THE SYNTHESIS OF SOME SULFUR HETEROCYCLIC METALLOCENES

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By

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Appreciation is extended to those individuals who were kind enough to obtain the n.m.r. spectrum of a number of compounds which were synthesized in this research.

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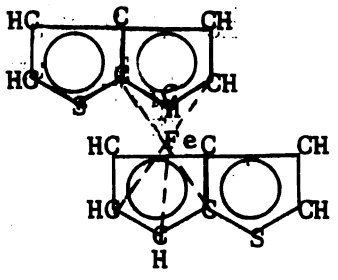
INTRODUCTION AND HISTORICAL

Ferrocene was first prepared in 1951 by Kealy and Paulson (1). The reaction between cyclopentadienylmagnesium bromide and ferric chloride was attempted in anticipation that the iron salt would oxidize the Grignard reagent to dicyclopentadienyl. This type of coupling reaction is known to occur with other Grignard reagents. For example, phenyl and benzyl magnesium halides yield diphenyl and dibenzyl respectively.

$$6RMg\ X + 2FeX_3 \text{ -- } 2Fe + 3R\text{-}R + 6Mg\ X_2$$

Thus while the expected product was not realized, ferrocene was discovered. The cobalt (2), chromium (3), manganese (4), ruthenium (5), and other metal analogs of ferrocene have since been prepared. The bicycloindenyl - iron and cobalt compounds were also synthesized shortly after ferrocene was discovered (6).

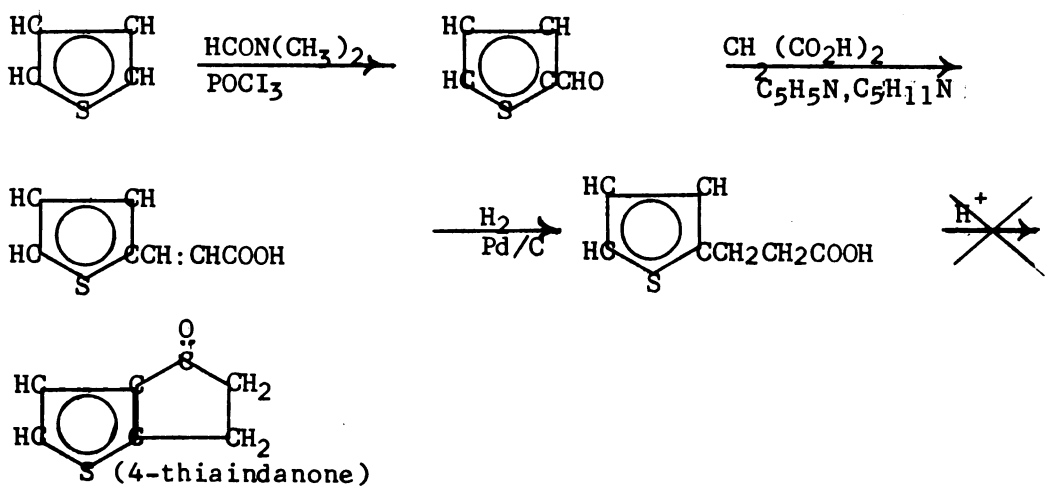
An examination of the chemical literature reveals that a great deal of work has been reported on substitution reactions of ferrocene and its analogs. There is no mention of studies to prepare a sandwich type compound incorporating a hetero atom somewhere in the molecule. It was, therefore, the purpose of the present work to snythesize bisthiaindenyliron,



and to investigate its chemistry and properties.

RESULTS AND DISCUSSION

The objective of this research was to develop methods for the synthesis of bisthiaindenyl iron and its alkyl analogs, and to investigate their substitution reactions. Sam and Thompson (7) reported the preparation of 4-thiaindanone* by the cyclization of 3-(2-thienyl)-propionic acid with polyphosphoric acid. The heterocyclic acid was obtained through a series of steps starting with thiophene.



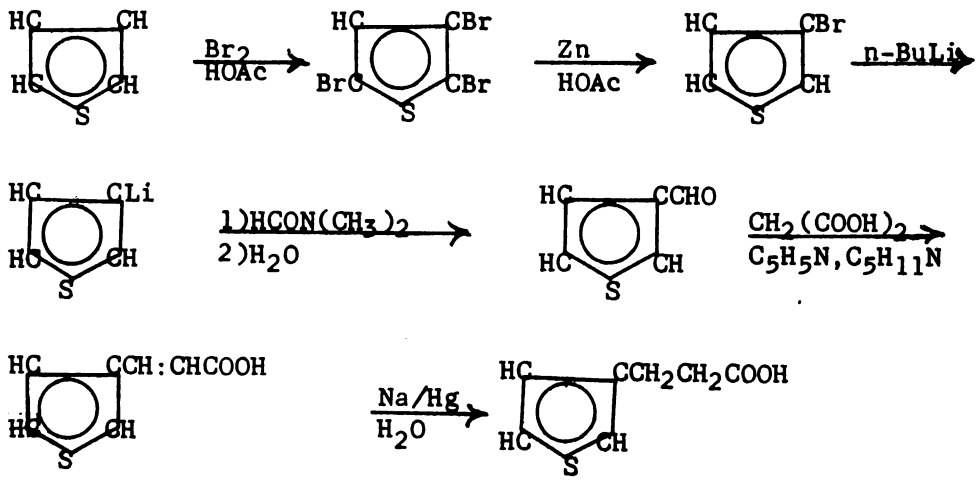
2-Thiophenecarboxaldehyde was prepared according to the procedure of Campaigne and Archer (8) in 57% yield. Reaction of the aldehyde with malonic acid produced the 3-(2-thienyl)-acrylic acid. The condensation was accomplished by two separate reaction procedures. Reaction of 2-thenal with malonic acid in acetic anhydride with potassium acetate as a catalyst produced a 43% yield of the desired acid (9). When the aldehyde was condensed with malonic acid in pyridine with piperidine also serving as a catalyst, a 98% yield of the acid was realized (10).

The acrylic acid was reduced with 10% sodium-lead alloy to give a 52% yield of the desired 3-(2-thienyl)-propionic acid (7), or alternately with hydrogen over palladium or carbon resulting in a quantitative conversion

*Extensive use will be made of the nomenclature suggested for these compounds by Sam and Thompson (7)

to the saturated acid. When attempts were made to prepare 4-thiaindanone by cyclization of the heterocyclic propionic acid with polyphosphoric acid, no product could be isolated (7). A private communication from Professor Sam disclosed that he also was unable to repeat the work he had earlier reported.

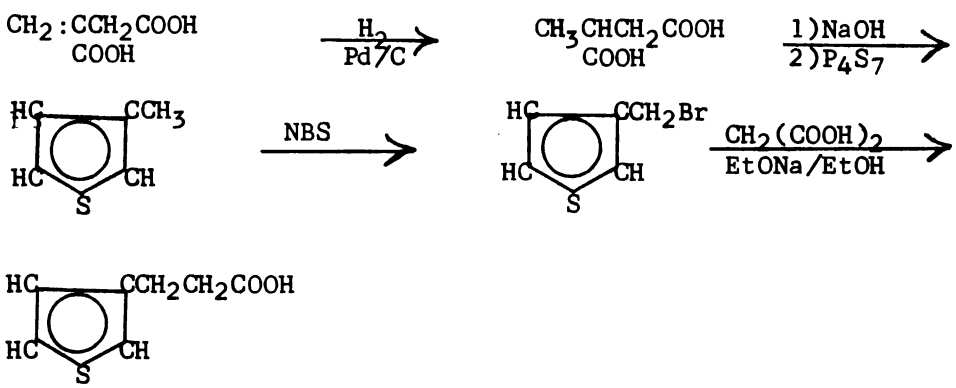
Since the product of the attempted cyclization of the 2-(thienyl)-propionic acid was a resinous polymeric material, it was assumed that cyclization involving the 2-position instead of the 3-position would increase the possibility of obtaining a thianindanone. The only known synthetic method for building up the necessary side at the 3-position of thiophene utilizes a 3-halothiophene.



