THE SYNTHESIS OF THE ENDOTHIOBICYCLO RING SYSTEM BY MEANS OF THE DIELS-ALDER REACTION

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Robert Eugene McComb
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This is to certify that the

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THE SYNTHESIS OF THE ENDOTHIOBICYCLO RING SYSTEM
BY MEANS OF THE DIELS-ALDER REACTION

presented by

ROBERT EUGENE McCOMB

has been accepted towards fulfillment
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O-169

ABSTRACT

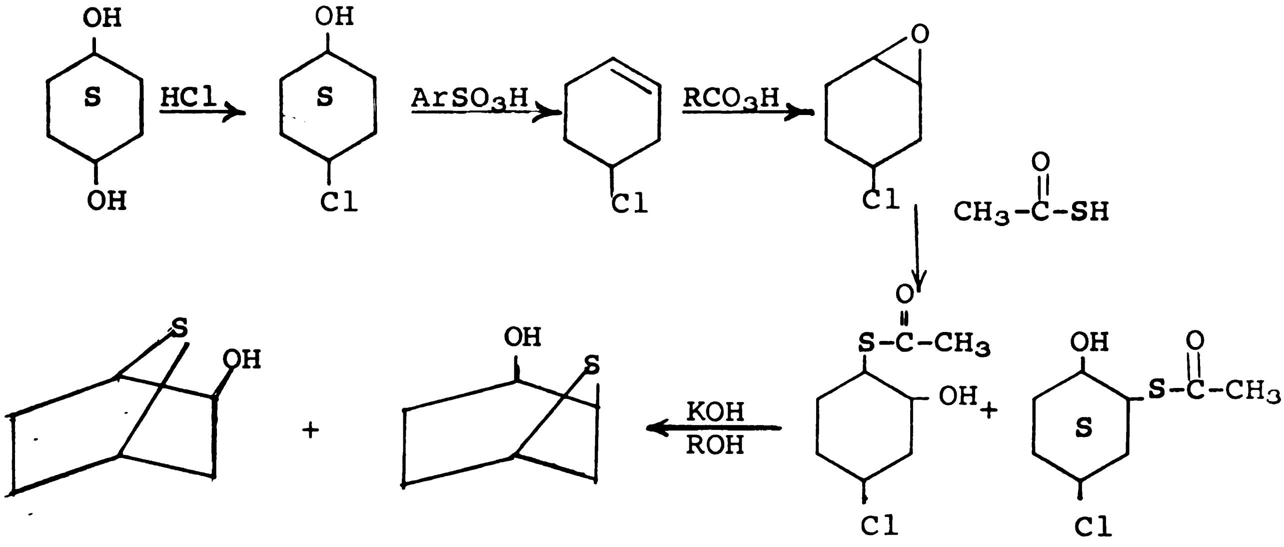
THE SYNTHESIS OF THE ENDOTHIOBICYCLO RING SYSTEM BY MEANS OF THE DIELS-ALDER REACTION

By

Robert Eugene McComb

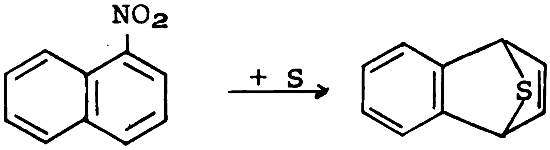
The present investigation was undertaken with two main objectives; namely, to develop synthetic procedures for the synthesis of endothiobicyclo compounds wherein a sulfur atom bridges a six membered ring at the 1,4-positions and to investigate their chemical and physical properties.

Attempts to synthesize 1-hydroxy-7-thiobicyclo[2.2.1]-heptane were unsuccessful.



However, from this series of reaction a new compound; 4-chlorocyclohexene oxide (4-chloro-7-oxo-bicyclo [4.1.0]heptane) was obtained.

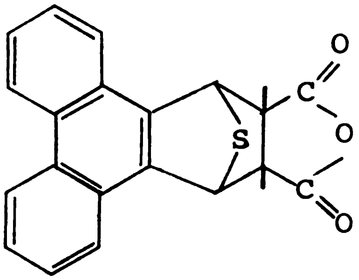
Efforts to prepare 1,4-thianaphthalene [1,4-endothionaphthalene] by the reaction of sulfur with 1-nitronaphthalene by the Herzfelder method (3) were also unsuccessful.



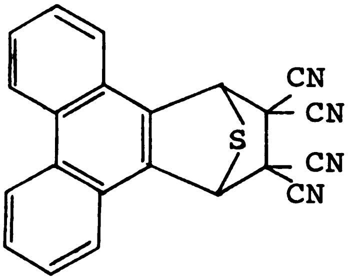
The next experimental approach to obtaining the endothiobicyclo compound was by a Diels Alder type reaction using 3,4-disubstituted thiophene and thiophene with very reactive dienophiles such as tetracyanoethylene and benzyne. A number of 3,4-disubstituted thiophenes were made as intermediates for the series of Diels Alder reactions; 3,4-dimethyl-, 3,4-dimethoxy-, 3,4-diphenylthiophene, 4,5,6,7-dibenzoisothionaphthalene and 4,5,6,7-tetrahydrobenzo [C]-thiophene (3,4-tetramethylenethiophene).

The re-evaluation of thiophene as a diene in the Diels Alder reaction was undertaken. Attempts to react thiophene with acrylonitrile, acrylic acid, methyl acrylate, dimethyl acetylenedicarboxylate, acetylene dicarboxylic acid, maleic anhydride and tetracyanoethylene under a variety of reaction conditions were unsuccessful. Attempts to interact 3,4-dimethyl-, 3,4-dimethoxy-, and 3,4-diphenylthiophene with maleic anhydride and tetracyanoethylene under various experimental conditions were also unsuccessful.

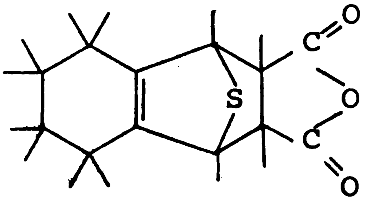
The 4,5,6,7-dibenzoisothionaphthalene and 4,5,6,7-tetrahydrobenzo[C]thiophene both reacted with maleic anhydride and tetracyanoethylene to give the following products;



5,6,7,8-dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalene-(2,3) anhydride (9),

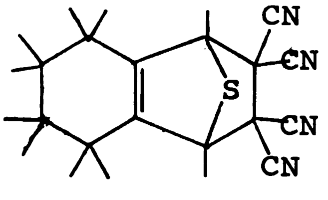


5,6,7,8-dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene;



1,2,3,4,5,6,7,8-octahydro-1,4-endothionaphthalene(2,3)anhydride

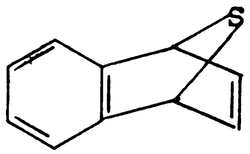
and



1,4,5,6,7,8-hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene.

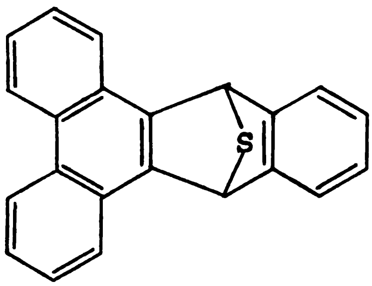
The last series of reactions investigated was the reaction of benzyne with thiophene and/or its derivatives; 3,4-dimethyl-, 3,4-dimethoxy-, and 3,4-diphenylthiophene. The 3,4-disubstituted thiophenes reacted with benzyne but attempts to isolate the 2,3-disubstituted-1,4-dihydro-1,4-endothionaphthalene products were unsuccessful.

Thiophene did react with benzyne to yield several products; 2- and 3-phenylthiophene, 2,3-, 2,4-, 2,5-, and 3,4-diphenylthiophenes were isolated in small yields. The 1,4-dihydro-1,4-endothionaphthalene (m.p. 78.5-80.0°)

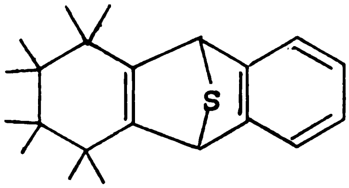


was isolated (6 to 13%) and characterized. It was found to be very unstable at ambient conditions. Its stability was improved by storing it below 0° (2-3 months).

The final two disubstituted thiophenes, 4,5,6,7-dibenzoisothionaphthalene and 4,5,6,7-tetrahydrobenzo[C]thiophene, were reacted with benzyne to give the following products,



6,7,8,9-dibenzo-5,10-dihydro-5,10-endothioanthracene which appears to be very stable at ambient conditions and



5,6,7,8,9,10-hexahydro-9,10-endothioanthracene which also appeared to be stable at ambient conditions.

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The Society of Sigma Xi

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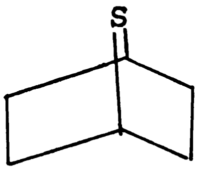
INTRODUCTION

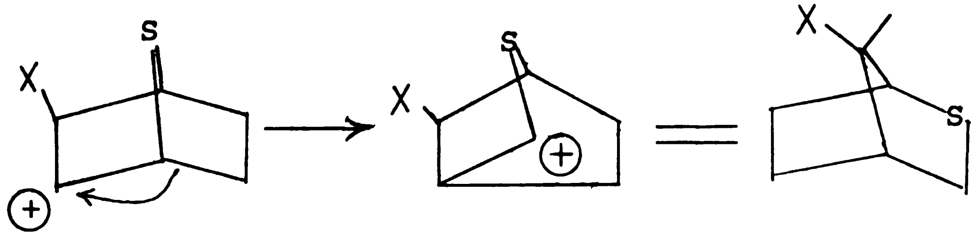
The present investigation was undertaken with the dual objectives of developing synthetic procedures to obtain bicyclic sulfur compounds, wherein the sulfur atom bridges a six membered ring at the 1,4-positions, and to investigate their chemical and physical properties.

The parent structure of compounds of this general type is 7-thiabicyclo[2.2.1]heptane.



Its synthesis has been reported by the late Dr. Birch and his collaborators working at the British Petroleum Institute (1).

