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THE LITHIUM-AMINE REDUCTION
OF THIANAPHTHENE AND SOME
OF ITS DERIVATIVES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY

Jay P. O'Brien

1962

THESIS

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THE LITHIUM-AMINE REDUCTION
OF THIANAPHTHENE AND SOME
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By

JAY P. O'BRIEN

A THESIS

Submitted to the College of Science and Arts
of Michigan State University of Agriculture
and Applied Science in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

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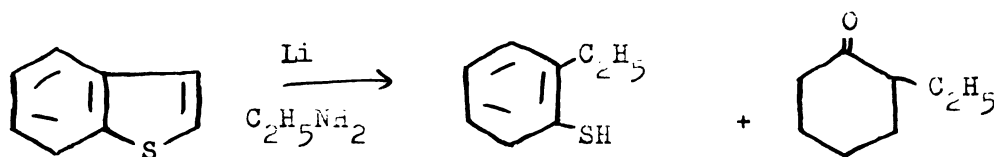
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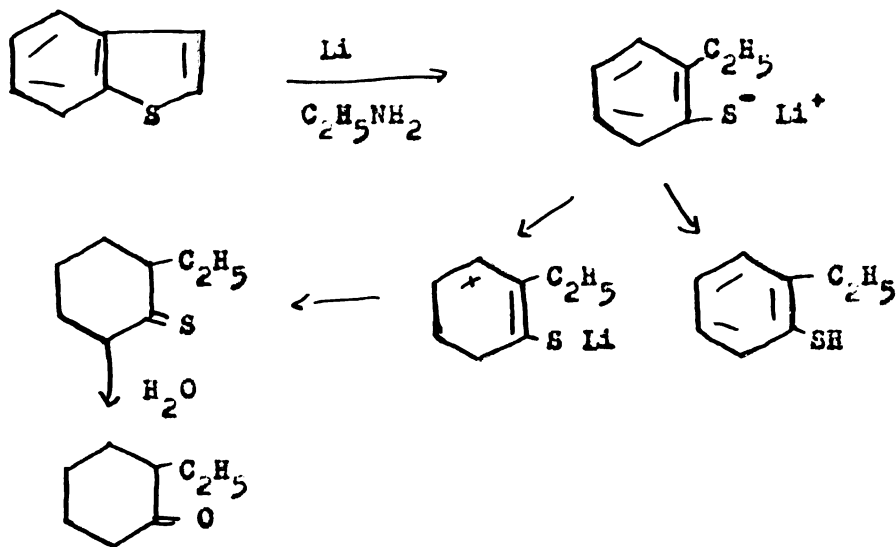
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ABSTRACT

The reduction of thianaphthene using a lithium-aliphatic amine system was investigated as possible synthetic route to partially reduced thianaphthenes. The reduction was found to involve cleavage of the carbon-sulfur bond in the heterocyclic ring to yield o-ethylthiophenol and 2-ethylcyclohexanone, in the case of thianaphthene.



The o-ethylthiophenol was established as an intermediate in the process by its isolation and reduction with lithium-ethylamine to 2-ethylcyclohexanone. Attempts to isolate additional intermediates by using various diluting agents, ethanol, piperidine, and morpholine or by lowering the reaction temperature (-60) and reducing the reacting time (three hours and one hour) only increased the yield of o-ethylthiophenol at the expense of 2-ethylcyclohexanone. These observations suggest the following reasonable mechanism for the reduction.



To alter the nature of the heterocyclic carbon-sulfur bond, methyl groups were placed in various positions in the thianaphthene nucleus. The 2-methyl, 3-methyl and 3,5-dimethyl thianaphthene derivatives were prepared. Each yielded the corresponding mercaptan and ketone by reductive cleavage with the metal-amine system. It was noted that as the +I effect of the ring substituents increased the amount of ketone was decreased very probably due to an increase in the electron density of the benzenoid ring.

The 2-fluorothianaphthene was prepared by fluorinating 2-lithiumthianaphthene with perchloryl fluoride (-10 to 0°). The compound was characterized by nuclear magnetic spectra and analytical data. Reduction of this fluoroheterocyclic yielded

o-ethylthiophenol and 2-ethylcyclohexanone as the sole reduction products in very low yields.

The lithium-amine reduction of the parent heterocyclic, thiophene, yielded a small amount of an unidentified high boiling neutral product which possibly contained a carbonyl group. The acidic fraction was not investigated further due to the extreme odor of the possible product, n-butylmercaptan.

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INTRODUCTION

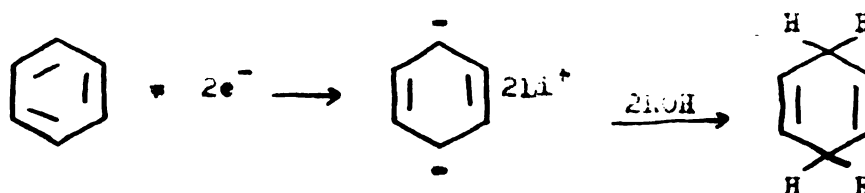
The present investigation was undertaken to determine the effect of the lithium-aliphatic amine reductive system on thianaphthene as a possible synthetic route to partially reduced heterocycles. To alter the nature of the heterocyclic carbon-sulfur bond, methyl substituted thianaphthenes and the 2-fluorothianaphthene were also reduced using the lithium-amine system.

HISTORICAL

The partial reduction of aromatic compounds using metal-liquid ammonia, and alcohol combinations has been known for some time as the Birch reduction. Metals usually employed are the alkaline and alkaline earths.

Liquid ammonia is very similar to the low molecular weight alcohols as a solvent for organic substances. The metals dissolve in the liquid ammonia to give deep blue colored solutions. The alcohol functions as a diluent or cosolvent and alters the solubility and rate of the reaction. In addition to alcohols, ammonium chloride, morpholine, piperidine, tetrahydrofuran, and ether have been used as cosolvents(1).

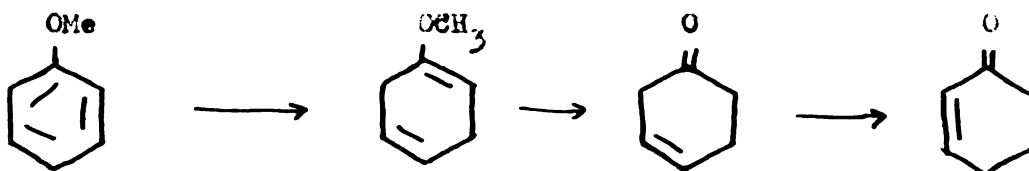
The essential step in the metal ammonia reduction is the addition of the two electrons to the aromatic compound in a stepwise manner. It is rather difficult to determine whether the addition of the first electron or the second is the rate determining step. The negatively charged molecule is associated with positive ions derived from the metal supplying the electrons. The charged specie may possibly be an intermediate. This charged specie then reacts with the cosolvent to pick up two protons and give the partially reduced compound.



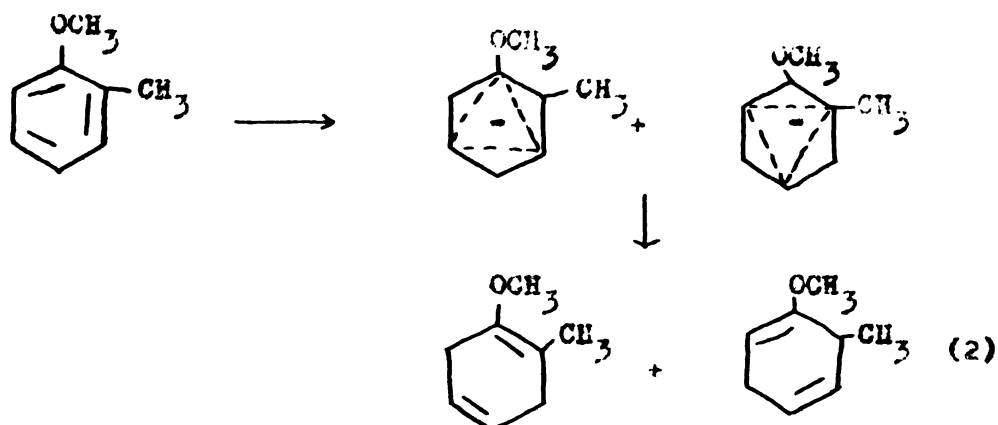
An acidic proton is needed which probably comes from the alcohol. (2)

Such reduction mixtures have been known to cleave aliphatic ethers to alcohols and alkanes. In the cleavage an alkoxide ion and carbanion are formed. If the anions are intermediates then the R group containing the less electron donating groups or more electron attracting groups should appear as the alkane.

The cleavage of anisole with sodium, ammonia, and alcohol leads to a vinyl ether which is cleaved to give a ketone.



Adding two electrons to o-methylanisole will yield two systems; one in which the electron is equally distributed to the 1,3,5 positions and the other to the 2,4,6 positions. The hydrogens will add to the 3 and 5 positions first since these are of greatest electron density. Then hydrogens will add α , β to the 3 and 5 positions giving two isomeric products.



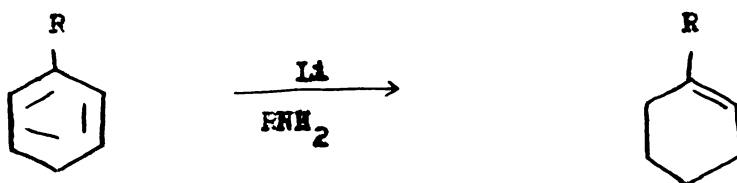
In 1952 Benkeser (3) observed that a certain quantity of lithium was absorbed by an aromatic hydrocarbon and in 1955 (4) he reported the high selectivity of the lithium-amine reduction system. Lithium metal dissolved in low molecular weight amines such as methyl and ethyl amines to give the characteristic deep blue colored solutions. The aromatic systems are reduced to monocyclohexenes by such reducing systems. An organo-lithium intermediate is postulated since a definite ratio of lithium is absorbed per mole of aromatic compound reduced.

Other amines which have successfully been used in these reductions include *n*-propyl, isopropyl, and *n*-butyl. However, due to the solubility of lithium metal decreasing in these amines as the molecular weight of the amines increase, the reduction was slower and a mixture of intermediate products were isolated.