To obtain a 3-bromothiophene it was necessary to first prepare 2,3,5 -tribromo - or 2,3,4,5-tetrabromothiophene. Bromination of thiophene with three equivalents of bromide produced 2,3,5 -tribromothiophene which was reduced to 3-bromothiophene with zinc dust and acetic acid in 70% yield (11). When zinc powder (60-200 mesh) was used the reaction proceeded more slowly and a sizable quantity of the material obtained was the dibromide.

When n-butyl lithium was reacted with 3-bromothiophene in anhydrous ether at -70°, a solution of 3-litho thiophene was obtained. Reaction of the lithio salt with dimethylformamide followed by hydrolysis gave the crude

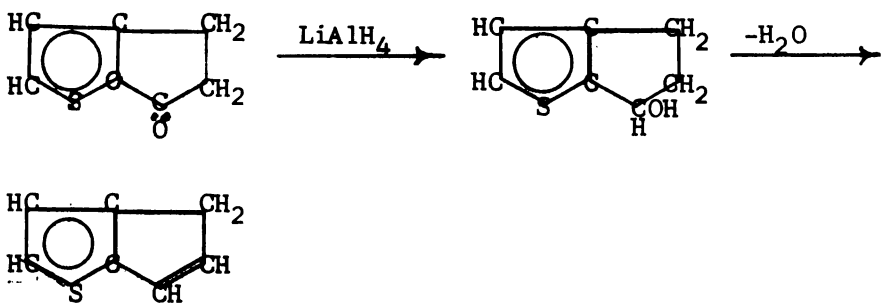
3-thiophenecarboxaldehyde in an 88% yield (12). This aldehyde was found to be rather difficult to purify and the results were not readily duplicable. Conversion of the aldehyde to 3-(3-thienyl)-acrylic acid was accomplished, in much the same way as the 2-isomer was synthesized, in a 98% yield. The unsaturated heterocyclic acid was reduced to the corresponding propionic acid with sodium amalgam in a 62% conversion. Attempts at catalytic hydrogenation with palladium on carbon as a catalyst were unsuccessful. The acid was also obtained from the reaction of 3-thenyl bromide with sodio-diethylmalonate in absolute ethanol. The series of reaction started with itaconic acid.



Itaconic acid was reduced under hydrogen using palladium on carbon as a catalyst. The disodium salt of the resulting methylsuccinic acid was reacted with phosphorus heptasulfide to obtain 3-methylthiophene in a 51% yield (13). Considerable difficulty was encountered in the conversion of 3-methylthiophene to 3-thenyl bromide (14). The benzoyl peroxide free radical initiator was recrystallized by dissolving it in chloroform, adding an equal volume of methanol, and filtering off the fine crystalline needles. The brominating agent, N-bromosuccinimide, was crystallized from acetic acid and set aside in an open beaker for at least two days to allow free bromine to escape. These precautions, coupled with rapid stirring of the reaction mixture under vigorous reflux, were not sufficient to prevent considerable nuclear bromination. Nuclear brominated products were obtained each time the reaction was

attempted, even though extensive precautions were taken with respect to purity of reagents and exactness of prescribed procedure. Some 3-thenyl bromide was obtained in each case; however, it was always contaminated with the other isomer. Isomer separation was effected under reduced pressure in an 18 inch Vigreaux column.

The 3-(3-thienyl)-propionic acid was obtained in a 42% yield by a malonic ester synthesis (7). The acid was best purified by distillation followed by recrystallization from ligroin. 3-(3-Thienyl)-propionic acid was cyclized to 6-thiaindanone in a 55% yield using polyphosphoric acid as the catalyst and reaction media (7). This reaction was found to produce the maximum yield when 0.1 mole of the heterocyclic acid, dissolved in 100 ml. of chlorobenzene, was cyclized in 400 g. of polyphosphoric acid at 130-135°. The ketone was reduced and the resulting alcohol dehydrated to give 5-thiaindene.



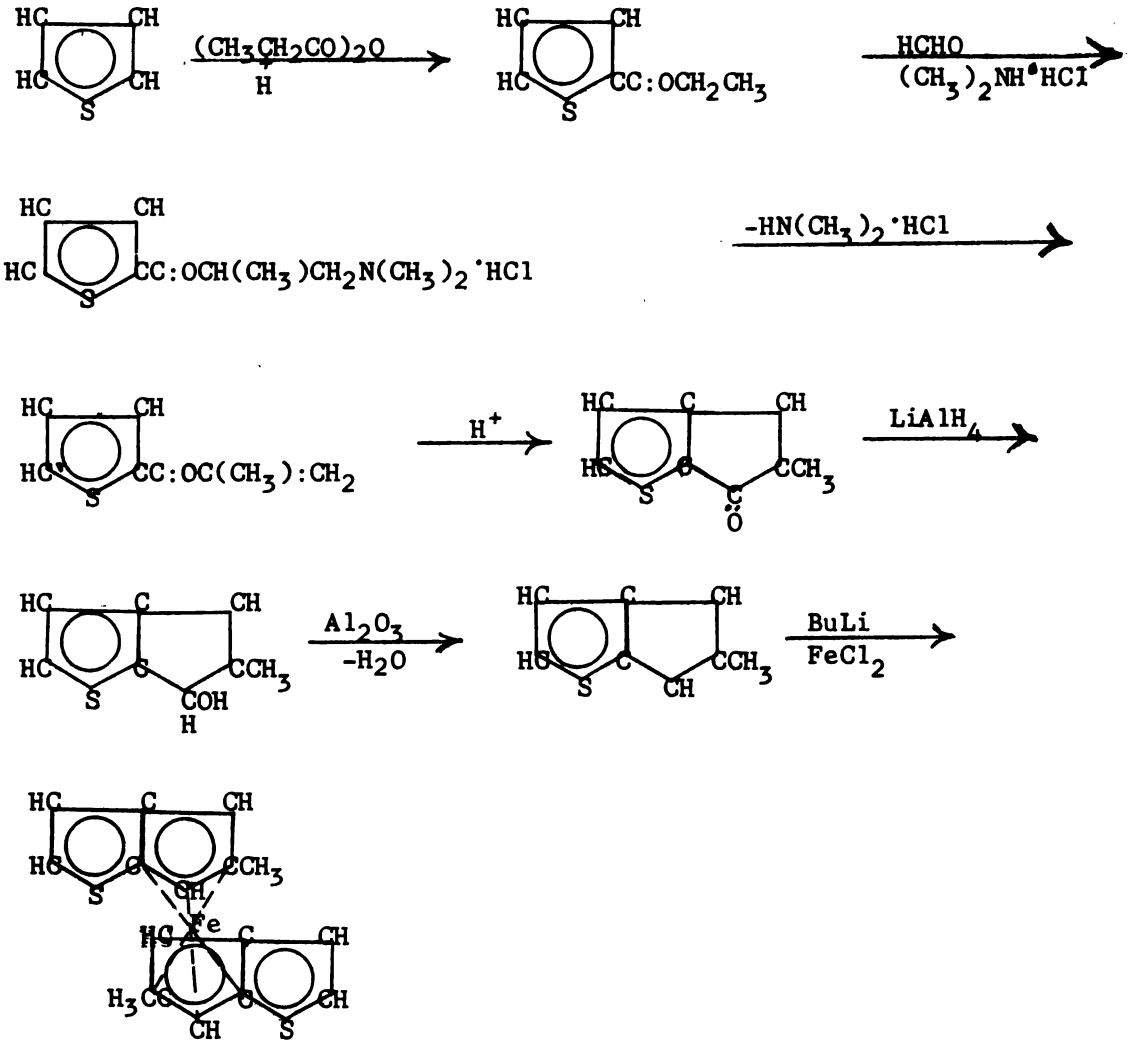
Reduction of the cyclic ketone to the corresponding alcohol was best accomplished with lithium aluminum hydride in ether. The alcohol is stable to basic solutions and only slowly darkened when exposed to the air. When the alcohol was contacted by an acid, a red solution was obtained and a gummy tar separated. The reaction occured even with exposure to acetic acid, suggesting that polymerization via a readily formed carbonium ion had taken place. 6-Thiaindanol was dehydrated in a 70% yield by passing the alcohol through an alumina column at 300°. In this manner a bright yellow liquid was obtained which showed no hydroxyl absorption in the infrared. The compound is fairly

stable and may be stored in the refrigerator for several days without noticeable decomposition; however, it darkens rapidly at room temperature.

