about 2.0 g. I.R. (III) (unreacted (from layer acidified) M.P. 169-172°C blks. ferrocene ether) recovered) I.R. (I) b) after attempted recrystal- b) recrystallization from lization from methanol- dioxane-water. benzene. M.P. 162-163°C M.P. 170-173°C blks.</p> <p>c) ether soluble. I.R. (V, VI). M.P. 169-172°C blks.</p> <p>d) ether insoluble. I.R. (II). d) other insoluble. M.P. 165-173°C blks.</p>			

TABLE II

Infrared Data

<u>No./3microns</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
0			5.7-6.1 m	7.1 m		9.0 s	10.0 s		12.3 s
I			5.85 6.0 vs vs	7.1 s	8.0 s	9.0 9.3 ms ms	10.0 ms		12.2 s
II			5.85 6.0-6.1 m vs	6.9 7.3-7.4 ms s	8.0 s	9.0 9.3 m ms			12.2 s
III			5.85 6.0 wm vs		7.9-8.0 m	9.0 wm			12.1 m
IV	3.3 wm		5.85 6.0 wm vs	7.1 wm	7.9-8.0 8.6 m m	9.05 9.3 wm m			12.1 m
V	3.3 m		5.85 6.0 m s		8.0 ms	9.05 9.3 wm m			12.1 ms
VI	3.3 m		5.8 6.0 ms vs	7.25 7.55 m m		8.9 ms	10.06 wm		12.25 s

References
(3) 3.03-3.45
-COOH

5.85-5.9 6.0
-CO-OH R-CO-

6.94-7.4 7.6-8.6
-COOH -COOH

9.0 9.95
presence of both
indicates mono-substitution

(11)

TABLE II (cont'd)

All solutions approximately 10 %, data corrected for solvent.

<u>No. (of spectrum)</u>	<u>Sample, solvent, and origin</u>
0	Ferrocene (CHCl_3), Ethyl Corp.
I	Ether Soluble (CHCl_3), from Procedure 2
II	Ether Insoluble (KBr pellet), Procedure 3
III	Original acid yield (nujol, paraffin oil), Procedure 4
IV	Ether Soluble (nujol), Procedure 3
V	Ether Soluble (nujol), Procedure 4
VI	Ether Soluble (1, 4 dioxane), Procedure 4

TABLE III

Ultra-violet Data

<u>Sample</u>	<u>U.V.</u> <u>200</u> m-microns	<u>300</u>	<u>Vis.</u> <u>400</u>	<u>500</u>
Ferrocene	205 260	325	440	
Orig. acid	204 225 270	340	455	
ether soluble	203 225 268	335-340	not taken	
ether insoluble	205 225 268	340	455	