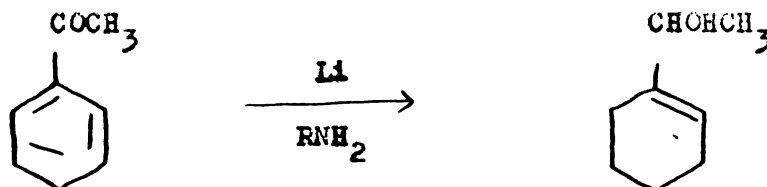
The difference between the lithium-amine and sodium-ammonia systems is considerable. Anisole when reduced with lithium, methylamine, and ethanol as solvent yields 95% of 3,4-dihydro-

anisole while sodium, ammonia, and ethanol yields the fission product α, β -cyclohexenone. However, use of just a lithium and ethyl-amine results in a mixture of cyclohexanol and cyclohexanone. (4) Biphenyl yields cyclohexylbenzene on reduction with sodium and ammonia while a 49% yield of 1-cyclohexylcyclohexene is obtained with lithium and methylamine, and a 92% yield of 1-cyclohexylcyclohexene is observed using morpholine as a cosolvent. Naphthalene when reduced with lithium and ammonia gives only tetralin, but with lithium and ethylamine a 90% yield of $\Delta^{9,10}$ octalin and 10% $\Delta^{9,1}$ octalin is observed (4).

Benkeser (5) reduced a series of mono alkyl substituted benzenes using the lithium-amine system. Using methyl, ethyl, isopropyl, and t-butyl benzenes he found that the most stable olefin was formed in all cases. However as the bulk of the alkyl group and its +I effect increased the yield of reduction product decreased.

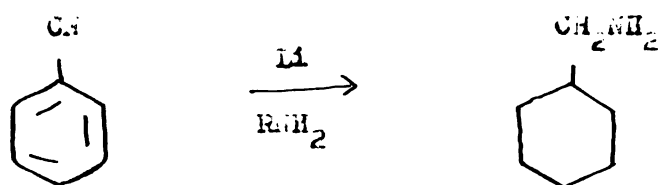


The same reduction system was found to reduce phenyl ketones to cyclohexenyl alcohols.

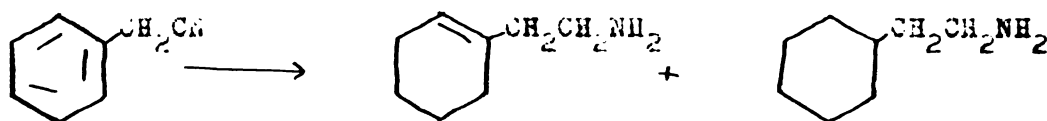


Phenol is reduced with the lithium-amine system in yields of 96% of cyclohexanone using only a slight excess of lithium and rapid hydrolysis. The mechanism is probably reduction of the aromatic ring to a cyclic monolefin, vinyl alcohol, which tautomerizes to the ketone. Using a very large excess of lithium a mixture of cyclohexanol and cyclohexanone is obtained (4).

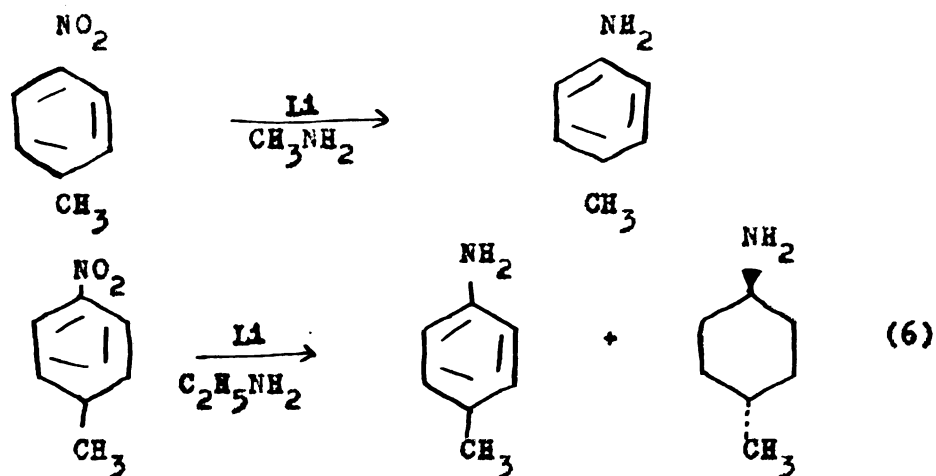
Aromatic nitriles are reduced to a saturated amine using the lithium-amine system.



47%
Benzonitrile is the only case, as yet, in which a monolefin was not produced. This may possibly be due to the electron withdrawing effect of the nitrile which reduced the electron density in the aromatic ring, thus, favoring complete reduction. The monolefin if produced could polymerize and account for the tarry by-products. However, if the nitrile group is removed from the ring by a single carbon a monolefin is produced.



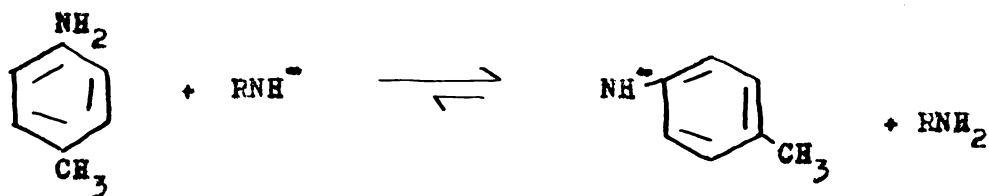
Nitrobenzenes when reduced with lithium and methylamine yield anilines. However, with ethylamine a mixture of anilines and cyclohexyl amines are formed.



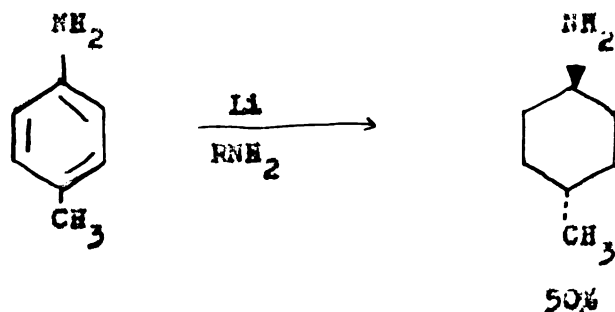
The failure of the ring to undergo further reduction is due to the fact that when the nitro group is reduced there is an increasing amount of, $\text{RNH}^- \text{Li}^+$, anide ions being formed which are in equilibrium with the anilide ions,



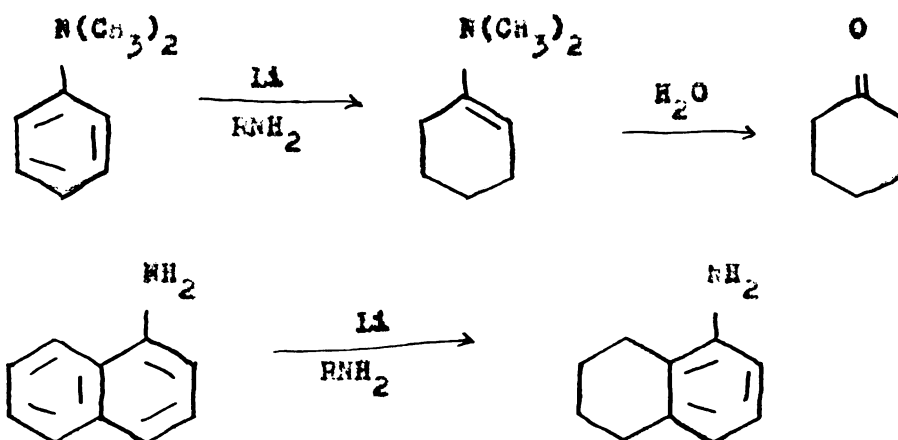
Since the anide ion is a stronger base than the anilide ion, the equilibrium will lie to the right.



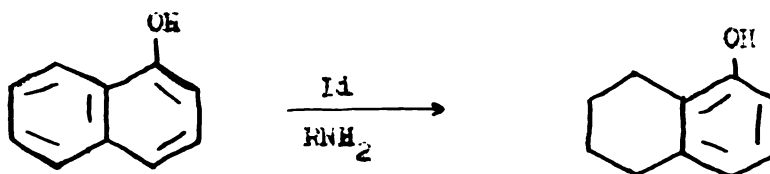
Formation of the anilide ion is analogous to the case of benzyl alcohol which is reduced to toluene while the salt of the alcohol is not, due to the development of a negative charge on the oxygen in a basic media. The amine alone is reduced to cyclohexylamine,



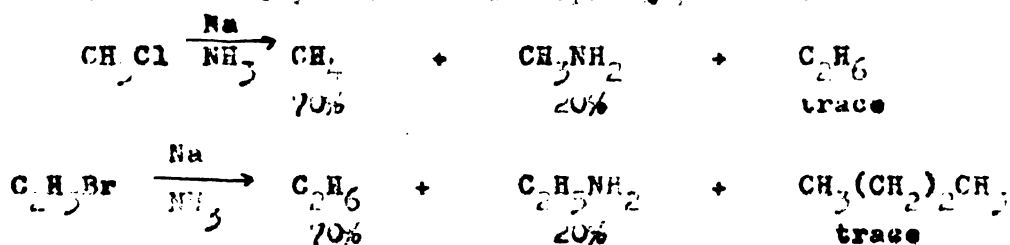
since there is no alkyl amide ions formed initially. However, as amide ions are formed the reduction stops, accounting for the low yield of reduction product. N,N -dimethylaniline, however, is reduced to cyclohexanone which can be explained by the formation of a vinyl amine and its hydrolysis to the vinyl alcohol followed by tautomeric rearrangement to the ketone (7).



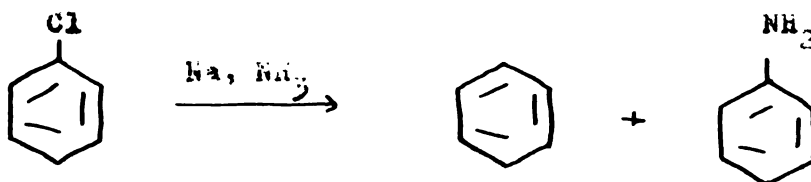
Thus, it is clear that the formation of a negative charge on a group attached to an aromatic ring will inhibit reduction of the ring by the lithium-amine combination.



The reduction of the alkyl halides with sodium and ammonia yields primarily the hydrocarbon, in addition to some amine and the expected Wurtz coupling product.



The reduction of aromatic halides likewise gives the hydrocarbon and the corresponding amine. The amine being produced by a benzyne intermediate (6).