Bisthiaindenyliron was prepared in a manner similar to that used for the preparation of bisindenyliron described by King (15). The thiaindene was reacted with n-butyl lithium to give the lithio salt. The salt was reacted, in tetrahydrofuran under nitrogen, with ferrous chloride, which had been prepared by reducing ferric chloride with iron. A maroon solid, which was easily isolated following completion of the reaction, immediately separated from the solution. The solid was stable at room temperature but slowly decomposed on being heated above 160°. It was sublimed at 100-130°/0.2mm. to yield a red microcrystalline solid. The n.m.r. of this compound was consistent with the proposed laminate structure. The hydrogen ratios were approximately 1:1:2:1 in close agreement with expected valves and the τ values were very close to those given for bisindenyliron. Solutions of the sulfur heterocyclic ferrocene analog are not stable to air and a brown solid, probably ferric oxide, slowly separates from solution. It is believed that the best yields would be obtained if the reaction solvent was removed under reduced pressure, and the residue was subjected to sublimation at 110-120°/0.02mm. This would permit separation of the product, from inorganic salts and organic residues, with a minimum of exposure to the air and solvents. A small amount of brown residue always remains following sublimation, and persists even after resublimation. The identity of the residue, which is insoluble in both the organic solvents ether, ethanol, chloroform and benzene, and water, is uncertain.

It was anticipated that a sulfur heterocyclic ferrocene could also be prepared via cyclization of 2-thenoyl ethene. The synthesis of 2-(2-thenoyl)-propene and its subsequent cyclization to 5-methyl-6-thiaindanone was already known (16). In order to take full advantage of the above mentioned reference bis (5-methylthiaindenly) iron was prepared through a series of steps starting

with thiophene.



2-Propionylthiophene was prepared in a manner similar to that used to prepare 2-acetylthiophene (19). A Mannich reaction using paraformaldehyde and dimethylamine hydrochloride was run on the 2-propionylthiophene. When the product of this reaction was subjected to steam distillation, 2-(2-thenoyl)-propene was obtained in a 67% yield (17).

The vinyl ketone was cyclized using cold concentrated sulfuric acid as a catalyst and reaction media. Best yields were obtained when the heterocyclic alkenone was slowly poured into the stirred sulfuric acid instead of being added dropwise over an extended period of time. Yields as high as 81% were obtained in this cyclization (16). The ketone was reduced to the alcohol

with lithium aluminum hydride in 75% yield. The alcohol was rapidly polymerized to a red insoluble material when exposed to acidic solutions, and it slowly turned brown on standing.

The alcohol was dehydrated to the corresponding unsaturated compound by passing it through an alumina column at 300°. Yields as high as 84% of the dehydration product, a bright yellow mobile liquid, were obtained. The synthesis of bis(5-methylthiaindenyl)iron was accomplished in 47% yield in the same manner as that used for the preparation of bisthiaindenyliron. The properties of this maroon solid are very similar to those of the previously described π complex. The calculated hydrogen ratio for this compound is 1:1:2:3 and the determined ratios are 1.00: 1.03: 1.92: 2:82. The aromatic hydrogen peaks occur at τ values very similar to those for bisindenyliron (15). The n.m.r. spectrum of this compound was consistent with the proposed laminate structure. Preparation of heterocyclic ferrocene analogs via 2-acylated thiophenes is considerably shorter and simpler than the route involving the 3-substituted thiophenes.

The same series of reactions were conducted with 2-acetylthiophene; however, attempted cyclization of 2-thenoyl ethene was unsuccessful. The heterocyclic alkene would not cyclize in cold sulfuric acid nor in hot phosphoric acid. It is possible steric requirements may have to be satisfied before this type of vinyl ketone can cyclize. The presence of a side chain methyl group has proven to be satisfactory for this type of cyclization and it may be that a halogen will function similarly. The halogen should be readily removed during the reduction of the cyclic ketone to yield the alcohol, 6-thiaindanol.

Several attempts were made to acetylate bis(5-methylthiaindenyl)iron. With acid catalysis in the presence of air the iron III cation was obtained, whereas in an inert atmosphere attempted acelylation resulted in destruction

of the molecule. With a reducible catalyst such as stannic chloride, an iron III salt was obtained both in the air and under a nitrogen atmosphere. Use of a nonreducible catalyst under nitrogen, such as aluminum chloride, produced only polymeric materials.

When the π complex was treated with two equivalents of n-butyl lithium followed by an excess of dimethylformamide, a solid was isolated which displayed a carbonyl absorption in the infrared. This material was too insoluble in organic solvents to permit the determination of an n.m.r. spectrum. Elemental analyses of the compound suggested that it was in fact a mixture of products.

Reaction of the lithium salt of 5-methyl-5-thiaindene with half a mole equivalent of titanium tetrachloride resulted in the eventual isolation of bis(5-methylthiaindenyl) titanium dichloride in a 20% yield.

The n.m.r. spectra of the two iron π complexes are similar to that of bisindenyliron which exhibits resonances (CS_2 solution) at 3.20τ (singlet), 5.54τ (doublet), and 6.08τ (triplet) (15).

Although, while all of the objectives of this investigation were not completely realized due to the properties of the compounds involved, a new type of π complex was successfully synthesized opening up an entirely new field of Thiophene chemistry.

EXPERIMENTAL

2-Thiophenecarboxaldehyde, C_5H_4OS:M.W112.15

The procedure of Campaigne and Archer (8) was modified for the preparation of this heterocyclic aldehyde. A 2 l. three-necked flask equipped with a mechanical stirrer and addition funnel was charged with a solution containing 168g. (2.0 moles) of thiophene in 184g. (2.44 moles) of dimethylformamide. The stirred solution was cooled to 0° by immersion in an ice bath, and 384g. (2.44 moles) of phosphorusoxychloride were added dropwise to it during a period of one hour. The reaction mixture was then carefully heated on the steam bath to initiate a vigorous exothermic reaction evolving hydrogen chloride gas. Occasional cooling in an ice bath was required to moderate the reaction. When the exothermic reaction had subsided, the mixture was heated on the steam bath for an additional hour to complete the reaction. The black solution was cooled to 0° and poured into a two liter beaker half-filled with cracked ice, and a pound of sodium acetate was added. The organic fraction was separated from the dark red mixture by steam distillation. The impure heterocyclic aldehyde was separated from the water, dried over anhydrous sodium sulfate, filtered, and vacuum distilled, b.p. 75-77° at 15 mm., to obtain 127 g. (1.1 moles, 57%) of a light pink colored liquid.

3-(2-Thienyl)-acrylic acid, $C_7H_6O_2S$:M.W.154.19

In the preparation of this acid the procedure of King and Nord (10) was followed. A 208g. (2.0 mole) quantity of malonic acid, 112g. (1.0 mole) of 2-thiophenealdehyde, 500 ml. of pyridine, and 10 ml. of piperidine were heated on the steam bath for four hours, during which a rapid evolution of carbon dioxide occurred. The yellow solution was acidified by pouring it into two liters of four molar hydrochloric acid. The crude acid product separated immediately, and when the mixture had cooled to 0°, it was recovered by filtration and air dried to give 150g. (0.98 mole, 98%) of crude acid as white platelets, m.p. 142-144. Literature value, 143-144 (10).

3-(2-thienyl)-propionic acid, $C_7H_8O_2S$:M.W.156.20

A 15g (0.1 mole) quantity of the acrylic acid was dissolved in 200 ml. of methanol and 4g. of 5% palladium on carbon were added. The reaction mixture absorbed a maximum of 0.1 mole of hydrogen in an hour at 50 p.s.i. pressure and 25°. The solution was filtered and the filtrate was evaporated to dryness. The solid residue was recrystallized from petroleum ether (b.p. 60-90°) to obtain 12g. (0.08 moles, 80%) of colorless needles, m.p. 45-47°. Literature value, 48-49° (7).