Interest in these types of bicyclic sulfur compounds was concerned with the effects of the sulfur atom on the reactivity of the bicyclo system under conditions which could give rise to a carbonium ion type of rearrangement, either classical or non-classical as in the non-hetero system, norborane

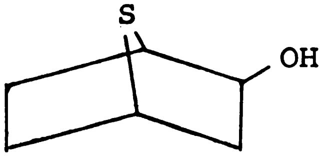


or cause the sulfur bridge to open by hydrolysis, oxidation or other chemical reactions.

It was anticipated that an investigation of the reactions of thiobicyclic compounds would permit a determination of whether their physical and chemical properties are related to *d* orbital overlap of the sulfur atom and/or its participation effects in the total properties of such compounds.

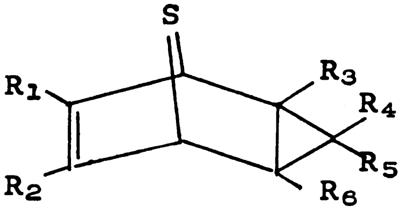
To experimentally study the reactions of a thio-bicyclic compound, it should have some functional group or reactive center present in its structure, e.g., unsaturation or a functional group. The reactive center should be of such a nature as to promote the formation of an ion while the functional group should help elucidate the structure of the products of its reactions, and help account for any structural rearrangements occurring during its reaction.

A structure permitting an experimental approach to this problem would be a substituted 7-thiobicyclo[2.2.1]heptane, namely, 1-hydroxy-7-thiobicyclo[2.2.1]heptane

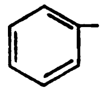


The presence of the hydroxyl group could be utilized to introduce a double bond into the thiobicyclo structure through the Chugaev reaction, or a simple xanthate decomposition.

An alternate approach to obtaining a reactive bicylic sulfur compound seemed possible through the Diels-Alder reaction. With the renewed interest in this reaction due to the development of newer and very reactive dienophiles, such as benzyne, tetracyanoethylene, dicyanoethylene and perfluorobutyne (2), it was anticipated that thiophene or some of the 3,4-disubstituted derivatives might be made to undergo the Diels-Alder type reaction and yield the thio-bicyclo type compounds,

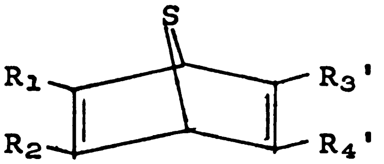


$R_1=R_2=H$, CH_3-, CH_3O-,

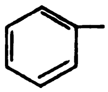


$R_3=R_4=R_5=R_6=$ -CN

or

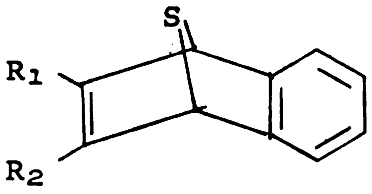


$R_1=R_2=$ H-, $CH_3]$, CH_3O-,

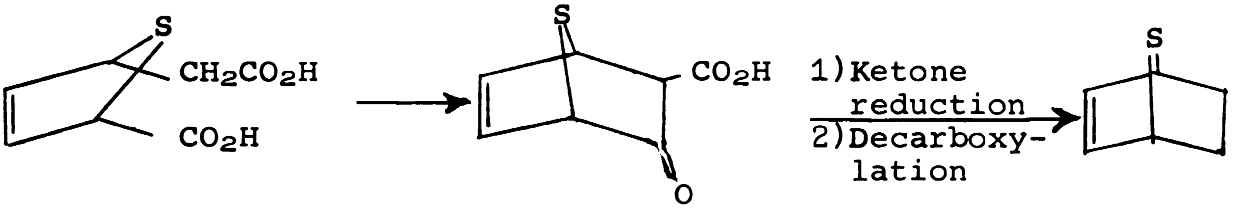


$R_3'=R_4'=$ -CN, $-NO_2$, $-CF_3$

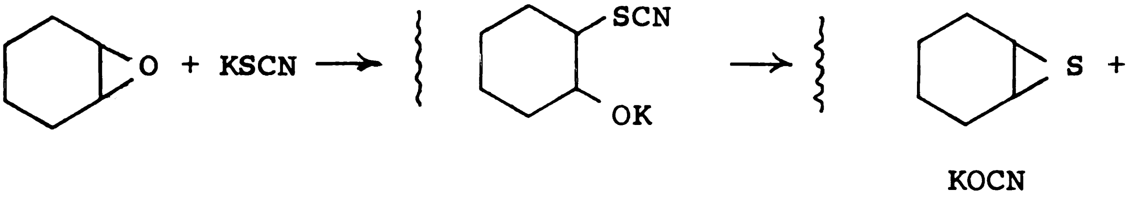
or



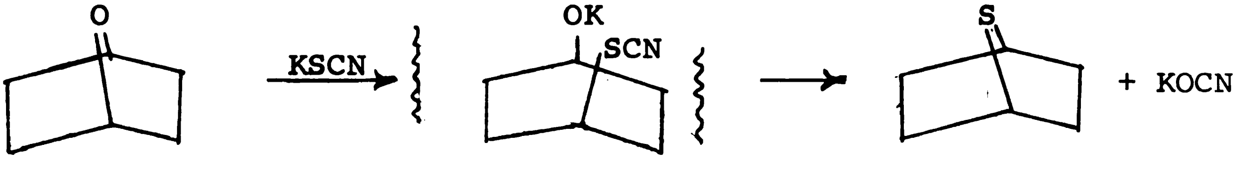
Other possible experimental approaches suitable to obtaining the desired thio-bicyclo compounds would be the Dickman condensation of a dicarboxydihydrothiophene



Furan and its derivatives readily undergo a Diels-Alder reaction. The treatment of such adducts with thiourea or thiocyanate ion might be utilized to exchange the oxygen by sulfur in reactions similar to those reported by Van Tamlen (2)



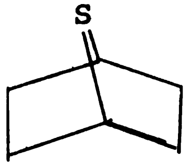
and extended to



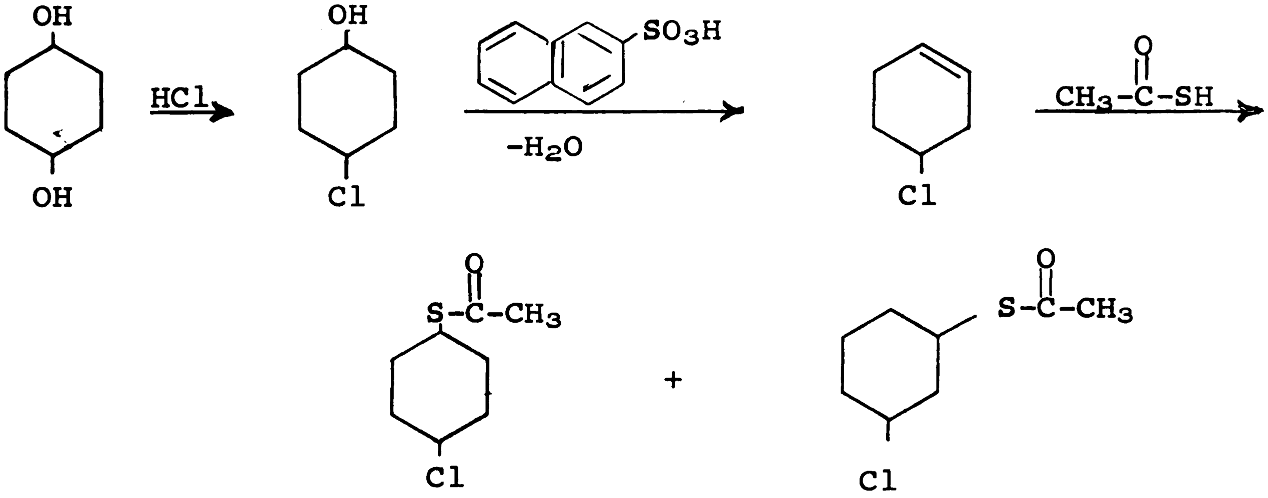
HISTORICAL

Several references to thiobicyclo compounds, endothiobridge or epithiobridge, have appeared in the chemical literature.

Birch and co-workers (1) isolated and characterized, 7-thiobicyclo[2.2.1]heptane

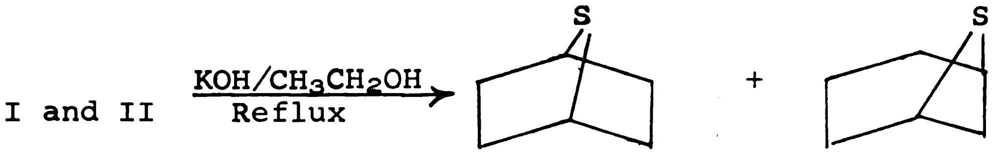


from eastern Mediterranean crude oils and in further research were able to synthesize this compound in a series of reactions starting with cyclohexane[1,4]diol.



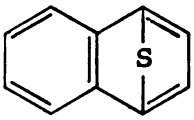
I

II

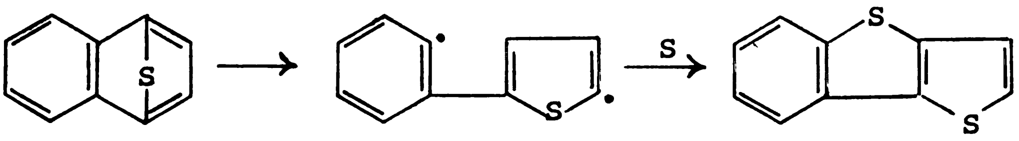


I'   II'

A Herzfelder in 1895 reported the synthesis of 1,4-thianaphthene [1,4-Epithionaphthalene] by pyrolyzing a mixture of 1-nitronaphthalene and sulfur (3). He assigned this material the endo structure

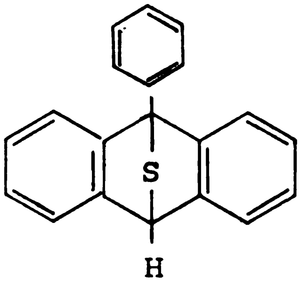


Hartough and Meisel (4) proposed that such a structure even if initially formed would be very unstable due to the presence of double bonds at the bridgehead carbon atoms, and that these would be readily opened by an attack of a second sulfur atom to yield the following compounds,

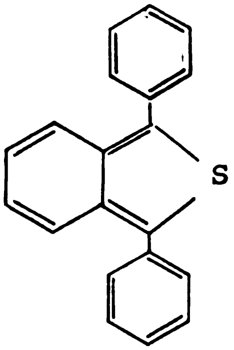


At present the existence of the proposed endothiobridged compound has not been substantiated by synthesis or proof of structure.