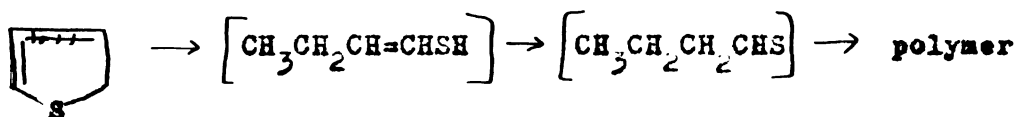


Organic sulfur compounds are extremely difficult to reduce with hydrogen and a platinum or palladium catalyst due to the poisoning effect of sulfur on these catalysts. Thiophene has been reduced (9) to tetrahydrothiophene using molybdenum sulfide as the catalyst. Butane, hydrogen sulfide and n-butylmercaptan were also isolated from the hydrogenation products. Using a large excess of palladium catalyst, the reductive hydrogenation of thiophene yielded only tetrahydrothiophene. In 1951 Birch and McAllan (10) treated thiophene with a

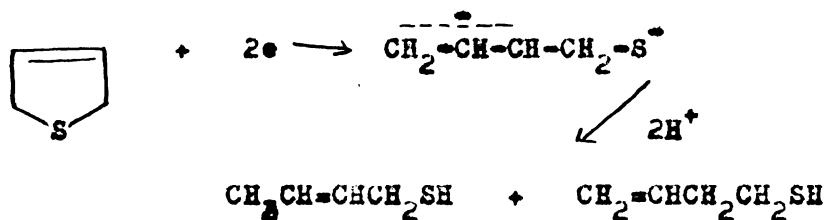
sodium, ammonia, alcohol mixture yielded 40% of a mixture of the 2,3 and 2,5 dihydrothiophene.



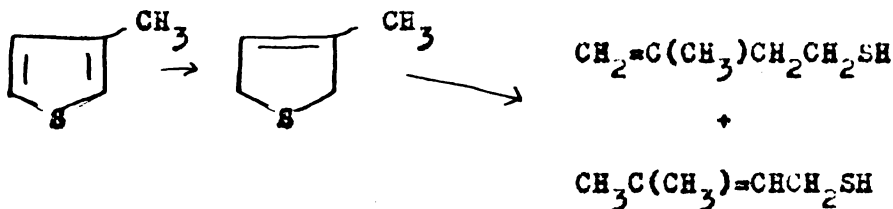
The 2,3 dihydro compound was very susceptible to polymerization. Upon further reduction of the 2,3 dihydro compound only polymeric material was obtained, which can be explained by the following mechanism assuming ring cleavage.



The 2,5-dihydrothiophene on further reduction was converted to a mixture of unsaturated mercaptans.

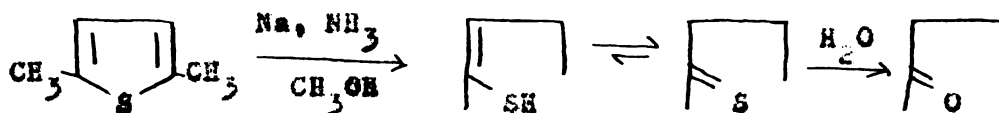


In 1951 Birch (11) also reduced 3-methylthiophene to 3-methyl-2,5-dihydrothiophene which could be further reduced to a mixture of unsaturated mercaptans.



The reduction of 2,5-dimethylthiophene using sodium, ammonia,

and methanol yielded only 2-hexanone, probably by hydrolysis of the intermediate thioketone.

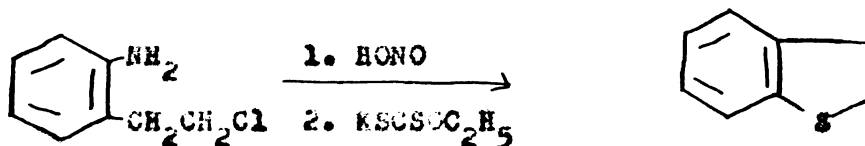


Using just sodium and ammonia or sodium and ethanol, n-butyl mercaptan is the sole product.

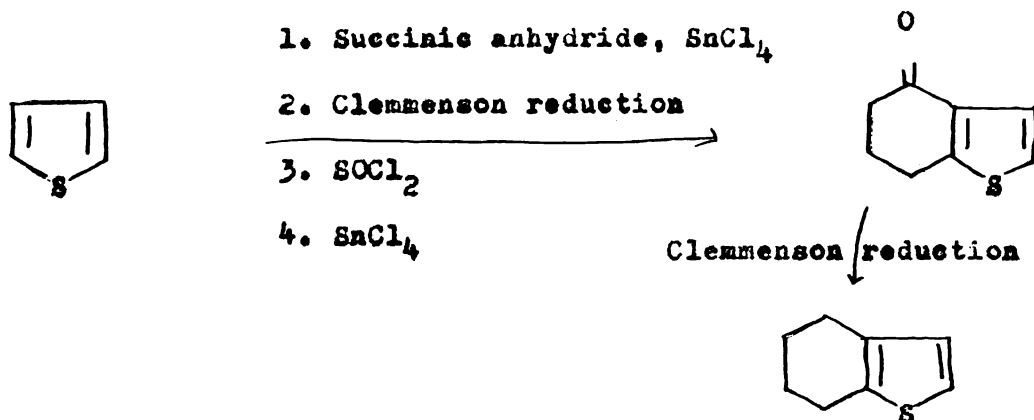
There is a single reduction system that will reduce thianaphthene to a partially reduced compound. Fricke and Spilker in 1925 (12) reduced thianaphthene with sodium and alcohol to obtain 2,3-dihydrothianaphthene and o-ethylthiophenol.

A Raney Nickel reduction in methanol will desulfurize thianaphthene to ethylbenzene (75%). Fricke and Spilker also reduced thianaphthene with hydrogen (11 atm., 438°) in the absence of a catalyst to obtain a mixture of products, o-ethylthiophenol, toluene, ethylbenzene, and benzene.

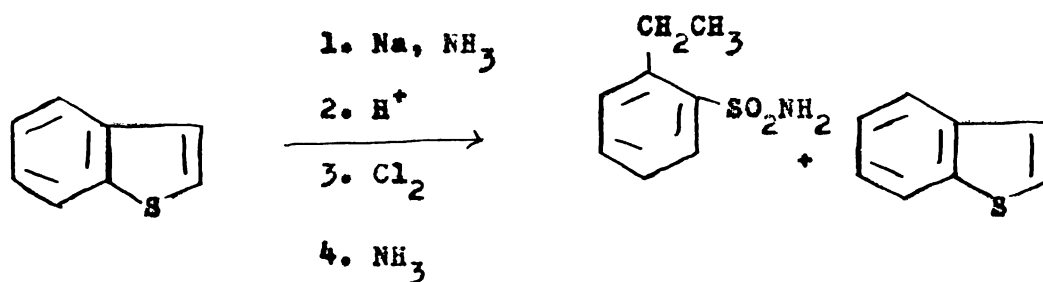
The 2,3-dihydrothianaphthene has also been prepared (13) by a ring closure procedure using o-amino-2-chloroethylbenzene; the amine following diazotization was treated with potassium ethyl xanthate.



The only other partially reduced thianaphthene reported was 4,5,6,7-tetrahydrothianaphthene. Its synthesis started with thiophene. (14, 15)



In 1959 (16) thianaphthene was reduced with sodium and ammonia, treated first with chlorine, then with acetic acid, and finally with ammonia to convert the reduction product, a mercaptan, to a sulfonamide. In addition to the sulfonamide, unreduced thianaphthene was also recovered.

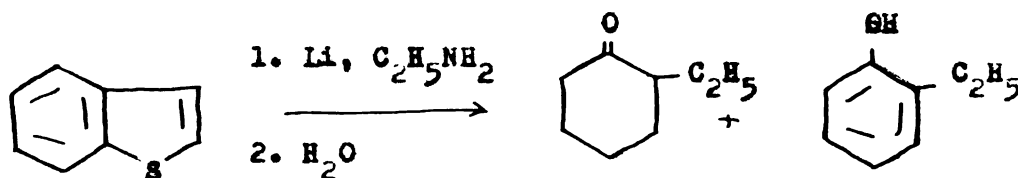


The 5-methyl derivative of thianaphthene was also reduced and yielded as the only reduction product reported, 2-ethyl-4-methylthiophenyl.

DISCUSSION

The reduction of thianaphthene using the lithium-ethylamine system of Benkeser was (5) investigated to determine whether this procedure was applicable to the synthesis of partially reduced thianaphthenes, and in particular to obtaining those not previously described. However, in every case studied, during the course of this work, one of the carbon-sulfur bonds underwent fission.

Due to the increased reducing power of the lithium-ethylamine system over the sodium-ammonia one, reduction of the benzenoid ring was also accomplished. The reduction of thianaphthene when treated with lithium-ethylamine for ten hours at room temperature gave two fractions. The neutral fraction was identified as 2-ethylcyclohexanone, being obtained in 47.5% yield. Acidification of the aqueous phase of the reaction mixture with concentrated sulfuric acid yielded 29% of o-ethylthiophenol.

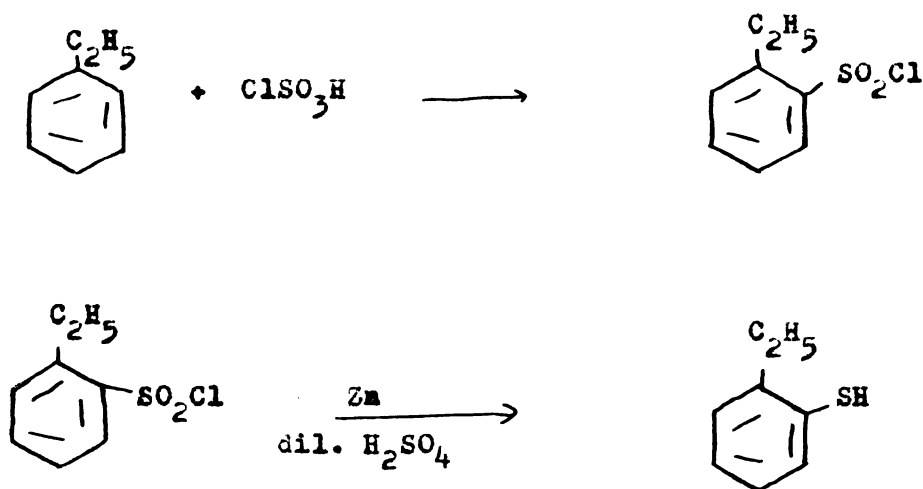


No unreduced thianaphthene was obtained.

The identity of the ketone was established by preparation of its known semicarbazide derivative. The cyclic ketone was also reduced with Raney Nickel in methanol to the corresponding

known alcohol. The o-ethylthiophenol identity was established by converting it to its known lead salt derivative and also by desulfurizing the mercaptan with Raney Nickel in methanol to obtain ethylbenzene.

It was shown that one of the intermediates in the reduction of thianaphthene is the mercaptan, o-ethylthiophenol, which then could be reduced to the corresponding mercaptan followed by its hydrolysis to yield the ketone. The o-ethylthiophenol was synthesized by an unequivocal method involving the chlorosulfonation of ethylbenzene with chlorosulfonic acid, and reduction of the acid chloride to the mercaptan with zinc and dilute sulfuric acid.