Attempted preparation of 4-thiaindanone

The procedure outlined by Sam and Thompson (7) was rigidly followed. A 10g. (0.065 mole) quantity of 3-(2-thienyl)-propionic acid was dissolved in 100 ml. of methylene chloride. This solution was slowly added portionwise to 200 g. of stirred polyphosphoric acid preheated to 120°. The addition of the methylene chloride solution required 15 minutes for completion and resulted in the formation of a black viscous mixture. After cooling the reaction mixture to 100°, it was poured over 200 ml. of cracked ice and extracted with four 100 ml. portions of ethylacetate. The combined extracts were washed twice with 100 ml. portions of 10% sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. Evaporation of the filtrate left a small amount (0.2g.) of unidentifiable black intractable material. Several variations in general reaction conditions failed to yield the desired product.

2,3,5-Tribromothiophene, C_4HBr_3S:M.W.320.85

Some variation in the procedure of Gronowitz (11) was used for the snythesis of this compound. A 420g. (5.0 mole) quantity of thiophene and 200 ml. of chloroform were placed in a 3 l. three-necked flask equipped with a mechanical stirrer and addition funnel. A cooling bath of running water was used throughout the reaction to control the reaction temperature. The addition

funnel was charged with 3420g. (15.1 moles) of bromine, and the halogen was added dropwise to the stirrer thiophene solution during 13 hours. Large quantities of hydrogen bromide gas were evolved during the addition of the bromine. Following the addition of the halogen, the reaction mixture was set aside overnight. It was then heated to 50° for five hours, after which the bromide was washed with a liter of three molar potassium hydroxide. The organic phase was separated and refluxed for seven hours with 290g. (5.2 moles) of potassium hydroxide in 600 ml. of ethanol. The solution was cooled and poured into a liter of water. The dense bromide solution was separated and the chloroform was removed under reduced pressure. The residue was not further purified but was used as such in the preparation of 3-bromothiophene.

3-Bromothiophene C_4H_3BrS:M.W.163.04

Using the procedure of Gronowitz (11), a 5 l. three-necked flask was equipped with a mechanical stirrer, condenser, and addition funnel. The crude tribromothiophene was placed in the funnel; the flask was charged with 1800 ml. of water, 800 ml. acetic acid, and two pounds of zinc dust. The stirred suspension was heated at its reflux temperature, and the bromide was added at such a rate that reflux was maintained when external heat was removed. Reflux was continued by heating for an additional ten hours. The 3-bromothiophene was removed by steam distillation, recovered from the aqueous distillate by extraction with ether, dried over anhydrous sodium sulfate, filtered, and finally fractionated to obtain 570 g. (3.6 moles, 75% from thiophene) of the pure halothiophene, b.p. 157-163°, n_D^{20}1.5908. Literature values, b.p. 160°, n_D^{20} 1.5919-1.5928 (11).

n-Butyl lithium C_4H_9Li:M.W.64.09

A 17.5g. (2.5 gram-atoms) quantity of lithium metal chips was placed in a 2 l. three-necked flask containing 400 ml. of dry ether. The reaction flask was equipped with an addition funnel, a mechanical stirrer, a low

temperature thermometer, and a nitrogen inlet tube. Under a nitrogen atmosphere, the stirred mixture was cooled to -10° in a dry ice-acetone bath; and, 157g. (1.15 moles) of n-butyl bromide in 200 ml. of ether were added dropwise during two hours. The blue mixture was stirred for an additional two hours at -10° to complete the reaction. It was then set aside in the refrigerator overnight.

3-Thiophenecarboxaldehyde C_5H_4OS:M.W.112.15

A method similar to that described by Taft (12) was employed to produce this aldehyde. The n-butyl lithium, prepared as described above, was cooled to -70° in a dry ice-acetone bath; and, a solution of 163g. (1.0 mole) of 3-bromothiophene in 100 ml. of ether was added dropwise during an hour and a half to the stirred solution, under a nitrogen atmosphere. A 100g. (1.26 moles) quantity of freshly distilled dimethylformamide in 100 ml. of ether was added dropwise to the reaction mixture during two hours. While maintaining the reaction temperature at -70°, stirring was continued for another six hours to complete the reaction. A considerable quantity of gray solid had separated from the blue solution at this point. The unreacted lithium chips, from the preparation of n-butyl lithium, were removed from the slurry; and the mixture was poured into a stirred saturated ammonium chloride solution. The yellow organic layer was separated, and the aqueous solution was extracted twice with 100 ml. portions of ether. The combined organic extracts were heated on the steam bath to remove solvent. The dark residue was vacuum distilled and the fraction boiling in the range 40-70°/1mm. was collected. Refractionation in an 8 inch Vigreaux column gave 99g (0.88 mole, 88%) of impure aldehyde boiling at 48-52°/1mm.. Literature value, 72-78/12mm. (19).

3-(3-Thienyl)-acrylic acid, $C_7H_6O_2S$:M.W.154.19

A 135g. (1.2 mole) quantity of 3-thiophenecarboxaldehyde, 250g. (2.5 moles) of malonic acid, 500 ml. of pyridine, and 10 ml. of piperidine

were heated on a steam bath for five hours, causing a rapid evolution of carbon dioxide. When the gas evolution had slowed (five hours) the solution was heated at its reflux temperature for a quarter of an hour. The volume of the reaction mixture was then reduced to 200 ml., by solvent removal under reduced pressure; and, the concentrated solution was added to 500 ml. of five molar hydrochloric acid, precipitating a solid. After being set aside overnight, the solid was removed by filtration and recrystallized from methylene chloride to yield 170g. (1.1 moles, 95%) of acid melting at 145-147°. Literature value, 149-150 (20.

Disodium methylsuccinate, $C_5H_6Na_2O_4$:M.W.176.10

A 130 g. (1.0 mole) quantity of itaconic acid was dissolved in 200 ml. of ethanol, containing two g. of 10% palladium on carbon, and hydrogenated. This solution absorbed a mole of hydrogen at 3-4 atmospheres after six hours in a Paar hydrogenator. The reaction solution was then filtered and the filtrate was evaporated to dryness. The solid residue was dissolved in concentrated sodium hydroxide containing two moles of base. The water was removed azeotropically with benzene, and the solid was separated as a fine powder by filtration. Benzene was removed from the solid by drying at 85° overnight.

3-Methylthiophene C_5H_6S:M.W.98.17

A modification of the procedure of Feldkamp and Tullar (13) was used to obtain this alkylthiophene. A 3 l. three-necked flask equipped with a mechanical stirrer, thermometer, gas inlet tube, straight bore reflux condenser, and a distilling head with an attached condenser, was charged with 300 ml. of mineral oil. The stirred oil was heated to 250° under a slow stream of carbon dioxide. A slurry of 180g. (1.2 moles) of disodium methylsuccinate and 200 g. (0.6 mole) of phosphorus heptasulfide in 500 ml. of mineral oil was added portionwise through the straight bore condenser during three quarters of an hour. The stirred reaction mixture was heated an additional half hour to

complete the alkylthiophene formation and the latter was recovered by distillation. The distillate was washed first with two 100 ml. portions of 10% sodium hydroxide then with 100 ml. of water. The organic layer was separated, dried over sodium sulfate, and distilled to obtain 50 g. (0.51 mole, 50%) of a clear liquid, b.p. 115-117°, n_D^{25} 1.5175. Literature values, 112-115° n_D^{20} 1.5170 ± 0.0005 (13).