A compound, 9-phenyl-9,10-dihydro-thio-9,10-anthracene having an epithiobridge

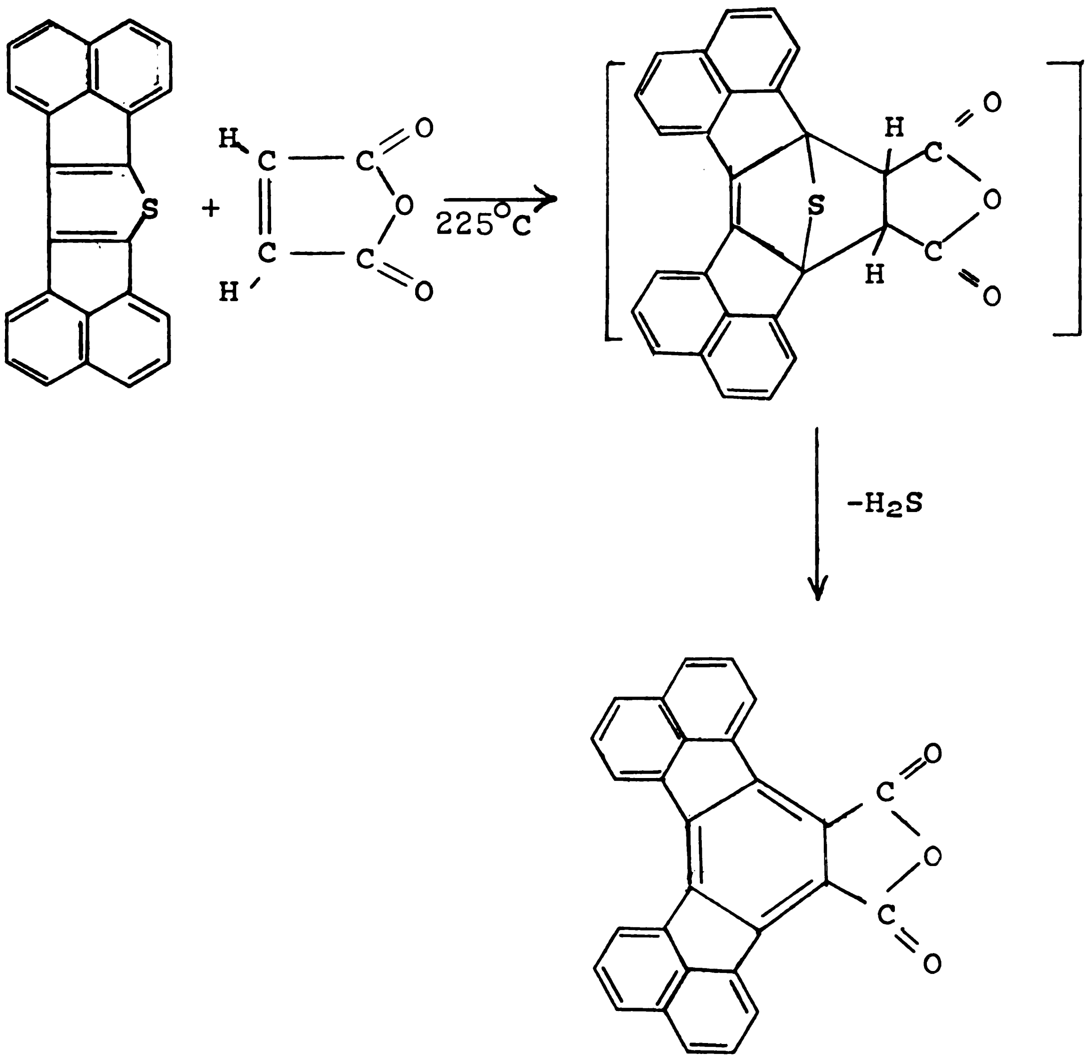


was reported by Bistrzycki and Brenken (5). Dufrasisse and Daniel (6) in 1937 demonstrated that the structure of this compound was actually 1,3-diphenylisothionaphthalene.



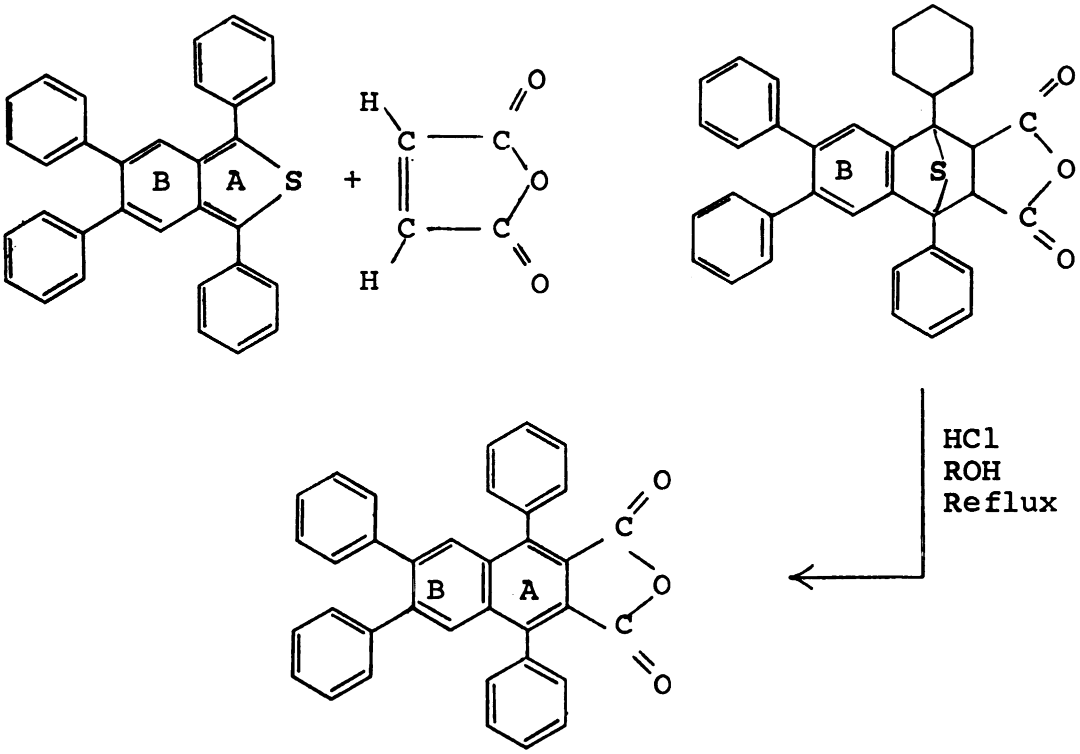
They also observed that 1,3-diphenylisothionaphthalene failed to undergo a Diels-Alder reaction with maleic anhydride as did its oxygen analog, 1,3-diphenylisobenzofuran.

In 1939, Clapp (7) reported the reaction of dinaphthylene-thiophene with maleic anhydride. However the Diels-Alder adduct was never isolated due to the drastic, experimental conditions required to bring about the reaction. The structure of the product could only be explained by assuming that a Diels-Alder reaction had occurred in which the adduct loses hydrogen sulfide to form the dinaphthylene phthalic anhydride



A very reasonable basis for the formation of such a product is that once the epithiobridge was formed the driving force or resonance energy gain resulting from the loss of hydrogen sulfide lead to the formation of a "new" benzene ring. Clapp found in the same investigation that thionessal would not undergo a Diels-Alder reaction with maleic anhydride.

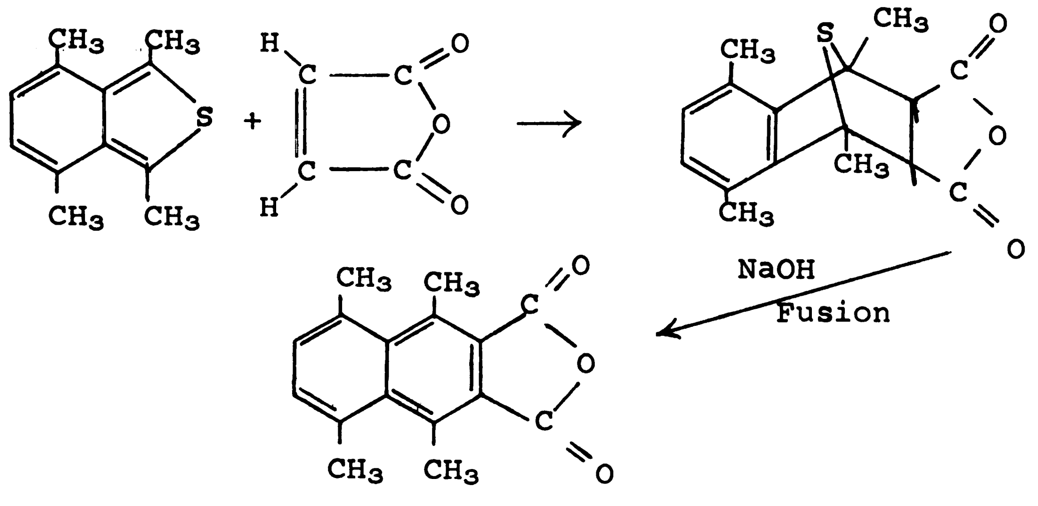
In 1943, Allen and Gates (8) in their studies of the reactivity of complex thiophene derivatives reported the formation of a compound having an epithiobridge by reacting 1,3,5,6-tetraphenylisothionaphthalene with maleic anhydride. They isolated an adduct and found that it lost hydrogen sulfide when refluxed with alcoholic hydrogen chloride.