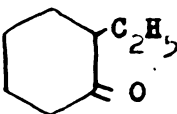
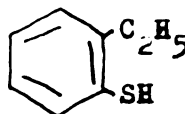


The mercaptan, o-ethylthiophenol, was then reduced to 2-ethylcyclohexanone with lithium-ethylamine in a 15.9% yield.

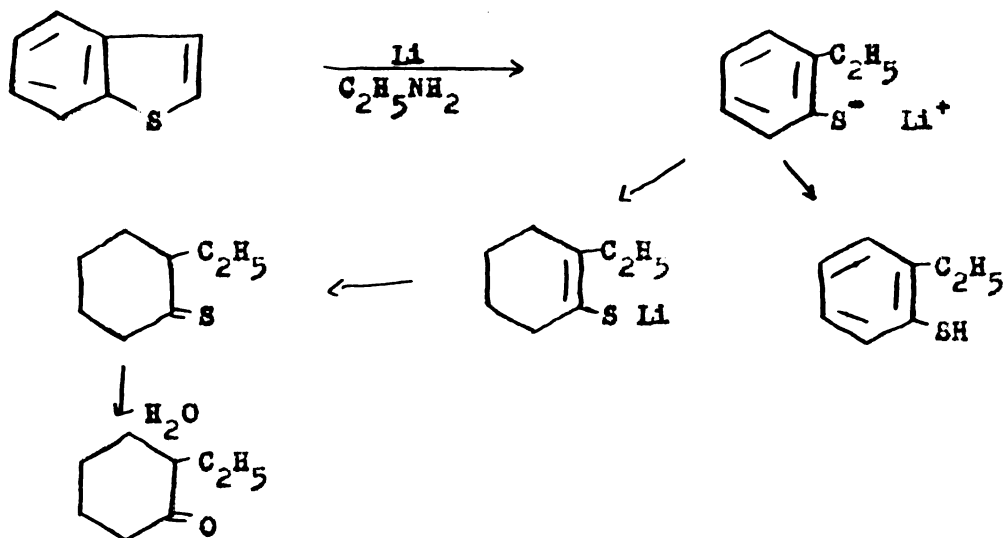
Attempts to isolate additional intermediates in the reduction of thianaphthene by adding various diluting reagents, ethanol, morpholine, and piperidine only decreased the yield of ketone and increased the yield of mercaptan (Table I). The thianaphthene reduction was also conducted at a lower temperature (-60) and the reaction time was reduced to periods

TABLE I

Reduction of Thianaphthene with the Lithium-Ethylamine
System and the Effects of Various Cosolvents
on the Reduction

Reaction		Yield %	
Cosolvents	Time hr.		
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none	8	47.5	29.0
C ₂ H ₅ OH	3	20.0	78.0
N(CH ₂) ₅	3	trace	59.5
O(CH ₂) ₄ N	3	41.5	54.0

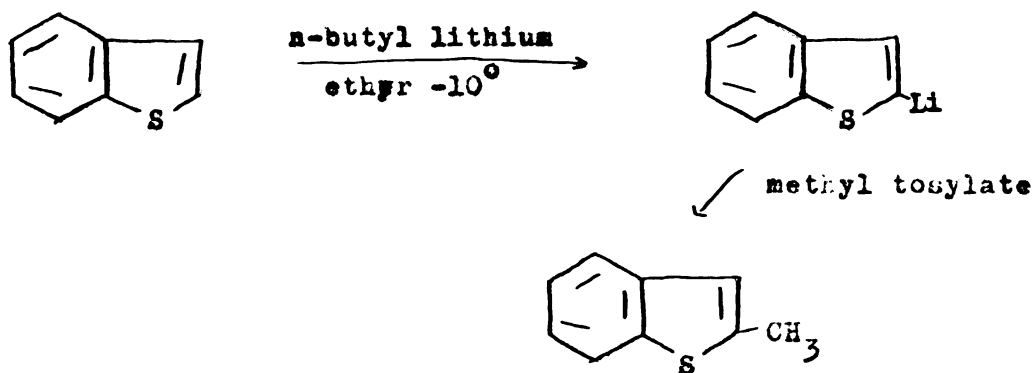
of three hours and one hour. In each case o-ethylthiophenol was the only major product isolated. A trace of impure 2-ethylcyclohexanone was also isolated. The reasonable mechanism, based on these observations, for the lithium-amine reduction of the sulfur heterocyclic can be suggested.



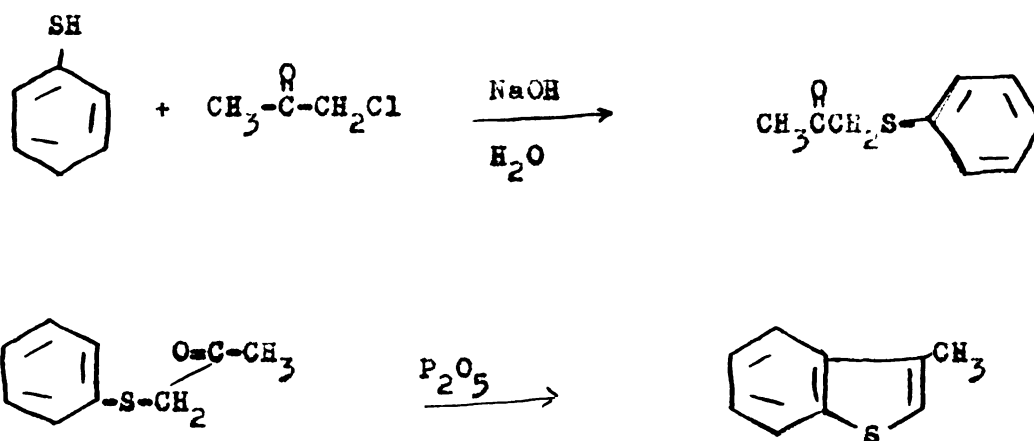
The negative charge associated with the mercaptan sulfur would probably increase the electron density of the ring, similarly to the case of the anilide ion in the reduction of nitrobenzene (?). Such an increase in the electron density would probably prohibit complete reduction to the thioenolate anion.

In an effort to increase the strength of the carbon-sulfur bond an electron donating group, methyl, was substituted in the various positions of the thianaphthene nucleus.

The 2-methylthianaphthene was obtained following the procedure of Heyd (18).



The isomeric 3-methylthianaphthene was prepared by a ring closure reaction of acetyl phenyl sulfide with phosphorous pentoxide.



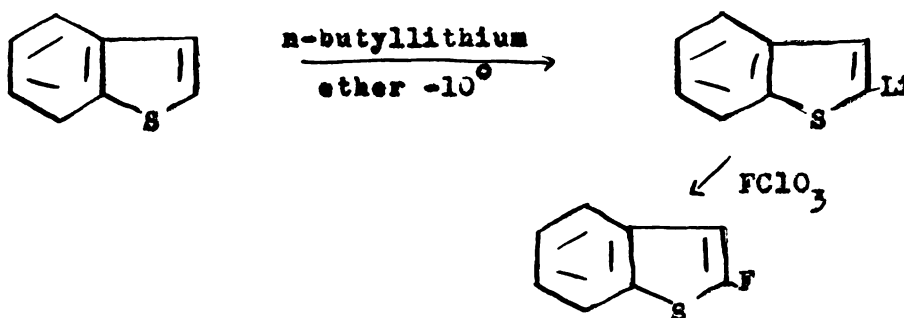
The dialkylthianaphthene, 3,5-dimethylthianaphthene, was synthesized employing the above procedure and using p-methylthiophenol as the initial starting material.

The three alkyl derivatives of thianaphthene were subjected to the reduction procedure, of treatment with lithium-amine,

identical to the reduction procedure of thianaphthene itself. The results are summarized in Table II.

Examination of this data indicates clearly that there is a decrease in the yield of the ketone as the +I effect or the number of electron donating groups present on the arene nucleus increases. Such a result can be accounted for the fact that as the +I effect increases, the electron density of the ring is increased, which in turn makes it more difficult to reduce the ring.

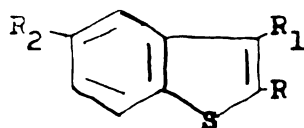
The effect of an electron withdrawing group on the carbon-sulfur bond was studied. The 2-Fluorothianaphthene was synthesized by the direct fluorination of 2-lithiumthianaphthene with perchloroyl fluoride. This new procedure for the introduction of fluorine into arenes and in particular into heterocyclic systems was developed partially during the course of the present investigation.



Due to the similarity of the boiling point and refractive index of the 2-fluorothianaphthene, an organic qualitative test for fluorine was attempted on this material using zirconium-alizarin test paper. (26). This failed to give a

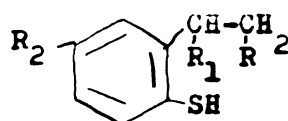
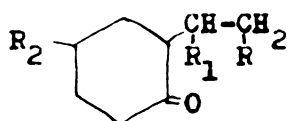
TABLE II

Reduction of Alkyl Substituted Thianaphthenes



Yield %

Substituent

 $R = \text{CH}_3$

53.0

33.0

 $R_1 = R_2 = \text{H}$ $R = R_2 = \text{H}$

17.5

60.5

 $R_1 = \text{CH}_3$ $R = \text{H}$

9.0

39.0

 $R_1 = R_2 = \text{CH}_3$

positive result. The infra-red spectra of thianaphthene and 2-fluorothianaphthene were determined and are shown in figures I and II respectively. The spectra are similar but not identical. The nuclear magnetic resonance spectra of thianaphthene and its 2-fluoro derivative were also determined and are shown in Figures III and IV. Integration of the areas under the two sets of peaks of thianaphthene are, 2 to 1, for the four benzenoid hydrogens and the two thiophene hydrogens respectively. The integration of the areas under the two sets of peaks of the 2-fluorothianaphthene were, 4 to 1, for the four benzenoid hydrogens and single thiophene hydrogen respectively. The single hydrogen on the thiophene ring of 2-fluorothianaphthene is split into a doublet by the fluorine.

The negative qualitative fluorine test was possibly due to the difficulty in breaking the carbon-fluorine bond to yield sodium fluoride, and may also be due to the small amount of fluorine present in the compound. The quantitative halogen analysis for the mono-fluorinated thianaphthene was in agreement with the theoretical amount.