3-Thenyl bromide, C_5H_5BrS:M.W.177.07

The method of Campaigne and Tullar (14) was followed to obtain this material. A 30g. (0.31 mole) quantity of 3-methylthiophene, 100 ml. of benzene, and 0.6g. of freshly crystallized benzoyl peroxide were placed in a 1 l. three-necked flask equipped with a mechanical stirrer and two reflux condensers. The stirred solution was heated at vigorous reflux, and a dry mixture of 50g. (0.30 mole) of recrystallized N-bromosuccinimide and 0.6g. of benzoyl peroxide was added in portions during 20 minutes. Each portion of this mixture introduced through the straight bore condenser caused a great deal of foaming. After adding the solid mixture, the red solution was cooled in an ice bath, filtered to remove succinimide, and concentrated under reduced pressure. The residue was fractionated, using an 18 inch Vigreaux column, to obtain 20 g. of a material boiling below 70°/3mm., n_D^{25} 1.5752. A second fraction of 14g. boiling at 70-80°/3mm. was collected, n_D^{25} 1.6015. The latter fraction was highly lachrymatory; and based on boiling point and refractive index, it was assumed to be 3-thenyl bromide. Literature values for 3-thenyl bromide, b.p. 75-78°/1mm., n_D^{25} 1.604 (15). Literature values for 2-bromo-3-methylthiophene, b.p. 27°/1.8mm., n_D^{25} 1.571. Thus it appears that the initial fraction was mainly nuclear brominated compound.

Preparation of sodium amalgam

A sodium amalgam was prepared by placing 23g. (1.0 gram-atom) of sodium metal in a liter beaker with 100 ml. of mineral oil. The addition of

67g. of mercury caused an exothermic reaction to occur. This mixture was heated at 200° until a homogeneous metallic solution was obtained. After cooling, the mineral oil was decanted from the solid amalgam. The amalgam was immediately washed with pentane to remove adhering mineral oil, broken into medium sized pieces, and stored in a sealed bottle.

3-(3-Thienyl)-propionic acid, $C_7H_8O_2S$:M.W.156.20

A. From 3-thenyl bromide

The procedure of Sam and Thompson (7) was followed in the preparation of this acid. A 14.5g. (0.62 gram-atom) quantity of sodium metal was dissolved in 300 ml. of absolute ethanol. To this stirred sodium alkoxide solution, 115 g. (0.65 mole) of diethylmalonate were added in one portion, followed by 113 g. (0.64 mole) of 3-thenyl bromide added dropwise during 10 minutes. During the addition of the heterocyclic bromide, copious quantities of solid precipitated from the solution with the evolution of considerable heat. The stirred mixture was heated at its reflux temperature for six hours, and 100g. of potassium hydroxide dissolved in 150 ml. of water were slowly added through the funnel. This stirred solution was again heated at its reflux temperature for a day. The volatile solvents were then removed under reduced pressure. The residue was dissolved in water, and the solution was acidified with concentrated hydrochloric acid. The organic material was removed by extraction with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was distilled under reduced pressure, and the fraction boiling in the range 130-150°/1.2mm. was collected. The solid which formed upon cooling was recrystallized from hexane to obtain 41g. (0.27 mole, 42%) of a pure product melting at 60-62°. Literature value, 61-62° (16).

B. From 3-(3-thienyl)-acrylic acid

A 97g. (0.63 mole) quantity of the corresponding acrylic acid was dissolved in two liters of one molar sodium hydroxide in a 3 l. three-necked flask. The flask and contents were cooled with a water bath; and, two gram-atoms of sodium as a 23% sodium amalgam were added portionwise to the stirred solution during 45 minutes. When the reaction subsided, 100 ml. of concentrated hydrochloric acid and 100 g. of amalgam were added. During the next eight hours, concentrated acid was added as needed to maintain a moderate evolution of hydrogen. The reaction mixture was stirred overnight then made alkaline to litmus. The organic layer was dissolved in 100 ml. of chloroform and separated. The aqueous layer was washed four times with 25 ml. portions of chloroform; these chloroform fractions were combined, and the solvent was removed by evaporation. The residue was extracted repeatedly with hot hexane until only a brown intractable resin remained. The solid, which was obtained by cooling and concentrating the hexane solution, was recrystallized twice from hexane to obtain 61g. (0.39 moles, 62%) of product, m.p. 61-62°. Literature value, 61-62° (16).

6-Thiaindanone, C_7H_6OS:M.W.138.19

A procedure similar to that described by Sam and Thompson (7) was used in the preparation of this compound. A stirred 400 g. quantity of polyphosphoric acid in a 1000 ml. beaker was heated to 130°. A solution of 30.8g. (0.2 mole) of 3-(3-thienyl)-propionic acid in 100 ml. of chlorobenzene was added to the mineral acid during five minutes. The black solution was stirred and heated an additional 25 minutes to complete the reaction. The reaction mixture was allowed to cool to 100° and poured into rapidly stirred mixture of ice and water. When the hydrolysis was complete and all the ice had melted, 200 ml. of ether was added to the rapidly stirred mixture. A hard solid residue was removed by filtration and washed several times with ether. The filtrate

was also washed several times with ether, and all the ether portions were combined. The deep red ether solution was decolorized with Norite, filtered, and evaporated to dryness. The solid residue was recrystallized from cyclohexane to obtain 15.3 g. (0.11 mole, 55%) of white needles melting at 94-95°. Literature value, 90-91° (7). The material showed a carbonyl peak at 6.05μ and no hydroxy absorption in the infrared.

6-Thiaindanol, C_7H_8OS:M.W.140.20

A 13.6g. (0.1 mole) quantity of the corresponding ketone was dissolved in 300 ml. of anhydrous ether and transferred to a liter flask containing 100 ml. ether and 5.0 g. (0.11 mole) of lithium aluminum hydride. The reaction mixture was heated at its reflux temperature for a day to complete the reduction. After decomposing the excess hydride with acetone, the ether solution was carefully poured into 200 ml. of rapidly stirred three molar sodium hydroxide. The organic fraction was separated from the milky-white aqueous portion. The aluminum hydroxide was removed by filtration through a fritted funnel, and both the precipitate and filtrate were washed twice with 100 ml. portions of ether. The combined ether washings and original ether washings and original ether extract were dried over anhydrous sodium sulfate, filtered, and concentrated on a steam bath. The residue was disilled under reduced pressure to yield 13g. (0.094 mole, 94%) of a pale green colored liquid boiling 93-95°/2mm., which solidified on being set aside for a few days, to give a solid which melted at 44-46°.

5-Thiaindene, C_7H_6S:M.W.:122.19

The dehydration of 6-thiaindanol was accomplished on a heated alumina column, prepared from a 25x7 cm. section of Pyrex tubing. A side arm for admitting nitrogen was attached about 8 cm. from the top, and glass wool was inserted 3-4 cm. from the bottom. The alumina column itself was 10 cm. in

length, and was packed with 8 mesh activated alumina, which had been dried under a stream of nitrogen for three hours at 400°. The column was heated to 300° and 8 g. (0.57 mole) of 6-thiaindanol were added dropwise through a burette during 45 minutes. Heating and nitrogen flow were continued for an additional 15 minutes after all the alcohol had been added. The yellow organic distillate and water were collected in a flask cooled in a dry ice-acetone bath. The organic material was dissolved in petroleum ether (30-60°) and separated from the water. The majority of the solvent was removed on the steam bath; and, the residue was vacuum distilled to obtain 4.9 g. (0.40 mole, 70%) of a bright yellow liquid, b.p. 55-62°/4.5 mm.

Bisthiaindenyliron, $C_{14}H_{10}FeS_2$:M.W.:298.21

A procedure similar to that reported by King (15) for the preparation of bisindenyliron was employed. A 0.39g. (0.0066 gram-atom) quantity of iron powder and 2.16 g. (0.0134 mole) of anhydrous ferric chloride were placed in a 100 ml. flask. A 50 ml. volume of tetrahydrofuran was added, resulting in the formation of a yellow solution and the liberation of heat. The mixture was heated at its reflux temperature, under nitrogen, for 3.5 hours to yield 0.02 moles of ferrous chloride. In a separate flask precooled in an acetone-dry ice bath, 4.8 g. (0.04 mole) of the thiaindene previously described were dissolved in 50 ml. of tetrahydrofuran. To this was rapidly added 30 ml. of 1.6 molar n-butyl lithium, causing the precipitation of a tan solid from the resulting red solution. The cold suspension was poured into the ferrous chloride solution, which had been cooled to -70°. This solution was stirred for 45 minutes at room temperature, then heated at its reflux temperature overnight, under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the dark red residue was washed with a mixture of methylene chloride and water. The red organic layer was separated, dried over anhydrous

sodium sulfate, filtered, and evaporated to dryness in vacuo. The residue was recrystallized from 1-2% solution of water in acetone to obtain 1.5g. (0.005 mole, 25%) of dark maroon colored needles. This material was further purified by sublimation at 110°/0.1 mm. The solid is stable in air but slowly decomposes above 150°. Organic solutions of the compound slowly lose their red color as a brown solid precipitates.