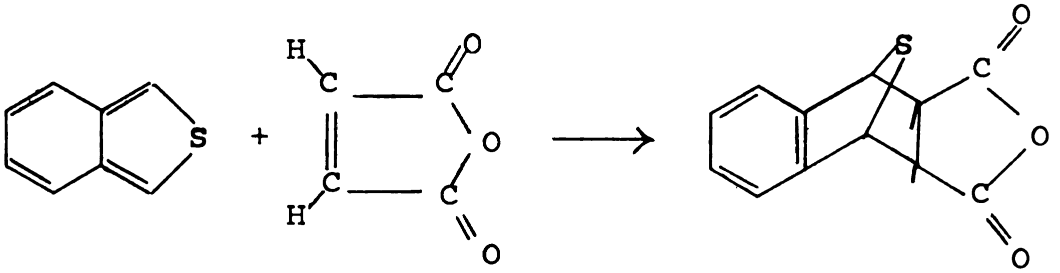
The postulated reason for the reaction of the substituted isothionaphthalene with maleic anhydride is the localization of the double bonds in the "thiophene" ring. It has lost its aromatic characteristics. Once the thiobridge is formed, it is very reactive and by refluxing in alcoholic hydrogen chloride the bridge sulfur is opened. The additional driving force of this reaction can be due to the formation of the "new" aromatic ring A. The reason for the tetraphenyl derivative reacting while the 1,3-diphenylderivative failed to react under Diels-Alder conditions (6) could be rationalized as due to a decrease in the resonance energy of ring B in the starting material caused by the 5,6-diphenyl groups and by the formation of the new aromatic ring in the tetraphenyl derivative whereas the 1,3-diphenylisothionaphthalene does not have these substituents on ring B to help decrease its resonance energy.

Thus, these investigations all report that attempts to employ thiophene or isothionaphthalene (benzo [C] thiophene) in the Diels-Alder synthesis fail unless the thiophene derivative is highly substituted and that where adducts are formed the sulfur bridge is easily eliminated as hydrogen sulfide, usually during the reaction.

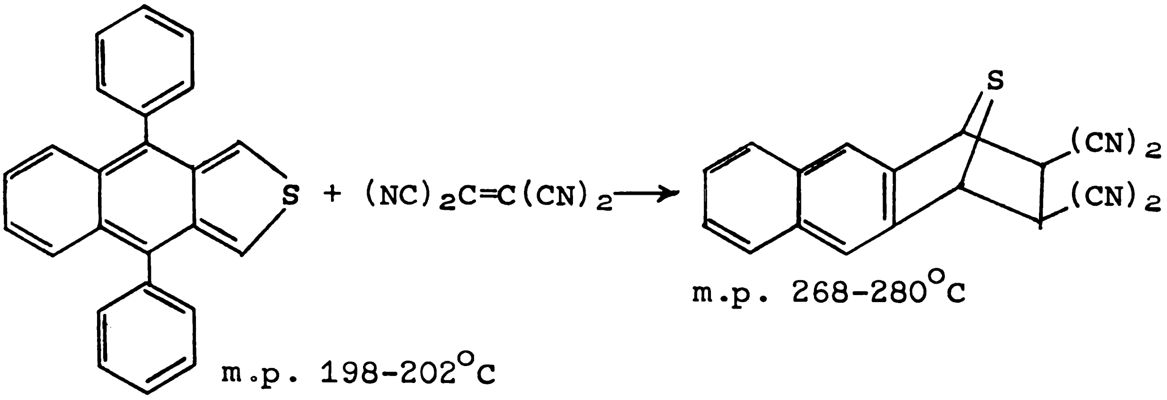
In 1954, Dann and co-workers (9,10,11) reported the reactions of substituted isothionaphthalenes with maleic anhydride to form endothiobridged compounds. The adducts were isolated and their chemical properties studied.



Recently two additional thiophene derivatives have been reported in the literature and both were found to undergo a Diels-Alder reaction with reactive dienophiles. Meyer and co-workers (12) reported a study of the synthesis of isothionaphthalene (benzo [C]thiophene) and its chemical properties. It undergoes a Diels-Alder reaction with maleic anhydride to form a 1,4-endothiobridged bicyclo compound.



Cava and Van Meter (13) in 1962 reported the synthesis of 1,3-diphenyl [5,6]benzoisothionaphthalene. This material was found to react with tetracyanoethylene to form a stable Diels-Alder adduct. The isothioanthracene did not react with maleic anhydride or n-phenylmaleamide to yield an adduct.

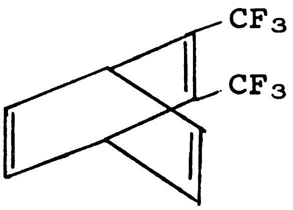


Complete literature references and reviews on the Diels-Alder reaction (14-28) are far too numerous to cite all of them. Thus only general references concerning this reaction are given in the bibliography unless a particular article had some special relevance to the present investigation.

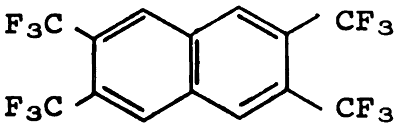
The literature references (14-28) report on numerous aspects, such as mechanisms and kinetics, of the Diels-Alder reaction and on the great variety of dienes and dienophiles that have been employed in this very general reaction.

Diels and others (27,28,29) have reported the failure of a Diels-Alder reaction to occur between thiophene and its "simple" derivatives with maleic anhydride and other "low reactive" dienophiles.

Thiophene derivatives as well as benzene derivatives show a tendency to react with dienophiles only if their derivatives are very complex, as was previously discussed, that is, substituted with benzo[C]thiophene(isothionaphthalene) or when the dienophile is extremely reactive as described for benzene reacting with perfluorobytyne (29). The initially formed adduct, 5,6-bis(trifluoromethylbicyclo[2.2.2]octatriene



was not isolated because it reacted with a second mole of the reactive perfluorobutyne and then rearranged to yield

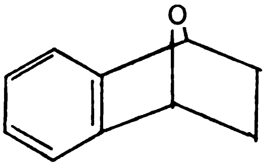


2,3,6,7 tetrakis(trifluoromethyl)naphthalene.

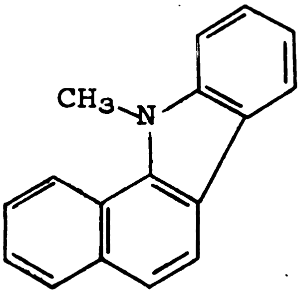
With the advent of new reactive dienophiles such as "benzyne" (30-42), Tetracyanoethylene (43,44) and perfluorobutyne (29) and a renewed interest in dicyanoacetylyene (45,46,48), it was anticipated that perhaps one or more of these dienophiles would react with thiophene or one of its 3,4-disubstituted derivatives to provide a simple direct synthetic route to the endothiobridged bicyclo compounds.

Of the reactive dienophiles, tetracyanoethylene and benzyne have been studied more extensively and as they were also readily available, these were utilized in attempts to synthesize the sulfur bridged compounds.

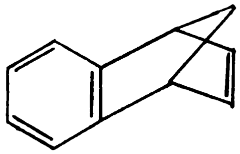
It has been reported that benzyne reacts with furan (35) to give an endo-oxo bridged compound



in good yield (46%). N-methyl pyrole likewise was found to react with benzyne (38) but the simple adduct was not isolated as it reacted with a second mole of benzyne followed by rearrangement of the product to give



Anthracene has been reported to react with benzyne to yield triptycene (33,37), while cyclopentadiene reacted with the same reagent to give endomethylene[1,4]dihydronaphthalene



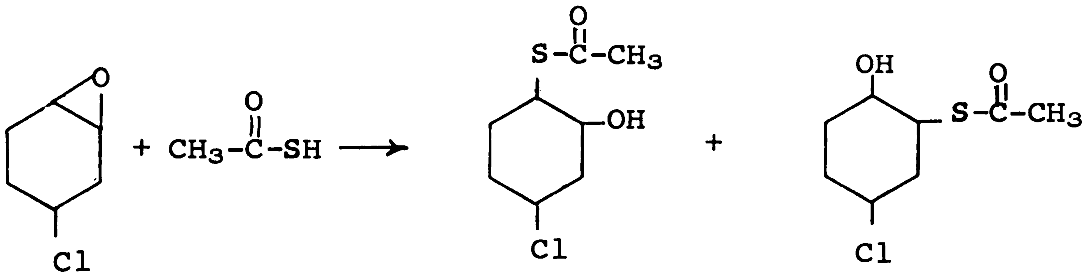
Because of this reactivity of benzyne and other examples of similar reactivity reported by Wittig, it was anticipated that benzyne would react with thiophene or one of its derivatives, whose aromaticity had been "reduced" by substitution, in the 3,4-position, to give the desired simple bicyclic sulfur bridged structure through a Diels-Alder reaction. Further, it was also anticipated that tetracyanoethylene because of its reactivity with dienes (47) would also yield an adduct with thiophene or one of the 3,4-disubstituted thiophenes.

DISCUSSION

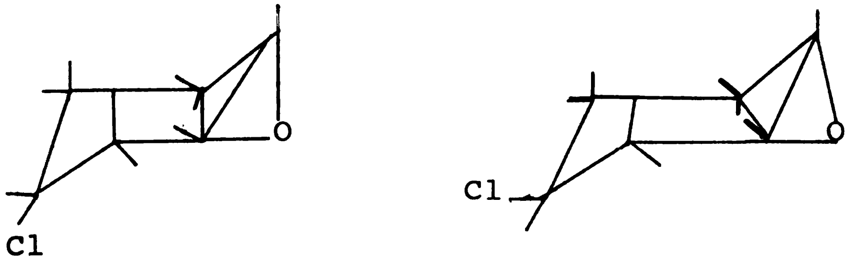
In order to study the reactivity of the sulfur atom in an endothiobicyclo compound, these compounds must first be obtained. The simplest member of the series, 7-thiobicyclo-[2.2.1]heptane was synthesized by Birch and co-workers (1). Its structure contained no other functional group besides the sulfur atom and for the purposes of investigating reactions taking place, such as ring openings and rearrangements, it was necessary to have some other functional group on the molecule.

Following the procedures of Birch (1), 4-chlorocyclohexene was prepared as an intermediate in the attempted preparation of 2-hydroxy-7-thiobicyclo[2.2.1]heptane. The 4-chlorocyclohexene was converted to 4-chlorocyclohexene oxide by peracetic acid (49,50). This is the first reported preparation of 4-chlorocyclohexene oxide. There appeared to be two fractions of material which had almost identical infrared spectra but differed in their boiling point. In a later communication, Taft (51) reported the preparation of 4-chlorocyclohexene oxide using p-nitroperbenzoic acid and apparently obtained only one compound. This compound's infrared spectrum, boiling point and refractive index agreed with a composite fraction of the material obtained in this study. An infrared spectrum of the latter material is shown in Figure I.