The 2-fluorothianaphthene was reduced in the lithium-alum procedure identical to the reaction of the parent thianaphthene. The reduction products obtained were identical to those isolated in the reduction of thianaphthene. However, the yields of the reduced products obtained were extremely low; 7.6% for 2-ethylchloronaphene and 11.9% for o-ethylthiophenol. These were the only organic compounds isolated from the reduction mixture. The infra-red spectra, nuclear magnetic resonance spectra,

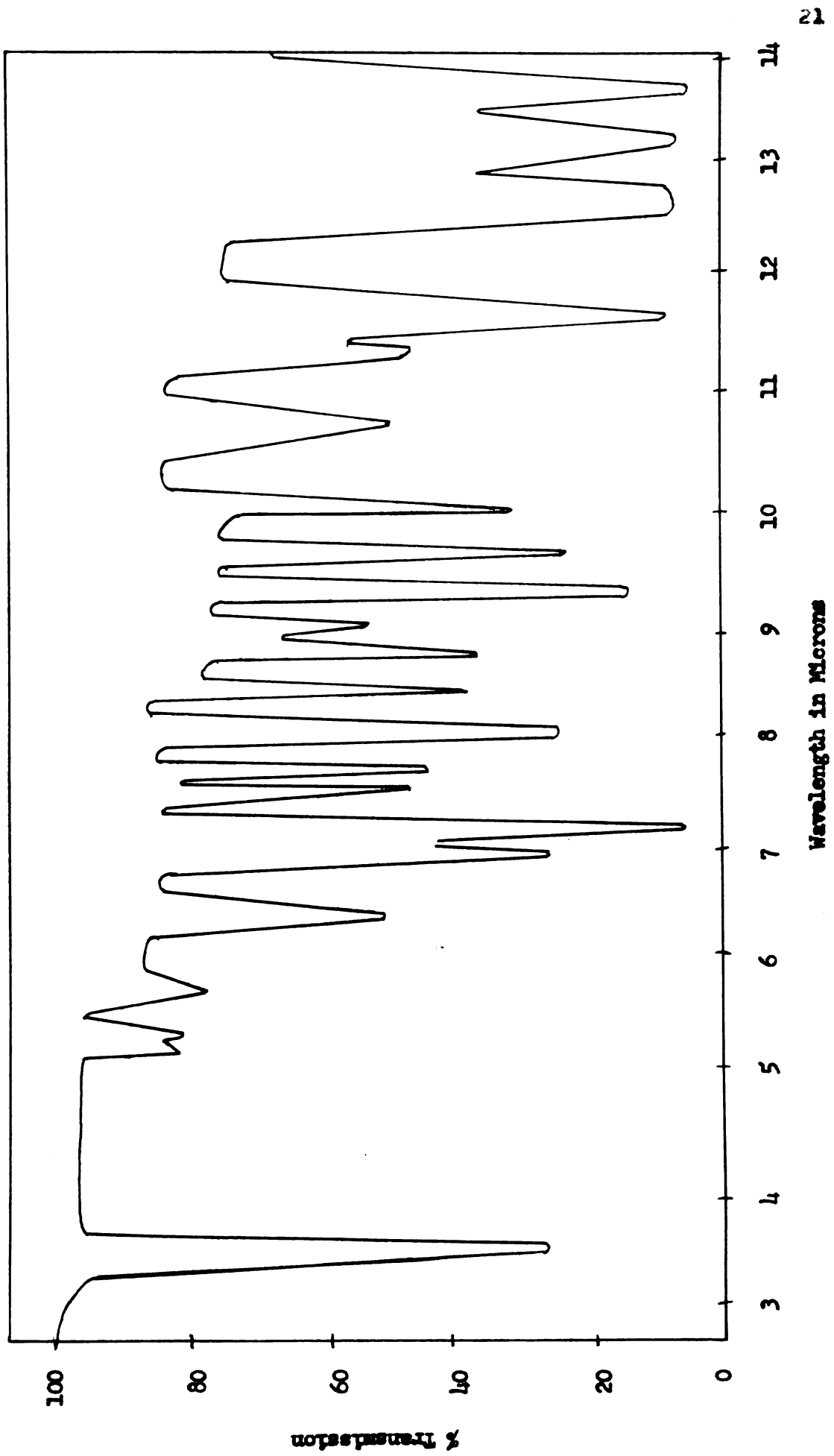


Fig. I Infra-red Spectra of Thianaphthene (neat)

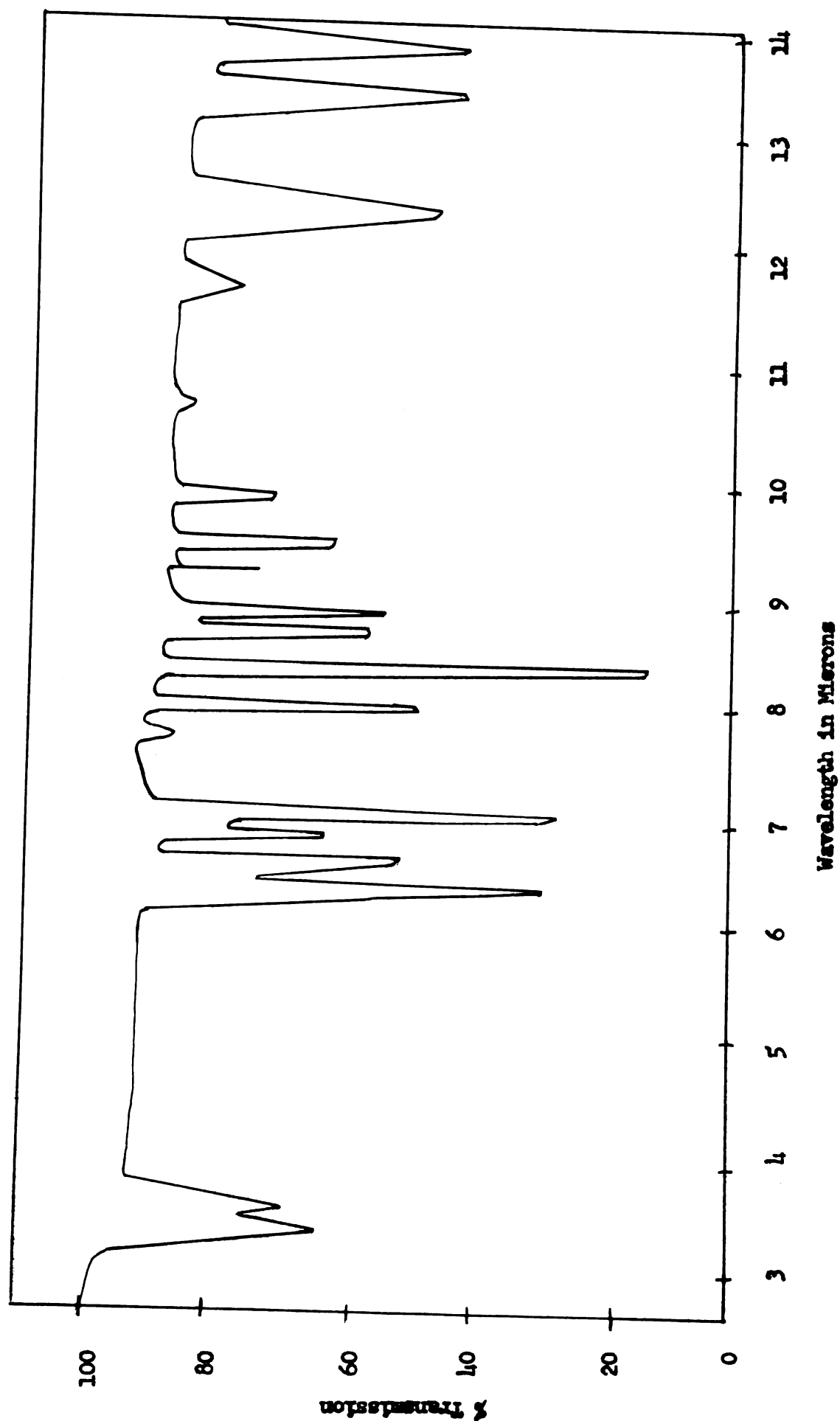
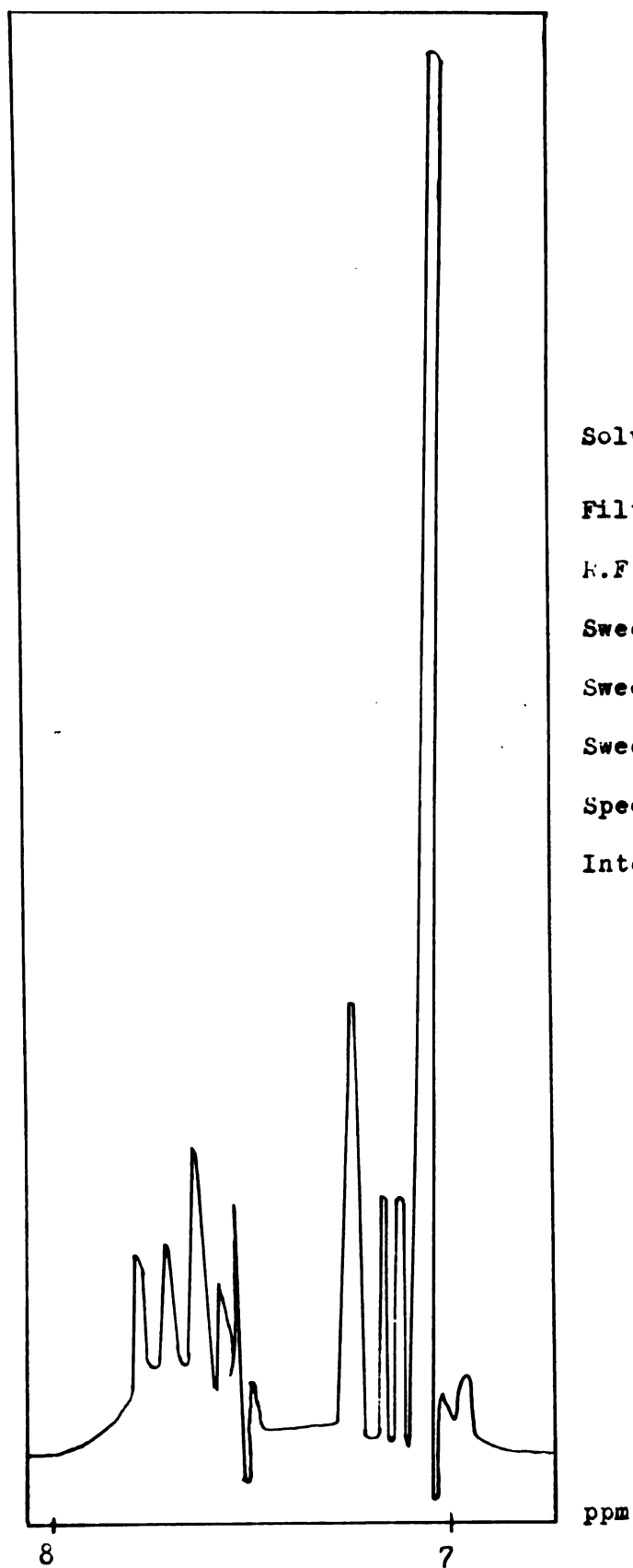


Fig. II Infra-red Spectra of 2-Fluorothiaphene (neat)



Solvent: CCl_4

Filter Bandwidth: 4 c.p.s.