Anal. Calc'd for $C_{14}H_{10}S_2Fe$: C, 56.34; H, 3.35;S,21.46; Fe, 18.79

Found:[1] C, 55.82; H, 3.56; S, 21.00; Fe, 18.30[2]

2-Propionylthiophene C_7H_8SO:M.W.140.20

This compound was prepared in much the same way that Hartough (22) outlined for 2-acetylthiophene. A 200 g. (2.4 moles) quantity of thiophene and 130 g. (1.0 mole) of propionic anhydride was heated to 70° in a liter three-necked flask. A 10 ml. volume of concentrated phosphoric acid was added, causing an exothermic reaction to occur. The stirred dark brown solution was heated at its reflux temperature, for two hours, then 200 ml. of water were added with vigorous stirring. The organic portion was separated and washed with 100 ml. portions of saturated sodium bicarbonate until the washings were basic (Hydrion B). Distillation of the thiophene solution gave 118 g. (0.83 mole, 83%) of a clear liquid boiling at 90-91°/5mm., n_D^{24} 1.5501. Literature values, b.p. 88°/7mm., n_D^{20} 1.5531 (23).

Dimethyl-2-(2-thenoyl)-propylamine hydrochloride $C_{10}H_{16}CINOS$: M.W. 233.77

To prepare this compound a modification of the procedure of Blicke and Burckhalter (21) was employed. A 290g. (2.04 moles) quantity of propionylthiophene, 180g. (2.18 moles) of 91% paroformadedyde, and 162g. (2.0 moles) of dimethylamine hydrochloride were added to 600 ml. of absolute ethanol. The

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[1]Analyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

[2]An average of four spectrophotometric determinations run in these laboratories.

reaction solution was heated on a steam bath for 12 hours under vigorous reflux to obtain a green colored solution. The ethanol was removed under reduced pressure, and the gummy residue was dissolved in 400 ml. of water. Insoluble organic material was removed by extraction with ether. The amine salt was not isolated but was used as an aqueous solution to prepare the next compound in the series.

2-(2-Thenoyl)-propene, C_8H_8OS:M.W.152.21

The aqueous solution of the Mannich base previously prepared was heated to boiling. A 250 ml. volume of organic matter was distilled from the solution and discarded. When the temperature of the distillate reached 100°, product collection was begun. When the volume of the solution had been reduced to 300-400 ml., steam was admitted to the system to accelerate the distillation. Approximately 3.5 l. of distillate were collected before organic material ceased to distill. The slightly lachrymatory vinyl ketone was separated from the water, dried over anhydrous sodium sulfate, filtered, and fractionated in an 8 inch Vigreaux column. Of the 257g. of material collected by steam distillation, 214g. (1.36 mole, 67%) distilled at 108-110°/15mm. n_D^{24} 1.5672. Literature value, b.p. 118-120°/19mm. (17).

5-Methyl-6-Thiaindanone, C_8H_8OS:M.W. 152.77

In a manner similar to Burckhalter and Sam (24), 75g. (0.49 mole) of the corresponding ketone were added to 400 ml. of rapidly stirred sulfuric acid forming a deep red solution. The temperature of the acid solution rose to 70°. After 45 minutes the reaction mixture had cooled to 50°, and it was poured over four liters of cracked ice. The pale yellow mixture was extracted several times with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and concentrated on a steam bath. The black residue was subjected to vacuum distillation to obtain 62.g. (0.4 mole, 81%) of a color-

less liquid, b.p. 95-100°/2mm; n_D^{25} 1.5818. Literature values, b.p. 95.5°/2mm., n_D^{20} 1.5808 (24).

5-Methyl-6-thiaindanol, $C_8H_{10}OS$:M.W.154.23

A 113g. (0.75 mole) quantity of 5-methyl-6-thiaindone was added during an hour to a stirred solution of 15g. (0.38 mole) of lithium aluminum hydride in 500 ml. of ether. The solution was heated at its reflux temperature for 12 hours. The excess hydride was destroyed with acetone, and the solution was carefully poured into 500 ml. of stirred three molar sodium hydroxide. The aluminum hydroxide was removed by filtration with a fritted glass funnel, and both the filtrate and precipitate were washed several times with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and concentrated on a steam bath. Distillation of the residue yielded 85g. (0.56 mole, 75%) of a viscous liquid, b.p. 82-84°/0.6mm. The infrared spectrum of this compound showed a hydroxyl absorption and no carbonyl peak.

5-Methyl-5-thiaindene, C_8H_8S:M.W.136.31

A 20g. (0.13 mole) quantity of the corresponding alcohol was released dropwise onto the previously described alumina column (page 17), during 45 minutes. The organic distillate was separated from the water by dissolving it in petroleum ether (30-60°). The ether extract was concentrated on a steam bath, and the residue was distilled under reduced pressure. A yield of 14.5g. (0.117 mole, 84%) was obtained, b.p. 57-58°/1mm.

Bis(5-methylthiaindenyl)iron, $C_{16}H_{14}FeS_2$:M.W.316.26

Anhydrous ferrous chloride was prepared by heating 5.53g. (0.033 mole) of ferric chloride and 0.92 g. (0.017 gram-atom) of iron powder in 100 ml. of tetrahydrofuran under nitrogen for four hours. In a separate flask, 13.6g. (0.1 mole) of the previously described 5-methylthiaindene in 200 ml. of tetrahydrofuran, were allowed to interact with 73 ml. of 1.6 molar

n-butyl lithium at -70°. The bright red solution was inediately added to the ferrous chloride. This mixture was stirred for an hour at room temperature and then heated at its reflux temperature for three hours under nitrogen. The solvent was removed on a steam bath, and the residue was washed with water to remove lithium chloride. The water insoluble residue was recrystallized from a solution of 1-2% water in acetone to obtain 7.9g (0.024 mole, 47%) of maroon colored platelets which decomposed slowly above 160°. Organic solutions of this compound slowly deposit a solid brown precipitate when exposed to air. Anal. Calc'd for $C_{16}H_{14}FeS_2$:C,58.85; H,4.29; S, 19.62. Found: C, 59.04; H, 4.50; S, 19.52.

Dimethyl-2-(2-thenoyl)-ethylamine hydrochloride $C_9H_{14}CLNOS$:M.W. 219.74

A mixture of 126 g. (1.0 mole) of acetylthiophene, 81g. (1.0 mole) of dimethylamine hydrochloride, 40g. (1.0 mole) of 91% paraformaldehyde, and 200 ml. of absolute ethanol was heated at its reflux temperature for 22 hours. On cooling the solution a solid crystallized and this was removed by filtration. The filtrate was concentrated and cooled to yield a second quantity of crystalline material. A total of 110 g. (0.05 mole 50%) of product was obtained, m.p. 179-183°. Literature value, 178-179 (17).

2-Thenoyl ethene, C_7H_6OS:M.W.138.19

A 20g. (0.09 mole) quantity of dimethyl-2-(2-thenoyl)-ethylamine hydrochloride was subjected to steam distillation with external heating to hold the volume of the reaction mixture at a low level. An 8g. (0.058 mole, 65%) quantity of a light yellow colored lachrymatory liquid was obtained by extraction of the distillate.