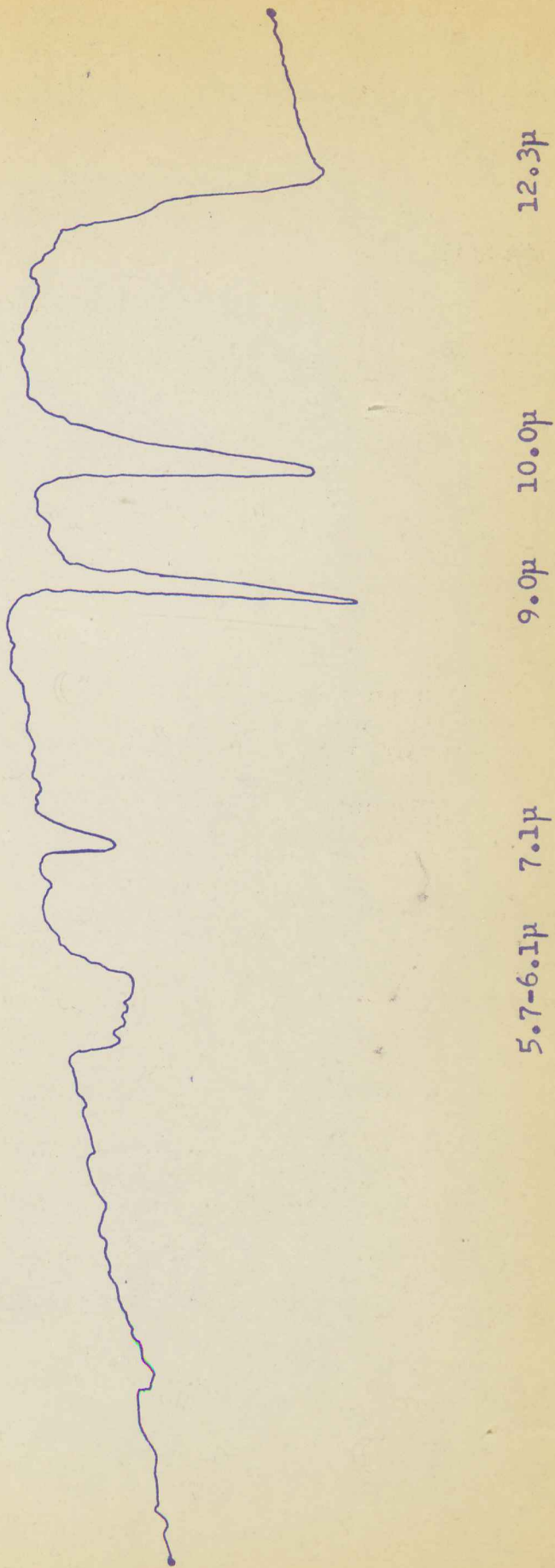
TABLE IV

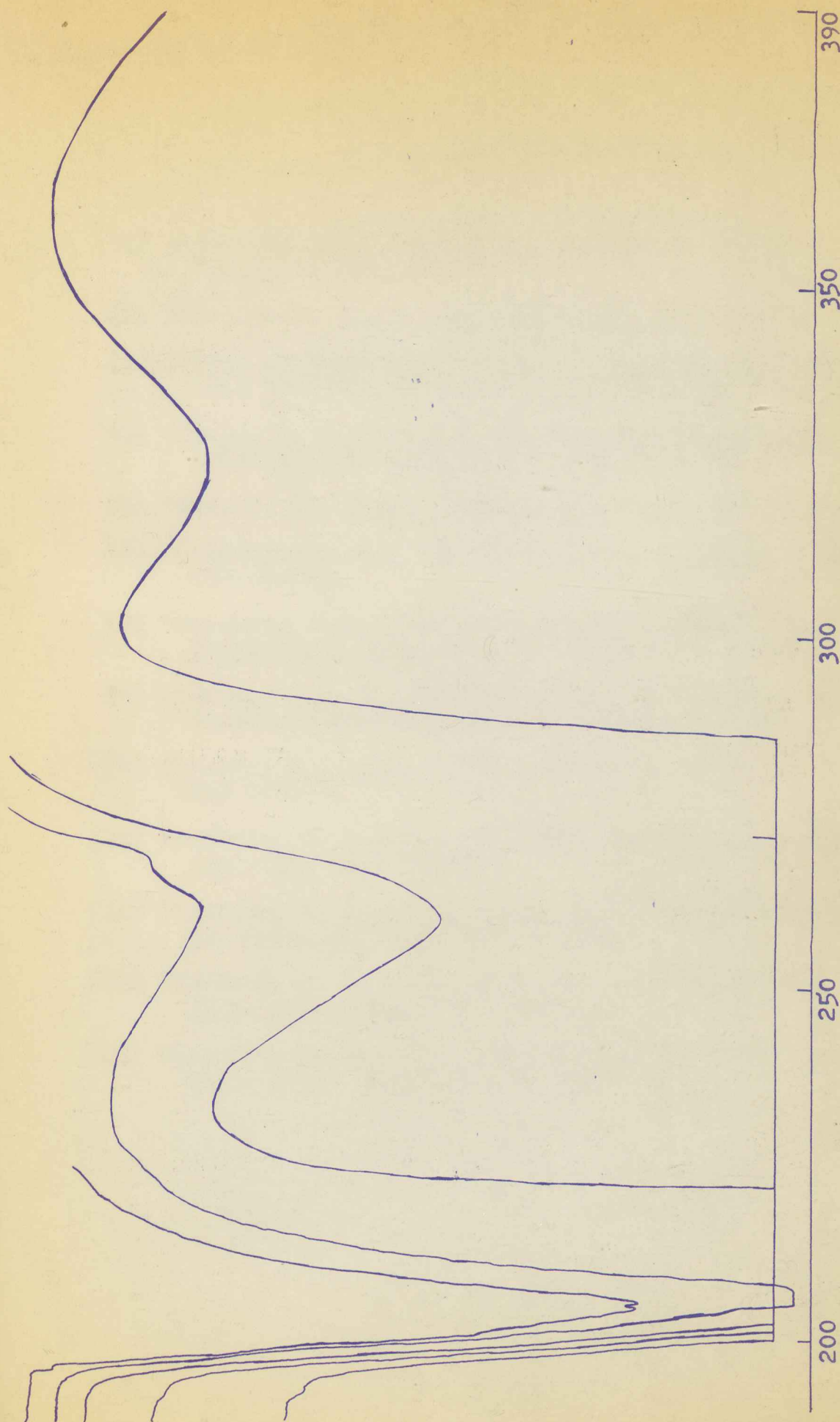
Solvents for Recrystallization

<u>Solvent</u>	<u>Cold</u>	<u>Solubility</u>	<u>Hot</u>
Acetone	v. sl. s.		sl. s.
Water	i.		i.
Chlorobenzene	i.		v. sl. s.
n-butanol	i.		sl. s.
1, 4 dioxane	v. sl. s.		sl. s.
Methanol	v. sl. s.		sl. s.
Benzene	v. sl. s.		sl. s.
Ethanol	v. sl. s.		sl. s.

INFRA-RED SPECTRUM OF FERROCENE

(2.0 - 14.0 MICRONS)





WAVELENGTH (MILLIMICRONS)

ULTRA-VIOLET ABSORPTION SPECTRUM FOR FERROCENE

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