R.F. Field: 0.03mG.

Sweep Time: 250 sec.

Sweep Width: 500 c.p.s.

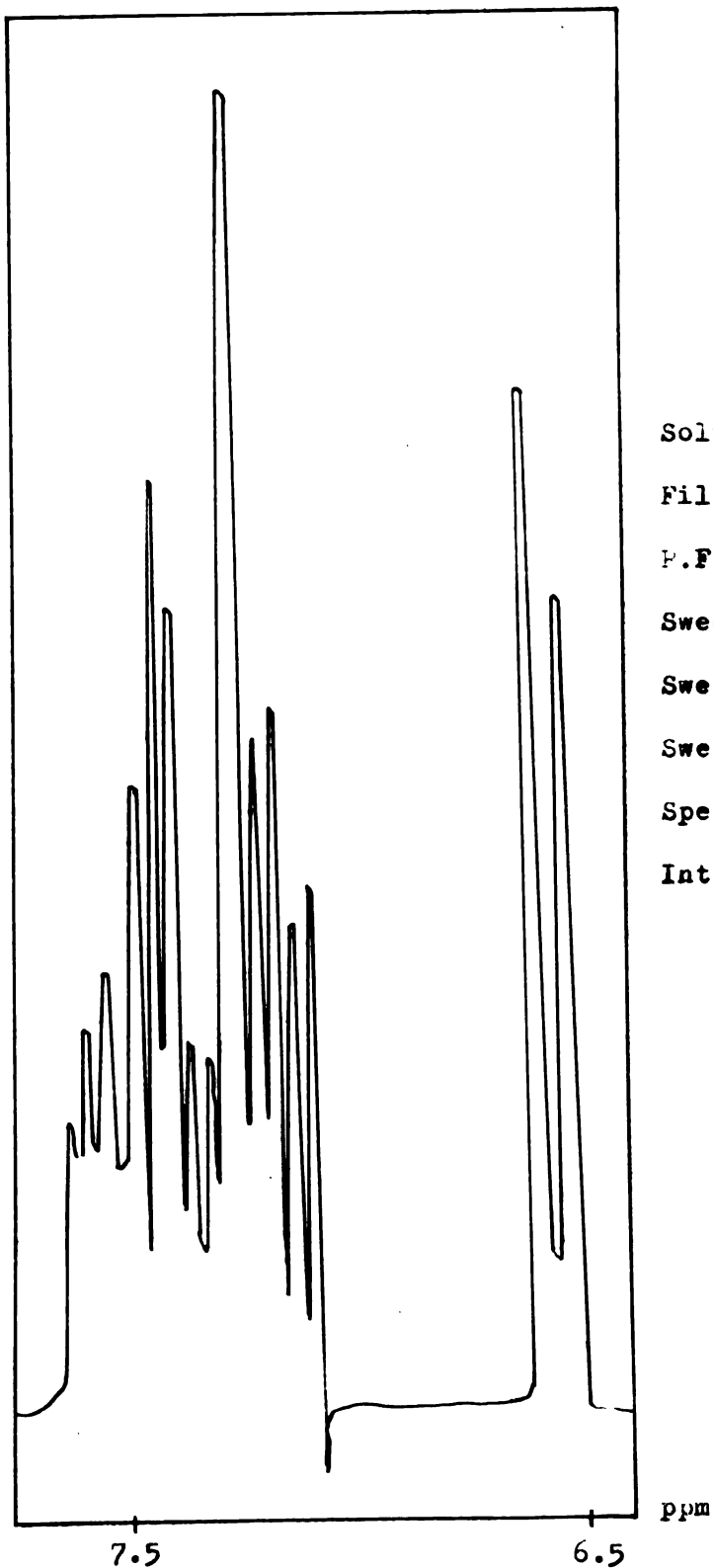
Sweep Offset: 0.000

Spectrum Amp.: 1.0

Internal Reference: $\text{Si}(\text{CH}_3)_4$

Fig. III Nuclear Magnetic Resonance

Spectra of Thianaphthene



Solvent: CCl_4

Filter Bandwidth: 2 c.p.s.

P.F. Field: 0.05mG.

Sweep Time: 250 sec.

Sweep Width: 500 c.p.s.

Sweep Offset: 0.000

Spectrum Amp.: 8.0

Internal Reference: $\text{Si}(\text{CH}_3)_4$

Fig. IV Nuclear Magnetic Resonance

Spectra of 2-Fluorothianaphthene

and the retention times of the vapor phase chromatography of the reduction products obtained from 2-fluorothianaphthene were identical to the products of the thianaphthene reduction. No unreduced 2-fluorothianaphthene was recovered from the reduction media nor was any acine from a possible benzyne intermediates observed to be present in the reduction products.

The reduction of thiophene using lithium-ethylamine yielded a small amount of a neutral product which could not be obtained in a sufficient degree of purity for proper identification. An infra-red spectra of the crude product indicated the possibility of a carbonyl group (5.85μ), which could be accounted for if ring opening had occurred giving rise to a thioaldehyde which on hydrolysis would yield an aldehyde. The acidic fraction obtained on acidification of the reduction product was not investigated further due to the extreme odor of the possible product, n-butylmercaptan.

EXPERIMENTAL

Reduction of Thianaphthene

To a 500 ml. three neck flask equipped with a mechanical stirrer, dropping funnel, dry ice condenser fitted with a calcium chloride drying tube, and a nitrogen inlet tube was added 250 ml. of ethylamine (which had been predried over sodium hydroxide pellets) and 8.3 g. (1.2 g. at.) of lithium chips. To the dark blue colored solution, kept at 0°, was added dropwise 13.4 g. (0.10 mole) of thianaphthene during a period of an hour. The reaction mixture underwent a color change from blue to tan to pale green, during a reaction period of eight hours. At this point unreacted pieces of lithium were removed from the reduction mixture with forceps. Decomposition of the amine was accomplished by cautiously adding ammonium chloride, until the solution became colorless. The reaction mixture was then set aside overnight to permit evaporation of the solvent.

The flask containing the solid residue was cooled in an ice-water bath and water was added dropwise until the solid dissolved. The aqueous solution was extracted three times with 100 ml. of ether. The combined ether extracts were washed with 100 ml. of water, dried over anhydrous magnesium sulfate, treated with Norit and filtered. The dried solution was concentrated on a steam bath, and the residue was fractionated

through a six inch Vigreux column, b.p., 75-77°/25mm.,
 180-184°/760mm., $n_D^{26.5} = 1.4520$, yield 6.0 g. (0.048 mole; 47.5%).
 The reported boiling point of 2-ethylcyclohexanone is
 182-183°/760 mm. and $n_D^{16} = 1.4528$ (20).

To the stirred aqueous fraction, after cooling it in an
 ice-water bath, was added dropwise 30 ml. concentrated sulfuric
 acid. The acidic solution was extracted three times with ether,
 and the ether extracts were combined, washed with 100 ml.
 of water, dried over anhydrous magnesium sulfate, treated
 with Norit, filtered, and concentrated on a steam bath.
 The residue was fractionated using a six inch Vigreux
 column, b.p., 90°/25mm., $n_D^{26} = 1.5654$. The yield was
 4 g. (0.029 mole; 29%). The literature values reported for
 o-ethylthiophenol are b.p., 210/760 mm. and $n_D^{20} = 1.5700$ (17).

The Reduction of Thianaphthene with Various Diluting Reagents

The general experimental apparatus used was the same
 as that described in the previous reduction reaction.
 To 160 ml. of ethylamine, predried over sodium hydroxide
 pellets, was added a solution containing 9.0 g. (0.067 mole)
 of thianaphthene dissolved in 20 ml. of 95% ethanol. A 7.0 g.
 (1.0 g. at.) quantity of lithium chips was added piece by
 piece to the later solution during a period of an hour.
 When all the lithium had been added the reaction mixture had
 taken on a blue coloration. This persisted for an hour and
 a half after which it changed to a dark grey. At this
 juncture 100 ml. of water was cautiously and slowly added
 to the reduction mixture. Additional water was then added

to dissolve the remaining solids. The resulting pale green colored solution was extracted with ether and the product was isolated in the manner described above. The residue was distilled using a six inch Vigreux column, to obtain 1.7 g. (0.013 mole; 20%) of a colorless product boiling at $180^{\circ}/760\text{mm.}$ and $n_D^{24} = 1.4530$.

The aqueous fraction was acidified and isolation of the organic product was accomplished in a manner identical to that described above, to obtain a colorless product boiling from $91-92^{\circ}/25\text{mm.}$ and $n_D^{23.5} = 1.5682$, yield of 7.2 g. (0.052 mole; 78%).

To 160 ml. of ethylamine, predried over sodium hydroxide, was added a solution containing 9.0 g. (0.067 mole) of thianaphthene dissolved in 20 ml. of morpholine. To this solution was added slowly 7.0 g. (1.0 g.at.) of lithium piece by piece during a period of an hour. Product isolation was conducted in a manner identical to that described above. The basic extract gave a product with the following properties; b.p. $74^{\circ}/25\text{mm.}$, $n_D^{22} = 1.4562$; yield 3.5 g. (0.028 mole). The acid extract gave a second product with these properties, b.p. $89/20\text{mm.}$, $n_D^{23} = 1.5685$, yield 5.0 g. (0.036 mole; 54%).

The above experiment was repeated substituting 20 ml. of piperidine for the morpholine. The basic extract gave only a trace of oil which was not obtained in sufficient quantity to distill. The acid extract yielded 5.5 g. (0.039 mole; 59.5%) of a product having a boiling point of $95^{\circ}/25\text{mm.}$ and $n_D^{24} = 1.5682$.

Proof of Structure of 2-ethyleyclohexanone

Reduction of the Ketone Group

To 25 g. of Raney Nickel suspended in methanol was added 4.35 g. (0.035 mole) of the ketone dissolved in methanol. The total volume of the reaction solution was 250 ml. This was allowed to reflux for three hours, cooled and the catalyst was removed by filtration and washed with methanol. The methanol solution was diluted with a liter of distilled water and extracted three times with 100 ml. of chloroform. The chloroform extracts were combined, dried over anhydrous calcium chloride, filtered, and concentrated on a steam bath. The residue was distilled using a six inch Vigreux column to obtain a product boiling at $180^{\circ}/760\text{mm.}$ and $n_D^{26} = 1.4642$, and yield 4.3 g. (0.034 mole; 96%). The literature values reported for 2-ethyleyclohexanol are b.p. $79^{\circ}/12\text{mm.}$ and $n_D^{21} = 1.4640$ (24).