Attempted preparation of 6-thiaindanone, C_7H_6OS:M.W.138.19

An 8g. (0.058 mole) quantity of 2-thenoyl ethene was added in one portion to 50 ml. of stirred concentrated sulfuric acid. This produced a black

solution which was stirred for an additional half hour before being poured over 300 ml. of cracked ice. Extraction of the mixture with ether yielded a lachrymatory liquid which slowly resinified, but failed to crystallize, upon standing.

Hot concentrated phosphoric acid was also used in an attempt to cyclize this compound; however, the results were the same as those obtained with sulfuric acid.

Attempted acelylation of bis(5-methylthiaindenyl)iron

A. Using phosphoric acid and acetic anhydride

The π complex (1.0g., 0.003 mole), 5.0 ml. of acetic anhydride, and 0.5 ml. of 85% phosphoric acid were heated on the steam bath for a half hour. A 50 ml. volume of water was added, and the insoluble brown solid which separated was removed from the green solution by filtration. The brown solid was not identifiable; its infrared spectrum showed an intense C-H peak and only shallow, very broad absorptions beyond 3.5μ. The spectrum is very similar to that of mineral oil in its simplicity.

B. Using boron trifluoride etherate and acetyl chloride.

A 0.9 g. (0.0016 mole) quantity of the π complex, 114μl. (0.0016 mole) of acetyl chloride, and 50μl. of 47% boron trifluoride etherate were placed in a flask containing 50 ml. of ether. After a day, the insoluble solid which separated was recovered by filtration and subjected to sublimation. In this manner 0.18g. of the starting material, identified by infrared, was obtained. A 0.12 g. quantity of a dark unsublimable powder, which dissolved in water to give a green solution, was also obtained.

C. Using phosphoric acid and acetic anhydride under nitrogen.

A stirred mixture of 0.5 ml. of phosphoric acid and 5.0 ml. of acetic anhydride was heated to reflux under nitrogen for 10 minutes. A 0.5 g. (0.0016 mole) quantity of the iron containing heterocyclic compound was added to this

acetylating mixture. The stirred reaction mixture was heated under nitrogen for an additional 20 minutes and then poured into 200 ml. of saturated sodium bicarbonate solution, which had been previously deaeriated. Methylene chloride was used to extract a brown solid from the colorless aqueous phase. This material proved to be unidentifiable and appeared to be polymeric in nature. The possibility of its being the desired product was eliminated through an infrared spectrum of the compound.

D. Using stannic chloride and acetyl chloride.

A 0.5 g. (0.0016 mole) quantity of the π complex was dissolved, under nitrogen, in 10 ml. of benzene containing 0.25 ml. (0.0035 mole) of acetyl chloride. When 100 μl of stannic chloride were added, a green precipitate formed. The stirred reaction mixture was heated, under nitrogen, for an additional half hour. A 0.5 g. quantity of green water soluble solid was recovered by filtration. Treatment of an aqueous solution of this compound with sodium borohydride resulted in the separation of an insoluble red material. The infrared spectrum of this red compound was the same as that of the starting material.

Reaction between bis(5-methylthiaindenyl)iron and bromine

A 0.5g. (0.0016 mole) quantity of the π complex was dissolved in carbon-tetrachloride and filtered. A 1.5 ml. volume of one molar bromine in carbon-tetrachloride was added to the red filtrate, causing the immediate precipitation of a green solid, weighing 0.60 g. This solid dissolved in water to give a green solution in which a red solid formed upon treatment with sodium borohydride. The infrared spectrum of the red precipitate was indistinguishable from that of bis(5-methylthiaindenyl)iron.

Reaction between bis(5-methylthiaindenyl)iron and boron trifluoride etherate.

A 0.5 g. (0.0016 mole) quantity of the π complex was dissolved in 25 ml.

of benzene containing 100 μl. of 47% boron trifluoride etherate. Precipitation of a dark solid was noticed immediately, and after 12 hours 0.29 g. of a solid was collected by filtration. The material was soluble in water yielding a green colored solution, which when treated with sodium borohydride liberated a red solid. This red material has an infrared spectrum which was indistinguishable from that of bis(5-methylthiaindenyl)iron.

Formalation of bis(5-methylthiaindenyl)iron

A 0.5 g. (0.0016 mole) quantity of the heterocyclic π complex was dissolved in 100 ml. of well stirred tetrahydrofuran and cooled to -15° under nitrogen. To this solution was added 2.2 ml. of 1.6 molar n-butyl lithium. A solid slowly separated from the red solution as it was warmed to room temperature. The solution was stirred at room temperature, under nitrogen, for a half hour in order to remove butane. At this point the solution was cooled to -25° and 2.0 g. (0.022 mole) of dimethylformamide in 10 ml. of tetrahydrofuran were added dropwise during 15 minutes. The solution became very dark during the addition of the amide. The solution was stirred for an additional half hour at room temperature before being poured into 100 ml. of saturated ammonium chloride solution. The dark precipitate was dissolved in methylene chloride to give a deep purple solution. This solution was dried over sodium sulfate, filtered, and evaporated to dryness. The residue was recrystallized from carbon disulfide to obtain 0.2g. of a black solid which showed a carbonyl absorption at 6.05 μ in the infrared. The relative insolubility of this compound in all solvents investigated prevented the determination of an n.m.r. spectrum. It was at first believed that this compound was the diformal derivative; however, the elemental analyses were neither suggestive of this possibility nor reproducible.

Anal. Calc'd for $C_{14}H_{18}FeO_2S_2$: C, 55.51; H, 3.66; S, 16.74

Found: C, 54.56, 53.79; H, 3.49, 3.78; S, 14.70, 15.80.

Bis(5-methylthiaindenyl)titanium dichloride, $C_{16}H_{14}Cl_2Ti$:M.W.325.09

A 6.8 g. (0.05 mole) quantity of 5-methyl-5-thiaindene was prepared by the method previously described (page 21). This was dissolved in 100 ml. of ether and treated, under nitrogen, with 0.06 mole of n-butyl lithium at -70°. A white solid precipitated immediately. Exposure of this compound to air turned it red. The ether-salt slurry was slowly added, under nitrogen, to a stirred solution of 4.8g. (0.025 mole) of titanium tetrachloride in 100 ml. of benzene. The solution became warm, turned red, and a green solid separated from the solvent. The suspension was stirred for an additional four hours to complete the reaction. The solvent was removed under reduced pressure; and, the residue was extracted, under nitrogen, with hexane in a Shoxlet extractor. The hexane extract was discarded, and the residue was subjected to extraction with chloroform for a day. When the chloroform solution was concentrated and cooled, 2.0g. (0.0051 mole, 20%) of a dark green solid was obtained. The green compound slowly decomposed upon heating and was not soluble enough in the organic solvents ether, ethanol, chloroform, benzene, dimethylsulfoxide, and carbon disulfide to permit determination of its n.m.r. spectrum.