The 4-chlorocyclohexene oxide on reaction with thioacetic acid yielded more than the two expected products; 4-chloro-2-hydroxycyclohexane-1-thioacetate and 5-chloro-2-hydroxycyclohexane-1-thioacetate.

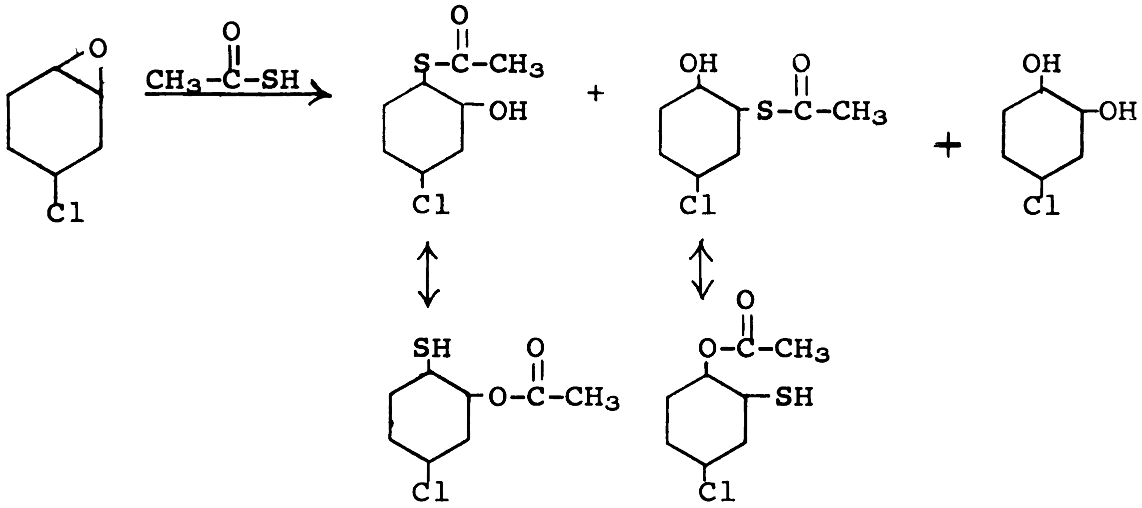


Gas-liquid chromatographic analyses of the reaction products indicated that five compounds were present. Attempts to separate these by liquid chromatographic methods yielded only three fractions. Several attempts were made to separate and identify the five products. It was originally believed that the 4-chlorocyclohexene oxide was obtained as cis-trans isomers.



These isomers, on reaction with the thioacetic acid, would yield four possible products. The fifth product was believed to be 4-chlorocyclohexane-1,2-diol.

Following communication from Taft (51) it was found that the previous distillation of the 4-chlorocyclohexene oxide had been in error. Therefore the five products could not be explained by cis-trans isomers. There have been references in the literature (53) on transesterification of thioacetates when adjacent to hydroxyl groups. The five products can thus be explained by the following reaction scheme.

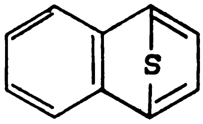


No analytical proof of the above compounds could be obtained except a series of infrared spectra and sulfur analysis. Attempts were made to carry out an ester analysis of the reaction products but these gave very erratic results.

The reaction product from the reaction of 4-chlorocyclohexene oxide and thioacetic acid, on being set aside over night, became a viscous brownish oil.

In a further attempt to prepare the 2-hydroxy-7-thiabicyclo[2.2.1]heptane, a freshly prepared reaction product of 4-chlorocyclohexene oxide and thioacetec acid was added to a refluxing ethanolic potassium hydroxide solution, which would, as reported by Birch (1), close the bridged "sulfur atom." The only product obtained by this procedure was an unidentifiable tar.

The next approach tried in attempts to prepare the bridged sulfur compound was that of Herzfelder (3) reported in 1895 for the syntheses of 1,4-thionaphthalene(1,4-epithionaphthalene). He reacted 1-nitronaphthalene with sulfur and by adding selective solvent admixtures to the reaction mixture precipitated an amorphous material (m.p. 155°) which he assigned the structure:



On repeating Herzfelder's procedures, no solid with a melting point of 155° could be isolated. Making use of all known product isolation techniques, such as liquid chromatography, vacuum distillation, etc., the attempts to isolate the epithionaphthalene were unsuccessful. All of the compounds which were obtained had sulfur analyses greater than 30 per cent while the theoretical sulfur content of epithionaphthalene is 20.2 per cent.

With the failure to isolate an endothiobicyclo-ring structure by the previous two methods, and the advent of the new very reactive dienophiles, tetracyanoethylene and "benzyne," the next approach was through the Diels-Alder reaction. It was anticipated that thiophene or one of its 3,4-disubstituted derivatives could be caused to undergo the Diels-Alder reaction and thereby yield the endothiobicyclo compound.

For this study, a series of 3,4-disubstituted thiophenes were required as intermediates. Thus, 3,4-dimethylthiophene (52), 3,4-diphenylthiophene (52), 3,4-dimethoxythiophene (70,73,74), 4,5,6,7-dibenzoisothionaphthalene (9) and 4,5,6,7-tetrahydrobenzo[C]thiophene were prepared by the method of Hinsberg (52).

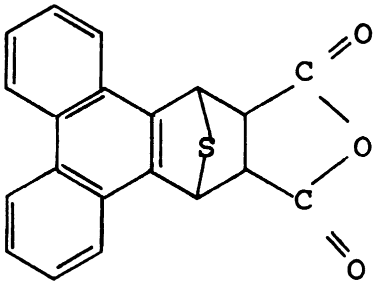
The 3,4-disubstituted thiophenes and thiophene were allowed to interact with various dienophiles, such as tetracyanoethylene, "benzyne" and maleic anhydride, and the materials isolated from the reactions were analyzed for possible Diels-Alder type reactions.

The first in the series of these reactions was the reevaluation of the reactivity of thiophene and some of the "common" dienophiles in attempts to obtain the Diels-Alder adduct.

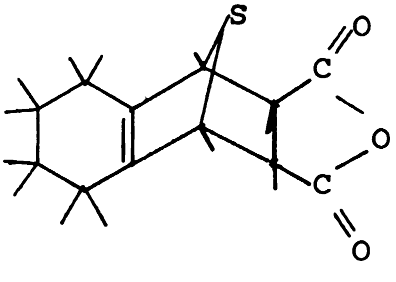
Thiophene was mixed with a dienophile; acrylonitrile, acrylic acid, methyl acrylate, dimethyl acetylenedicarboxylate, acetylenedicarboxylic acid, or maleic anhydride in tetrahydrofuran. The reaction conditions were at ambient temperature or at the reflux temperature of the solvent. As had previously been reported by Alder (21,24) and others (18) no evidence of a reaction could be ascertained.

The 3,4-disubstituted thiophenes, 3,4-diphenyl-, 3,4-dimethyl-, and 3,4-dimethoxythiophene, were similarly treated with maleic anhydride in a tetrahydrofuran solvent and again no evidence of a Diels-Alder reaction could be ascertained. In each case only starting materials were recovered.

The last two 3,4-disubstituted thiophenes, 4,5,6,7-tetrahydrobenzo[C]thiophene and 4,5,6,7-dibenzoisothionaphthalene, were allowed to interact with maleic anhydride and in each of the latter cases a product was obtained and identified. These compounds are 5,6,7,8-dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalene(2,3)anhydride (9),



and 1,2,3,4,5,6,7,8-octahydro-1,4-endothionaphthalene(2,3)-anhydride:



Their infrared spectra were obtained and are Figures II and III respectively.

Both of these compounds were refluxed with methanolic hydrogen chloride. In the case of the dibenzotetrahydro endothionaphthalic anhydride, no reaction occurred and only starting material was recovered. With the octahydroendothionaphthalic anhydride, a reaction did occur as evidenced by the evolution of hydrogen sulfide. The product, isolated from the reaction of octahydroendothionaphthalic anhydride with alcoholic hydrogen chloride, melted 130° higher than the starting material and qualitative sulfur tests indicated the absence of sulfur in the product. The most probable structure for this product is tetrahydronaphthalic(2,3) acid.

The test with methanolic hydrogen chloride has been used by Dann and co-workers (9,10,11), Birch (1) and Allen and Gates (8) for opening the 1,4-endothiobridge. Wittig and co-workers (34,35,36,38) also used the same method to open the 1,4-oxobridge compounds.

The above difference in the reactivity of the two endothiobridged compounds may be explained as due to the difference of resonance energy gained on loss of the thiobridge. For the complex dibenzotetrahydroendothionaphthalic anhydride, the gain in resonance energy of the whole molecule on the loss of the sulfur atom is of the order of one or two kilocalories. For the simpler octahydroendothionaphthalic anhydride, the gain in resonance energy is of the order of 50 to 55 kilocalories. Therefore the octahydroendothionaphthalic anhydride would convert to the tetrahydrophthalic acid or anhydride because of the driving force of this gain in resonance energy.

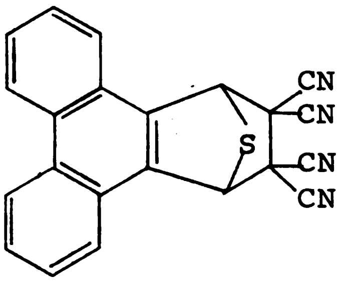
A sodium hydroxide fusion of each of these compounds led to the loss of the sulfur bridge and the expected products were obtained. The dibenzotetrahydroendothionaphthalic anhydride gave 5,6,7,8-dibenzonaphthalic anhydride, which was identified by its melting point and elemental analysis in agreement with the literature values (9) for this material.

The product from octahydroendothionaphthalic anhydride fusion with sodium hydroxide was tentatively identified by its elemental analysis and the observation that the melting point of this product was identical to the melting point of the product obtained from the methanolic hydrogen chloride reaction.

The above endothiobridge compounds were set aside for further study and another series of reactions was initiated with tetracyanoethylene and thiophene and its 3,4-disubstituted derivatives.