Preparation of the Semicarbazone

The derivative was prepared by dissolving 0.2 g. (0.002 mole) of semicarbaside hydrochloride and 0.3 g. (0.004 mole) of sodium acetate in a few drops of water. To the solution was added 0.2 g. (0.002 mole) of the ketone. Ethanol (95%) was added until the solution became clear, after which it was heated on a steam bath for 15 minutes, cooled, and filtered to obtain the crystalline product. The dried crystalline material was recrystallized

from a small amount of ethyl acetate. The product melted at 180° (uncorr.). The literature value reported for the melting point of this material is 157° (20).

Proof of Structure of o-ethylthiophenol

To a saturated solution of lead acetate in ethanol (95%) was added 0.5 ml. of the mercaptan. A characteristic yellow colored lead salt precipitated instantaneously. After three recrystallizations from ethyl acetate a sharp melting point of $147-148^{\circ}$ (uncorr.) was obtained. The melting point reported in the literature for this material is 147.5° (21).

An attempt to prepare a 2,4-dinitrophenylsulfide derivative of this mercaptan was unsuccessful.

An Attempt to Desulfurize the Mercaptan

To 10.0 g. (0.0725 mole) of the mercaptan was added 11.62 g. (0.0694 mole) of freshly redistilled triethyl phosphite. The reaction mixture was set aside at room temperature for a day and then slowly distilled. Two fractions were obtained; (a) b.p. $57^{\circ}/25\text{mm.}$, $n_D^{25} = 1.4128$; literature values for triethyl phosphite, b.p. $155^{\circ}/760\text{mm.}$, $n_D^{25} = 1.4115$ (22) and (b) b.p. $93-94^{\circ}/25\text{mm.}$, $n_D^{25} = 1.5692$; literature values for o-ethylthiophenol b.p. $210/760\text{mm.}$, $n_D^{20} = 1.5700$ (17).

To 25 g. of Raney Nickel suspended in methanol was added 4.4 g. (0.031 mole) of the mercaptan dissolved in methanol. The total volume of the reaction mixture was 300 ml. It was heated at its reflux temperature for three hours, cooled and the catalyst was removed by filtration and washed with methanol. The methanol solution was diluted with a liter of distilled water and extracted with three 100 ml. portions of chloroform. The chloroform extracts were combined, dried with anhydrous calcium chloride, filtered, and concentrated on a steam bath. The residue was distilled using a six inch Vigreux column, to obtain a product boiling at $35-37^{\circ}$ /25mm. and $n_D^{27} = 1.4930$, and yield 2.8 g. (0.026 mole; 85%). The literature values for ethyl benzene are b.p. $134-136^{\circ}$ /760mm., $n_D^{14.5} = 1.49828$ (28).

Preparation of o-ethylthiophenol

To 192.5 g. (1.65 moles) of well stirred chlorosulfonic acid, precooled to zero degrees in a dry ice-acetone bath, was added 54 g. (0.51 mole) of ethylbenzene during a period of 45 minutes, while holding the temperature of the acid between -5 and 0° . Following the addition of acid the reaction mixture was set aside in a refrigerator for 18 hours at 0° . The product was then poured with vigorous stirring onto 700 ml. of crushed ice and the oily layer was separated.

In a two liter three neck flask equipped with a mechanical stirrer, thermometer, condenser, and dropping

funnel was placed 1000 ml. of crushed ice and 325 ml. of concentrated sulfuric acid. The acid mixture was cooled in a dry ice-acetone bath to 0° . The sulfonyl chloride product from the above chlorosulfonation was added by means of a dropping funnel into the rapidly stirred acid mixture followed by addition of 163 g. (2.5 moles) of zinc. Following the addition of the zinc the mixture was allowed to warm to room temperature and then heated at its reflux temperature for five hours. It was then cooled, filtered, and the solid washed with ether. The filtrate was extracted three times with 100 ml. portions of ether. These were combined, dried with anhydrous magnesium sulfate, filtered, and concentrated on a steam bath. The residue was distilled using a six inch Vigreux column, to obtain a product, b.p. $95-96^{\circ}/25\text{mm.}$, $n_D^{28} = 1.5628$ in a yield of 54.2 g. (0.392 mole; 76.5%). The literature values for o-ethylthiophenol are b.p. $210/760\text{mm.}$, $n_D^{20} = 1.5700$. (17).

Proof of an Intermediate in the Reduction

Reduction of o-ethylthiophenol

The general experimental approach was the same as that utilized in the reduction involving thianaphthene. To 250 ml. of ethylamine, predried over sodium hydroxide, was added 7.25 g. (1.05 g. at.) of lithium metal chips. To the dark blue colored solution, externally cooled,

was added dropwise, 20.5 g. (0.15 mole) of o-ethylthiophenol during a period of an hour and a quarter. The total reduction time was ten hours. The reaction products were isolated in the manner already described. Basic fraction; b.p. 80-83° /29mm., $n_D^{29} = 1.4523$. Yield, 3.0 g. (0.024 mole; 15.9%). Acidic fraction; b.p. 94-95° /25mm., $n_D^{29} = 1.5621$. Yield, 10.0 g. (0.072 mole; 50%).

Reduction of thianaphthene at -60°

The experimental procedure used was that employed for the reduction described above. To 250 ml. of dried ethylamine, precooled to -60° with a dry ice-acetone bath, was added 8.3 g. (1.2 g. at.) of lithium metal chips. To the dark blue colored solution was slowly added 13.4 g. (0.10 mole) of thianaphthene during a period of an hour. The total reaction time was 3.5 hours and the reduction products were isolated in the manner previously described. Basic fraction; b.p. 76° /25mm., $n_D^{25} = 1.4521$. Yield was 1.0 g. (0.0079 mole; 7.9%) of 2-ethylcyclohexanone. Acidic fraction; b.p. 94° /25mm., $n_D^{26} = 1.5655$. Yield was 10.0 g. (0.072 mole; 72%) of o-ethylthiophenol.

Preparation of 2-Methylthianaphthene

To a 1 liter three neck round bottom flask equipped with a mechanical stirrer; dropping funnel, condenser with attached calcium chloride tube, and a nitrogen inlet tube was placed

9 g. (1.3 g. at.) of lithium metal chips and 200 ml. of anhydrous ether. A solution containing 82.2 g. (0.60 mole) of n-butyl bromide dissolved in 120 ml. of anhydrous ether was added during a period of one hour to the stirred, cooled (-10°) metal-ether suspension. To complete the reaction, stirring was continued for an additional 1.5 hours at -10° .

The purple colored n-butyl lithium solution was filtered through glass wool by nitrogen pressure into a previously cooled (-10°) 1000 ml. three neck round bottom flask. A 53.6 g. (0.40 mole) quantity of thianaphthene dissolved in 100 ml. of anhydrous ether was added during a 20 minute period to the stirred, cooled alkyl-metal mixture. The reaction was completed by stirring for an additional 1.5 hours at -10°C . To force the reaction to completion at this point the ether was removed by a water aspirator until solid material began to precipitate from solution. Then 100 ml. of anhydrous ether was added and evaporated again via the water aspirator. This procedure was repeated a third time to remove as much butane with the ether as possible.

A solution containing 74.4 g. (0.40 mole) of methyl-p-toluenesulfonate dissolved in 100 ml. of anhydrous ether was added dropwise to the 2-lithium thianaphthene during a period of a half hour while keeping the reaction temperature at 2° by suspension in an ice-water bath. Following the addition of the organic sulfonate the reaction mixture was stirred at its reflux temperature for a half hour. The mixture was then allowed to warm to room temperature and the brownish-red

colored solution was poured over 1 liter of ice chips. The ether layer was separated and the aqueous phase was extracted three times with 100 ml. portions of ether. The ether extracts were combined, dried with anhydrous magnesium sulfate, filtered, and concentrated on a steam bath. The residue was distilled using a six inch Vigreux column, to obtain a liquid product, b.p. $109-110^{\circ}/25\text{mm}$. The oily product on cooling solidified. It was recrystallized by dissolving it in a small amount of ligroin and cooling. The crystalline product was recovered by filtration and air dried, to obtain 22.0 g. (0.166 mole; 39%) of a pure product, m.p. $51-52^{\circ}$. The literature value for the melting point of 1-methylthiolanaphene is $51.5-52^{\circ}$. (18).

Preparation of Acetonylphenyl Sulfide

In a 1 liter three neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, and dropping funnel were placed 40.0 g. (1.0 mole) of sodium hydroxide dissolved in 100 ml. of distilled water. The alkaline solution was cooled to 25° and 110 g. (1.0 mole) of thiophenol was added quickly. To the stirred sodium thiophenolate solution, 92 g. (1.0 mole) of chloroacetone was then added during a half hour while holding the reaction temperature at $20-25^{\circ}$. To complete the reaction the mixture was stirred at room temperature for an hour following the addition of the chloroacetone. The product was extracted into 200 ml. of

ether, washed with 100 ml. of water, dried over anhydrous calcium chloride, filtered and concentrated on a steam bath. The crude product was distilled using a six inch Vigreux column to obtain 130 g. (0.785 mole; 78.5%) of a pure liquid product, b.p. $137^{\circ}/15\text{mm}$. The literature value reported for this sulfide is, b.p. $139-140^{\circ}/16\text{mm}$. (18).

Preparation of Acetonyl-p-tolyl Sulfide

The general experimental procedure used in the synthesis of this sulfide was the same as that used in the preparation of acetonylphenyl sulfide. A 32.2 g. (0.805 mole) quantity of sodium hydroxide was dissolved in 80.5 ml. of distilled water and placed in a flask. To the cooled (25°) alkaline solution was added 100 g. (0.805 mole) of p-toluenethiol. To the thiolate solution was added 74.2 g. (0.805 mole) of chloroacetone during a half hour period. The isolation of the pure sulfide was accomplished in a manner identical to that described in the previous synthesis. Physical properties of the product, b.p. $165^{\circ}/19\text{ mm.}$, yield 117.0 g. (0.65 mole; 80.7%). The literature value reported for the boiling point is $160-162^{\circ}/17\text{mm}$. (18).