Anal. Calc'd for $C_{16}H_{14}Cl_2S_2Ti$: C, 49.33; H,3.60; S,16.44

Found: C 49.56 H, 3.71 S, 16.39

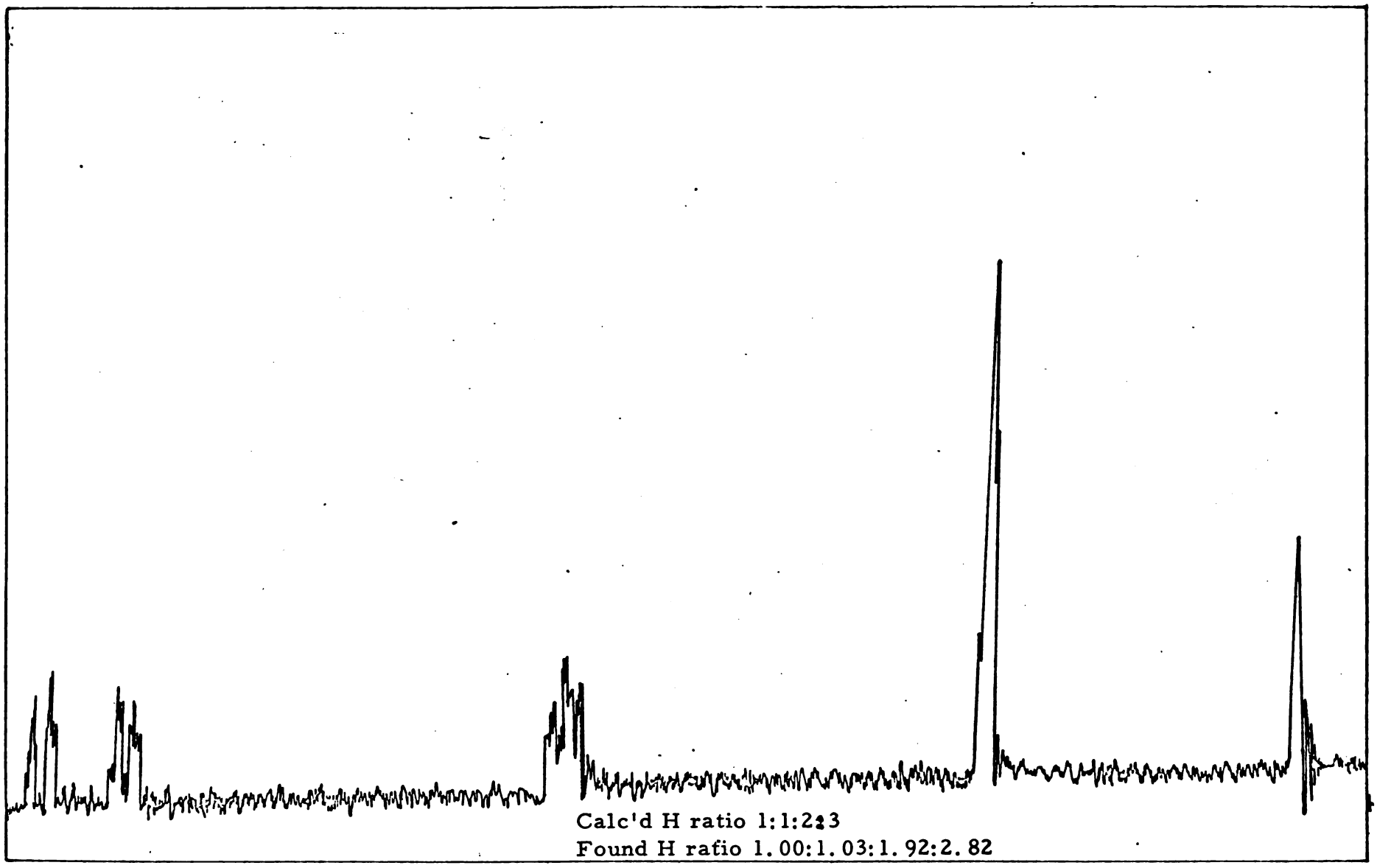
SUMMARY

Bisthiaindenyliron, bis(5-methylthiaindenyl)iron and bis (5-methylthiaindenyl) titanium dichloride were prepared for the first time and characterized. The 5-methyl substituted compounds were prepared via 5-methyl-6-thiaindanone, which in turn was prepared by the cyclization of 2-(2-thienyl)-propene. It was necessary to prepare bisthiaindenyliron by way of 3-(3-thienyl)-propionic acid, since the 2-thenoyl ethene failed to cyclize to the desired ketone.

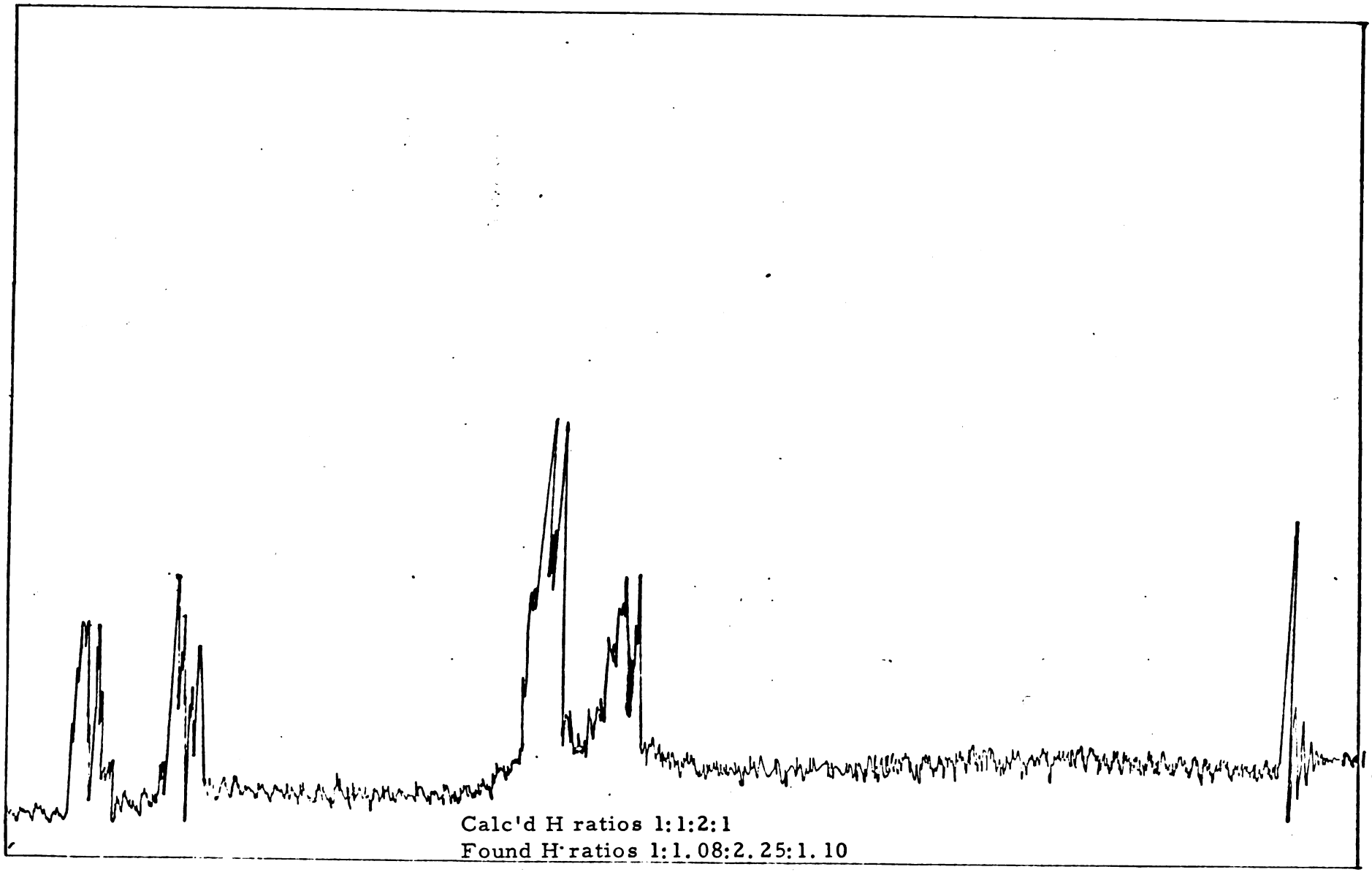
Several substitution reactions were investigated with the bis (5-methylthiaindenyl)iron; however, oxidation or polymerization usually resulted. Attempted formalation via the lithium salt and dimethylformamide produced a mixture of products. It was difficult to obtain n.m.r. data on the heterocyclic metallocene compounds due to their low hydrogen content and relative insolubility.

N. M. R. SPECTRA

A Varian A-60 n.m.r. spectrometer operating at approximately 35° was used to obtain all n.m.r. spectra. Tetramethylsilane was used as an internal reference standard. (τ=10.00)



N.M.R. Spectrum of bis(5-methylthiaindenyl)iron (CS_2 solution) . Sweep width of 500 c.p.s..



Calc'd H ratios 1:1:2:1
Found H ratios 1:1.08:2.25:1.10

τ=3.08 τ=3.63 τ=5.72 τ=6.16 T.M.S.

N.M.R. Spectrum of bisbisaindenyliron (CS_2 solution). Sweep width 500 c.p.s..

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