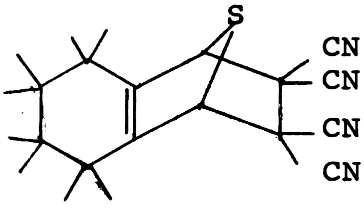
Tetracyanoethylene appeared to react with thiophene, 3,4-diphenylthiophene, 3,4-dimethylthiophene or 3,4-dimethoxythiophene, but on the application of isolation procedures to the reaction products the only isolatable materials were the starting materials and some tarry residues. The remaining 3,4-disubstituted thiophenes, 5,6,7,8-dibenzoisothionaphthalene and 4,5,6,7-tetrahydroisothionaphthalene, were caused to react with tetracyanoethylene and both compounds gave a reaction product.

The 5,6,7,8-dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene



appears to be a very stable compound at ambient conditions. After tentative identification of the product by elemental analysis, the product was set aside for further study.

The 1,2,5,6,7,8-hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene



was also isolated and identified by elemental analysis. However, it decomposed when kept at room temperature for two weeks. It appeared to be stable for three months at -40°.
This material was set aside also for further study.

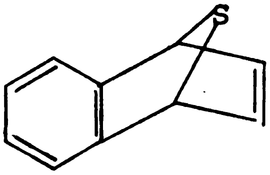
None of the previous attempts to prepare the endothiobicyclo compounds gave a simple bridged molecule of reasonably good stability. Therefore the last series of reactions investigated started with thiophene and the 3,4-disubstituted thiophenes reacting with "benzyne," in attempts to prepare the endothiobicyclo bridge compounds.

The first synthesis attempt in this series was the reaction of thiophene with benzyne. The materials isolated from this reaction indicated that benzyne had reacted with the thiophene in a very complex reaction. During the course of repeating the preparation it became evident that the following influenced the reaction, and type of product obtained; (1) the type of solvent used, (2) the presence of moisture, (3) the amount of oxygen in the nitrogen atmosphere, and (4) reaction temperature. A gas chromatographic analysis of the reaction products indicated that some twenty compounds could be present. The separation and identification of these proved to be extremely difficult if not impossible.

By liquid chromatographic techniques several products were isolated and identified as: 2-phenylthiophene (13%), naphthalene (10%), 3-phenylthiophene (5%), triphenylene (3-16%). By liquid chromatographic treatment of the vacuum distillation distillate, 2,3-diphenylthiophene (1%), 3,4-diphenylthiophene (1%), 2,5-diphenylthiophene (2%), 2-4-diphenylthiophene (1%), and many other solids and oils some of which contained sulfur, were isolated.

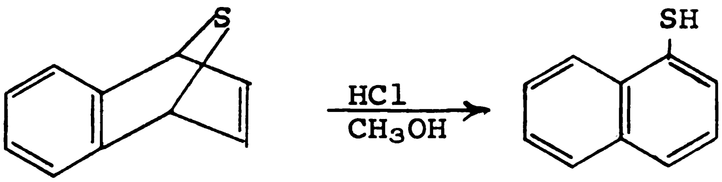
One of the fractions obtained from the vacuum distillation was a crystalline solid which melted in the range 78.5°-80.0°. The infrared spectrum of this compound was completely different from that of naphthalene and qualitative tests indicated the presence of sulfur. On obtaining its elemental analysis, it was found to have an empirical formula,

$C_{10}H_8S$. It was believed that this compound was the expected 1,4-dihydro-1,4-endothionaphthalene

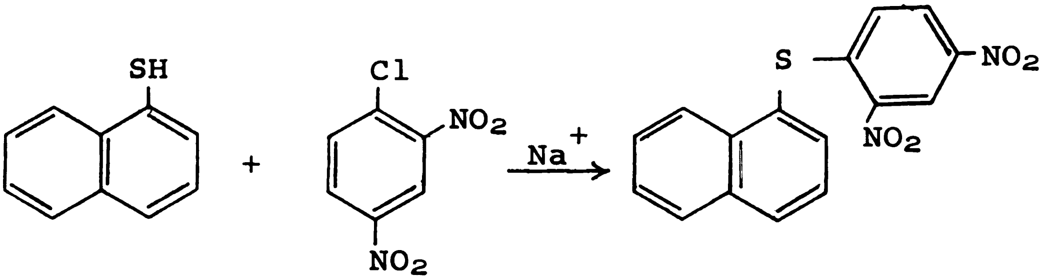


The infrared spectrum was obtained, Figure VI.

Upon reacting the 1,4-dihydro-1,4-endothionaphthalene with alcoholic-hydrogen chloride, the endothio bridge was



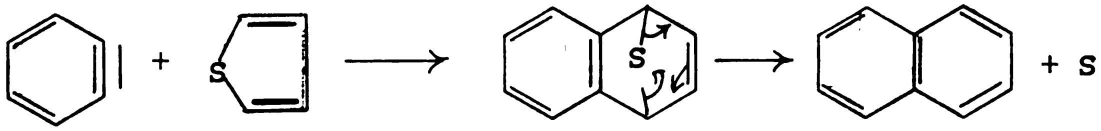
opened similarly to the opening of the oxo bridge found by Wittig and Pohmer (36) in the furan analogs. The product 1 or α-thionaphthalene was reacted with 2,4-dinitrochlorobenzene to give the expected thioether.



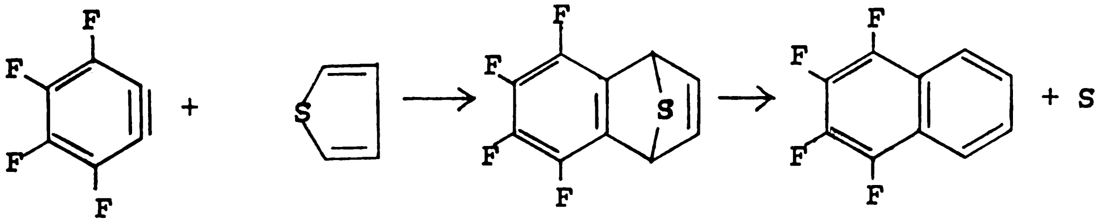
The thioether was identified by elemental analysis, mixed melting point and comparison of its infrared spectrum with that of an authentic sample of the 2,4-dinitrophenyl-1-naphthyl thioether.

A reasonable explanation for the number of products and their formation in the reaction of thiophene with benzyne follows.

Recently Diels-Alder reactions with thiophene and its simple derivatives have been reported (12,13,54,55,56). Fields and Meyerson (55) pyrolyzed phthalic anhydride in the presence of thiophene at 690°. The major products were naphthalene, benzothiophene, 2- and 3-phenylthiophene and bithenyl. Naphthalene was the major product and its formation could best be explained by the benzyne formed on pyrolysis, since it is a strong dienophile, adding 1,4- rather than 1,2- to the thiophene and at the high temperature this product decomposes to give naphthalene and sulfur. Fields and Meyerson (55) gave a mechanism for the formation of the products they obtained. The 2- and 3-phenylthiophene resulted from hydrogen abstraction; benzyne abstracts a hydrogen on the thiophene ring. Arnett (40) demonstrated benzyne would abstract hydrogens in a series of experiments with aliphatic and unsaturated aliphatic compounds. When thiophene was subjected to the same pyrolytic conditions only trace amounts of naphthalene were isolated (55).

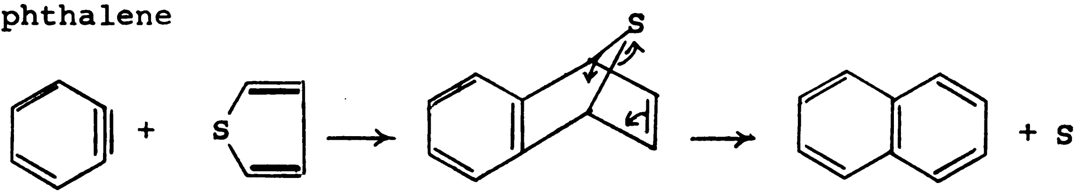


Callander et al. (54) obtained a Diels-Alder adduct from the reaction of tetrafluorobenzyne with thiophene. This adduct was very unstable and decomposed to give tetrafluoronaphthalene

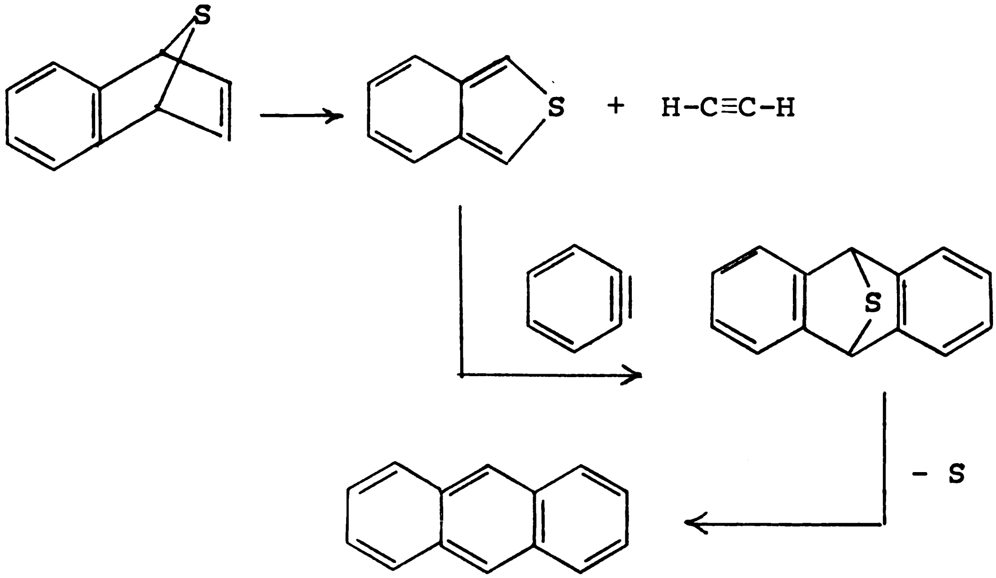


Finally Meyer et al. (12) and Cava et al (12,13) synthesized benzo[C]thiophene and found that it would readily undergo a Diels-Alder reaction with maleic anhydride (12,56) and N-phenylmaleimide (56). Therefore the products obtained from the relatively mild benzyne thiophene reaction in this study could be explained as hydrogen abstraction by benzyne (40,41,55) from the thiophene to yield the phenylthiophenes. Arnett (40) and Simmons (41) found this to be the case in unsaturated aliphatic hydrocarbons and Fields et al (55) found evidence of this process in the pyrolysis of phthalic anhydride in thiophene.