Preparation of 3-Methylthianaphthene

In a 500 ml. round bottom three neck flask equipped with a mechanical stirrer, reflux condenser, thermometer, and

dropping funnel were placed 22 g. (0.15 mole) of phosphorous pentoxide. In the dropping funnel were placed 66.5 g. (0.39 mole) of acetophenyl sulfide. Approximately one quarter of the sulfide was added initially to the reaction flask and the reaction mixture was cautiously heated with a Bunsen burner to initiate the reaction, which occurred when the reaction mixture had reached a temperature of 100°C . The exothermic reaction caused the reaction temperature to rise to about 200°C . and resulted in some decomposition. After allowing the reaction temperature to drop to 170° , the remainder of the sulfide was added dropwise to the reaction mixture after which it was stirred and heated at $160-180^{\circ}$ for an additional three quarters of an hour. The dark colored reaction mixture was cooled to room temperature and 200 ml. of water were added. The reaction was extracted with 100 ml. of ether. An emulsion formed which had to be filtered, washed with ether and the aqueous layer extracted three times with ether. The ether extracts were combined, washed with 100 ml. of water, dried with anhydrous calcium chloride, filtered, and concentrated on a steam bath. The crude product was distilled using a six inch Vigreux column to obtain the pure liquid product, b.p. $112/15\text{mm.}$, yield 23.5 g. (0.16 mole; 40.5%). The reported literature value for this compound is, b.p. $75-78^{\circ}/2\text{mm.}$ (13).

Preparation of 3,5-Dimethylthianaphthene

The general experimental procedure employed in the preparation of this material was the same as that used in

the preparation of 3-methylthianaphthene. The quantities of reactants used were, 55.0 g. (0.925 mole) of phosphorous pentoxide and 117.0 g. (0.65 mole) of acetyl-p-tolyl sulfide. The pure product had a boiling point of $132^{\circ}/25$ mm. The literature value reported for the boiling point of this material is $130-135^{\circ}/15$ mm. (13).

Reduction of 2-Methylthianaphthene

The general experimental procedure is the same as that used for the reduction of thianaphthene. The quantities of reactants used were, 250 ml. of dry ethylamine, 8.3 g. (1.2 g. at.) of lithium metal chips, and 14.8 g. (0.1 mole) of 2-methylthianaphthene. The total reduction time was ten hours. The reduction products were isolated in the manner previously described. Basic fraction; b.p. $92-93^{\circ}/25$ mm., $n_D^{26} = 1.4916$; yield 7.0 g. (0.053 mole; 53%). The literature values for 2-n-propylcyclohexanone are b.p. $199^{\circ}/760$ mm; $n_D^{25} = 1.4510$ (24). The semicarbazide derivative of the cyclic ketone was prepared in the manner described previously and recrystallized from ethyl acetate, m.p. $131-132^{\circ}$. The literature value reported for the melting point is 133.5° for this semicarbazide (24). The acidic fraction; b.p. 222° at atmospheric pressure and the refractive index was, $n_D^{26} = 1.5545$; yield 5.0 g. (0.033 mole; 33%). The literature value reported for the boiling point of this material is $219-221^{\circ}/730$ mm. (17).

Reduction of 3-Methylthianaphthene

The general experimental method used in this reduction was

identical to that used for the reduction involving thianaphthene. The quantities of reactants employed were 250 ml. of dry ethylamine, 6.5 g. (1.2 g. at.) of lithium chips, and 14.9 g. (0.1 mole) of 3-methylthianaphthene. The total reduction time was ten hours. The reduction products were isolated in the manner already described. Basic fraction; b.p. $80^{\circ}/1\text{mm.}$, $n_D^{26} = 1.4556$; yield 223 g. (0.017 mole; 17.5%). The literature values for the physical constants of 2-isopropylcyclohexanone are, b.p. $92^{\circ}/15\text{mm.}$, $n_D^{12} = 1.4585$ (24). The semicarbazide derivative of the cyclic ketone was prepared in the usual manner, and recrystallized from ethyl acetate, m.p. 166° . The literature value reported for the melting point is 187° for this semicarbazide (27). The acidic fraction; b.p. $107^{\circ}/20\text{mm.}$, $n_D^{26} = 1.5564$; yield 9.2 g. (0.061 mole; 60.5%). The literature value reported for 2-isopropylthiophenol is b.p. $225-227^{\circ}/760\text{mm.}$ (17).

Reduction of 3,5-Dimethylthianaphthene

The general experimental procedure was the same as that used for the reduction of thianaphthene. The quantities of reactants used were 250 ml. of dry ethylamine, 6.5 g. (1.2 g. at.) of lithium metal chips, and 16.3 g. (0.1 mole) of 3,5-dimethylthianaphthene. The total reduction time was ten hours. The reduction products were isolated in the manner previously described. Basic fraction; b.p. $90^{\circ}/25\text{mm.}$, $n_D^{26} = 1.4589$; yield 1.7 g.

(0.009 mole; 3%). The very small quantity of product isolated was insufficient to obtain an analytically pure sample for analysis. Acidic fraction; b.p. $110^{\circ}/25$ mm., $n_D^{26} = 1.5472$, yield 0.5 g. (0.009 mole; 3%). Calcd. for $C_{10}H_{14}S$: C, 72.29; H, 6.43; S, 19.23. Found: C, 72.57; H, 6.09; S, 19.13.

Preparation of 2-Fluorothianaphthene

The 2-methylanaphthene compound was prepared as described in the experimental procedure for obtaining 2-methylthianaphthene, except that in this case one-half the quantities of reactants were used.

Perchloryl fluoride gas was passed into the ethereal solution at $0^{\circ}C$. through a dispersion tube. The reaction was exothermic and the temperature was controlled by immersion in a dry ice-acetone bath and the rate of the addition of the gas. A white precipitate formed in the orange colored reaction solution giving it a yellow appearance. A blue glow was visible around the dispersion tube which brightened with an increased rate of flow of the gaseous perchloryl fluoride. The addition of gas was continued until the blue glow stopped, at which point nitrogen gas was passed through the reaction solution for about ten minutes to flush out excess perchloryl fluoride gas. The reaction mixture was then transferred to a two liter beaker and water was added to dissolve the precipitate. The solution was then made basic with sodium carbonate. The red

colored ether layer was separated and the aqueous phase was extracted with three 100 ml. portions of ether. The ether fractions were combined, washed with water until neutral, dried with anhydrous magnesium sulfate, filtered, and concentrated on a steam bath. The residue was distilled using a six inch Vigreux column to obtain a liquid product, b.p. $93-94^{\circ}/25\text{mm.}$, $n_D^{27} = 1.5910$, m.p. 20°C. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{SF}$: C, 63.16; H, 3.29; S, 21.05; F, 12.50. Found: C, 63.19; H, 3.51; S, 21.20; F, 12.67.

Reduction of 2-Fluorothianaphthene

The general experimental procedure employed in this reduction was the same as that used for the reduction of thianaphthene. The quantities of reactants used were 250 ml. of dry ethylamine, 8.3 g. (1.2 g. at.) of lithium metal chips, and 15.2 g. (0.1 mole) of 2-fluorothianaphthene. The total reaction time was ten hours. The reduction products were isolated in the manner already described. Basic fraction; b.p. $87^{\circ}/30\text{mm.}$, $n_D^{26} = 1.4527$, yield 2.5 g. (0.02 mole; 20%). The infra-red spectra was found to be identical to that of 2-ethylcyclohexanone. Acidic fraction; b.p. $87^{\circ}/24\text{mm.}$, $n_D^{26} = 1.5668$. A sample submitted to vapor phase chromatography gave the same retention time as o-ethylthiophenol. The yield of product was 2.5 g. (0.018 mole; 18%). The nuclear magnetic resonance and infra-red absorption spectra of the reduction product were identical with those of o-ethylthiophenol.

Reduction of Thiophene

The general experimental procedure used in this reduction was the same as that used for the previously described reductions of thianaphthene. To 250 ml. of anhydrous ethylamine was added 7.4 g. (1.05 g. at.) of lithium metal chips. To the dark blue colored metal-amine solution was added 12.6 g. (0.15 mole) of thiophene dropwise during a period of two hours. The total reduction time was ten hours. At the end of this period no lithium metal remained. The reaction products were isolated in the manner previously described. Basic fraction; b.p. range 66-77°/13mm. The yield of product was approximately 0.5 g. ($n_D^{24} = 1.4625$). An infra-red spectra of the product was determined and contained the following peaks (in microns) 3.4 (OH stretch), 6.0 (carbonyl), 6.9 (CH₂ deformation), 7.25 (CH₃ deformation). The product did not contain N, S, or halogen. The compound gave a small amount of precipitate with 2,4-dinitrophenylhydrazine. Unfortunately, insufficient amounts of the derivative or the original product could not be obtained for further identification and characterization work. Acidic fraction; a small quantity of the aqueous phase was acidified with dilute acetic acid and a solution of lead tetraacetate was added. An instant black precipitate was observed, which indicated the presence of sulfur, possibly in the form of a mercaptan. Further work was not carried out with the aqueous phase due to the possibility of isolating n-butylmercaptan.

Attempt to Desulfurize Aromatic Mercaptans with Triethyl Phosphite

Benzenethiol

To 11.62 g. (0.0694 mole) of purified triethyl phosphite was added 7.65 g. (0.0694 mole) of benzenethiol. The reaction mixture was set aside for a day at room temperature. The mixture was then transferred to a fractional distillation apparatus and heated to 150°C . at which temperature no volatile material was obtained. The distillation temperature was then raised to $150\text{--}175^{\circ}$ for twenty minutes and then to 200° at which point a distillate, b.p. $100\text{--}105^{\circ}$, was obtained. It was identified as a mixture of triethyl phosphite and benzenethiol.

p-Chlorothiophenol

The attempted desulfurization reaction was repeated using 11.62 g. (0.0694 mole) of triethyl phosphite and 10.00 g. (0.0694 mole) of p-chlorothiophenol. The initial fraction obtained by distillation of this mixture was 11.0 g. of a compound having a boiling point, $105\text{--}100^{\circ}/60\text{mm.}$, identical to that of triethyl phosphite.

Pentachlorothiophenol

To a 9.61 g. (0.0343 mole) quantity of triethyl phosphite was added 10.0 g. (0.0343 mole) of pentachlorothiophenol dissolved in 125 ml. of carbon tetrachloride. The reaction solution was refluxed on a steam bath for a day and then cooled to room temperature. A crystalline product was obtained

which melted at $229-232^{\circ}$. A mixture melting point of this material and pentachlorophenol did not depress the melting point below that of pure pentachlorophenol.

SUMMARY

1. Thianaphthene was reduced using the lithium-amine system to 2-ethylcyclohexanone and o-ethylthiophenol.
2. The o-ethylthiophenol was established to be an intermediate in the reduction of thianaphthene by this procedure.
3. The 2-methyl, 3-methyl, and 3,5-dimethylthianaphthene derivatives were reduced to yield the corresponding ketones and mercaptans.
4. The 2-fluorothianaphthene was prepared and reduced to o-ethylthiophenol and 2-ethylcyclohexanone as the sole reduction products indicating reductive cleavage of the carbon-fluorine bond.
5. Thiophene on reduction with lithium-amine yielded a small quantity of unidentified high boiling neutral product.

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