The explanation for the formation of naphthalene and the 1,4-dihydro-1,4-endothionaphthalene found in this study resulted from a Diels-Alder type reaction, which must be a 1,4-addition of the benzyne to the thiophene and because of the unstable nature of the adduct, it decomposed to give naphthalene



If the endothionaphthalene had undergone an inverse Diels-Alder reaction to yield acetylene and benzo[C]thiophene--Cava (56) and Meyer (12) reported that benzo[C]thiophene is very reactive--the benzo[C]thiophene would have in turn reacted with another benzyne molecule to give a Diels-Alder adduct

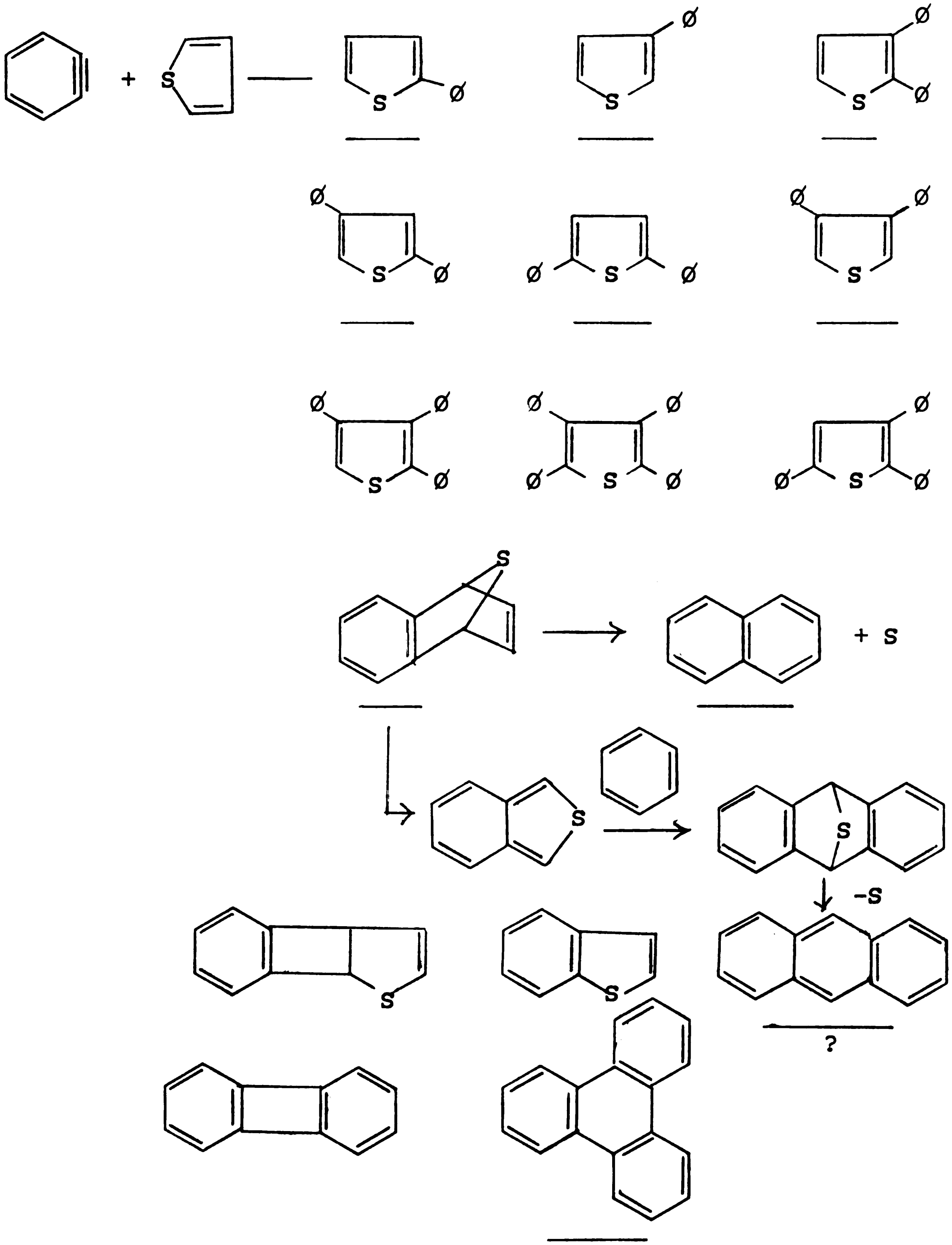


which in turn could lose sulfur to yield anthracene.
A solid believed to be anthracene in trace amounts was isolated from this reaction. The formation of benzo[C]thiophene was not favored by Fields (55), since the loss of a sulfur atom to yield naphthalene is energetically more favorable than the loss of acetylene to yield the less stable benzo[C]-thiophene.

A solid melting from 184 to 187° isolated from the reaction mixture was believed to be thionessal (tetraphenyl-thiophene) but an infrared spectrum comparison, and the large mixed melting point depression (168°) with an authentic sample proved the solid was not thionessal. Wittig et al. (33-38) had isolated diphenylene (m.p. 112-114^{o}) and triphenylene (m.p. 191-194^{o}) from their benzyne reactions. Diphenylene was not isolated in any of the reactions in this study but triphenylene was isolated.

The benzo[C]thiophene found by Fields and Meyerson (55) in their reaction of benzyne with thiophene was not isolated in this study but could possibly be present in the oily substance which contained sulfur and which had been separated by liquid chromatographic techniques.

The following is a scheme of products that might be obtained from the reaction of benzyne with thiophene--those unlined were isolated and identified in this study.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Considerable effort to isolate and identify the endothionaphthalene resulted in the identification of many of the reaction products but left many unidentified which did not contain sulfur.

Several other methods were used in attempts to obtain further proof of identity of the 1,4-dihydro-1,4-endothionaphthalene such as the phenylazide addition compound--n-phenyltriazole--used by Alder and Stein (24,58,59). This method did not give an identifiable reaction product. In addition alkaline permanganate oxidation (3) gave phthalic anhydride, and bromination (3) gave 1,4-dibromonaphthalene. These last two positive tests helped to substantiate that the 1,4-dihydro-1,4-endothionaphthalene had been formed.

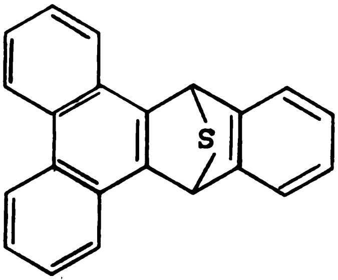
Following procedures similar to those used for thiophene; 3,4-dimethylthiophene, 3,4-dimethoxythiophene and 3,4-diphenylthiophene were caused to react with benzyne. Gas chromatographic analysis of the reaction products indicated that in each case a reaction had taken place because of the 7 to 11 absorption peaks. Some of the products isolated from these reactions did have sulfur as a constituent but attempts to isolate the 1,4-dihydro-2,3-disubstituted-1,4-endothionaphthalenes were unsuccessful.

To gain some insight on the assumption that the large number of reaction products in the reaction mixtures might be due to benzyne reacting with itself or o-fluorobromobenzene or some intermediate reactive species, the following reaction was undertaken. Using the same experimental procedures as were used with thiophene, a benzyne reaction was conducted in the absence of thiophene. Gas chromatographic analysis of this reaction product indicated three absorption peaks. Based on discussions of Wittig and Pohmer (35) and the physical properties of the three compounds isolated, they were tentatively identified as triphenylene (79%), biphenylene (6%) and O,O'-difluorobiphenyl (6%).

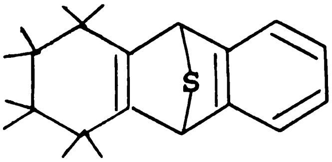
Thus this information and the fact that the triphenylene isolated from the reaction of benzyne with 3,4-disubstituted thiophenes was only 6 to 10%, indicates that thiophene derivatives had reacted but the adducts had decomposed by the loss of sulfur or had reacted with another molecule of benzyne.

The last two substituted thiophenes studied in this series of reactions, 5,6,7,8-dibenzoisothionaphthalene and 4,5,6,7-tetrahydroisothionaphthalene were caused to react with benzyne. Both of these thiophenes gave an identifiable reaction product.

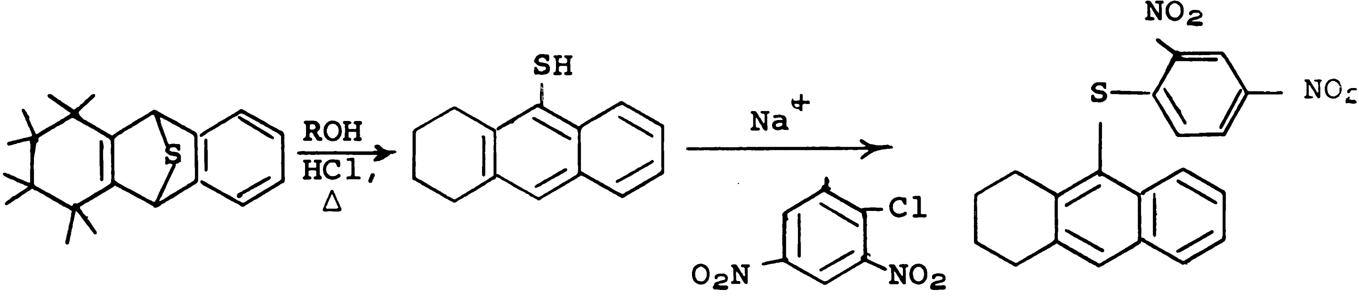
6,7,8,9-Dibenzo-5,10-dihydro-5,10-endothioanthracene



was tentatively identified by elemental analysis. Its infrared spectrum was obtained Figure VII. Attempts to make a derivative involving the sulfur of the thiobridge by opening the bridge with methanolic-hydrogen chloride, then reacting this product with 2,4-dinitrochlorobenzene were unsuccessful. During refluxing the adduct with the methanolic-hydrogen chloride the molecule lost hydrogen sulfide. The product isolated from the reaction appeared to be 6,7,8,9-dibenzo-5,10-dihydroanthracene by elemental analysis.



5,6,7,8,9,10-Hexahydro-9,10-endothioanthracene was tentatively identified by elemental analysis and appeared to be reasonably stable at ambient conditions. Its infrared spectrum was obtained Figure VIII. Attempts to prepare a derivative of the compound by opening the endothiobridge with methanolic-hydrogen chloride and reacting the resultant product with 2,4-dinitrochlorobenzene were also unsuccessful because the sulfur was lost as hydrogen sulfide during refluxing the adduct with the methanolic-hydrogen chloride. The product from this reaction was tentatively identified as

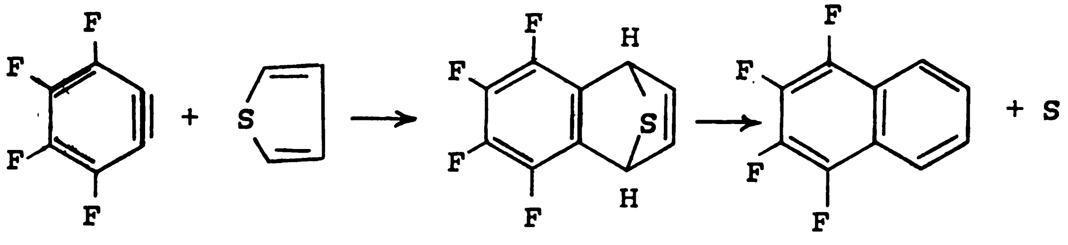


hexahydroanthracene by elemental analysis.

The present study with the recent reports of the Diels-Alder type reaction of thiophene (54,55) and its derivatives (12,13,56) yields either the stable adduct or the decomposition products through loss of sulfur, indicates that even under the right conditions and with a very reactive dienophile, thiophene does undergo a Diels-Alder reaction.

Most of the work in this study was spent in attempts to isolate the endothiobridged compound and very little work was done on the identification of the other reaction products. Identification of these products might have unequivocally demonstrated that the Diels-Alder reaction was the principle reaction. The other reaction products probably are the decomposition products of the adduct.

Callander, Coe and Tatlow (54) established that the very reactive tetrafluorobenzyne did react with thiophene at ambient conditions and the endothiobicyclobridged product from the reactive benzyne and thiophene was unstable and decomposed to yield tetrafluoronaphthalene



I

By liquid chromatographic techniques these investigators did isolate compound I whose n.m.r. was consistent with the structure 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-endothionaphthalene. The principle product was the tetrafluoronaphthalene and its formation could only be accounted for by a Diels-Alder type reaction.

All evidence reported in the literature and the results obtained in the present investigation indicate that benzyne reacts with thiophene and its derivatives to yield Diels-Alder type adducts. These products in some cases are very unstable and decompose to yield naphthalene derivatives (54,55,56).

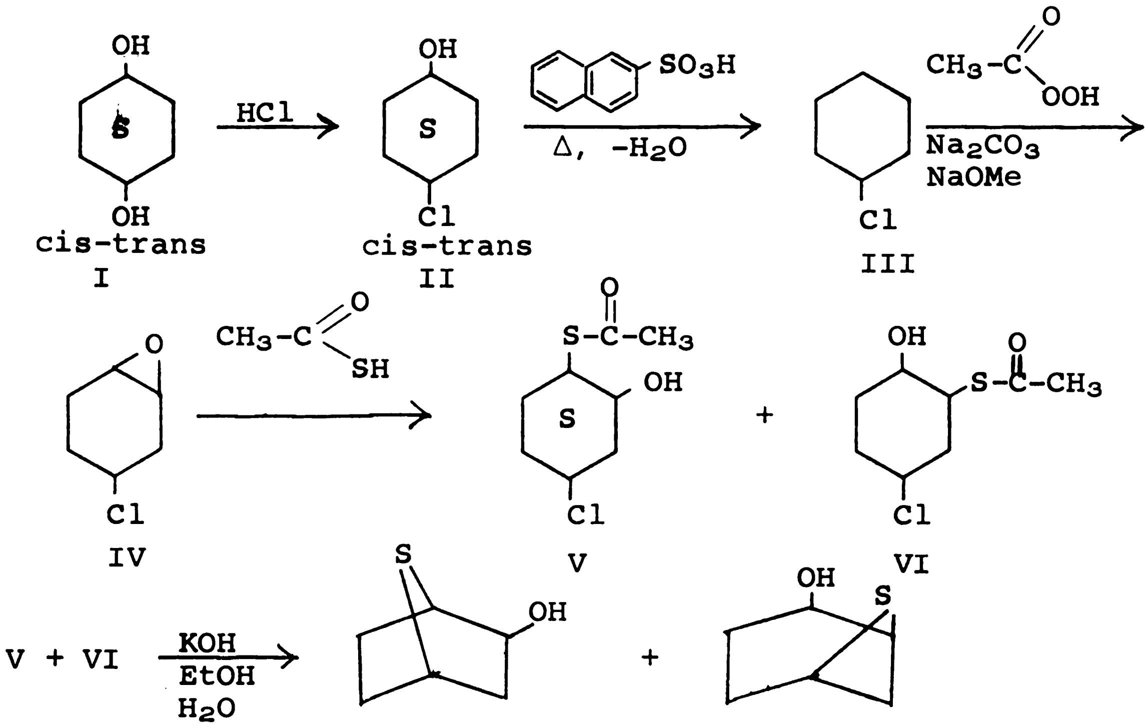
Further work on isolating and identifying the various other reaction products especially those from benzyne with 3,4-dimethyl-3,4-dimethoxy- and 3,4-diphenyl-thiophene will be necessary to establish that the Diels-Alder reaction did take place. Further it will be necessary to determine what electromeric effects the 3,4-disubstituents had on the reactivity of the thiophenes.

Arnett (40) and Simmons (41) in their studies of benzyne were able to demonstrate that benzyne abstracts hydrogen and yields phenyl substitution in various aliphatic systems. This is the most rational basis based on current evidence to account for the formation of the phenylthiophenes found in the reaction product of benzyne with thiophene.

EXPERIMENTAL

All melting points were corrected and were determined on a micro hot stage apparatus.

Attempted Preparation of 1-Hydroxy-7-thiabicyclo-[2.2.1]heptane (1)



Preparation of 4-Chlorocyclohexanol (II)

4-Chlorocyclohexanol, 1000 g. (6.64 moles), was prepared by the method of Owens and Robins (60) from 1,4-cyclohexanediol (I, Aldrich Chemical Co.) and concentrated hydrochloric acid in a 70-79% yield, b.p. 80-90°/5 mm. Hg. (literature value b.p. 96-106°/10 mm. Hg., b.p. 80-85°C/5 mm (60)) n_D^{20} 1.4941 (literature value n_D^{20} 1.4947 (60)).

Preparation of 4-Chlorocyclohexene (III)

4-Chlorocyclohexene, 350 g. (3.00 moles), was prepared by the method of Owens and Robins (60) from 4-chlorocyclohexanol (II) and β-naphthyl sulfonic acid in a 39-45% yield, b.p. 88-93°C/130 mm. Hg., n_D^{20} 1.4814 (literature values 51% yield, b.p. 88-98°C/140 mm. Hg. n_D^{20} 1.4822 (60,1)).

Preparation of 4-Chlorocyclohexene Oxide (IV)

In a 500 ml., three necked, round bottom flask equipped with an adapter, a reflux condenser, thermometer, stirrer, and a dropping funnel was placed 20 g. (0.171 mole) of 4-chlorocyclohexene in 100 ml. of chloroform. To this solution was added a mixture of 40 g. of 40% peracetic acid solution [Becco Chemical Div., FMC., 16 g. peracetic neat, 0.21 mole, corresponding to a 25% excess over the stoichiometric amount required for the reaction] (49) and 9 g. (0.11 mole) of anhydrous sodium acetate as a buffering agent. The reaction mixture was kept under constant stirring during a period of 2.5 hours while maintaining the reaction mixture temperature at 5°. The reaction mixture was stirred for an additional hour, until samples taken from the reaction mixture indicate no further decrease in their peracetic acid content.

The 4-chlorocyclohexene oxide was isolated from the reaction mixture by adjusting the pH to 7 with anhydrous sodium carbonate and separating the chloroform layer. The aqueous layer was extracted once with 25 ml. of chloroform. The chloroform was removed by distillation and the crude 4-chlorocyclohexene oxide obtained weighed 20 g. (0.15 mole, 88%). The crude 4-chlorocyclohexane oxide was fractionally distilled using an 18" helice packed column (50 x 1.5 cm, 3/16" Pyrex helices).

Two fractions were obtained, 8 g. (0.06 mole) b.p. $128\text{-}134^{\circ}$/130 mm. Hg. and 7 g. (0.053 mole) b.p. $140\text{-}150^{\circ}$/130 mm. Hg. and approximately 5 g. of a polymeric residue remained. The refractive index of the two fractions was identical, $n_D^{20} = 1.4915$. An infrared spectra determined between salt plates on a Model 21 Perkin Elmer double beam instrument indicated the presence of the epoxide group with a strong absorption at 11.9 μ (61) and a chloro substituent with absorption in 12-14 μ regions. The two spectra were almost identical and from all appearances the two fractions were identical.

It appeared that two isomers of the epoxide were obtained, the cis-trans isomers analogous to the diols.

The Second Preparation of 4-Chlorocyclohexene oxide (IV) (3-Chloro-7-oxabicyclo[4.1.0]heptane)

Using the method of Korach et al. (62) a second preparation of 4-chlorocyclohexene oxide was undertaken.

To a rapidly stirred suspension of anhydrous sodium carbonate (20 g., 0.18 mole) in a solution of 4-chlorocyclohexene (20 g., 0.17 mole) and 200 ml. of methylene chloride was added 35 g. of 40% peracetic acid solution (0.185 mole neat). The peracetic acid solution had been previously treated with 1 g. of anhydrous sodium acetate to neutralize the sulfuric acid present. The reaction temperature was maintained at 5° during 2.5 hours it required to add the peracetic acid solution. The reaction mixture was stirred an additional hour to complete the reaction. Titration of a filtered aliquot showed all peracetic acid had been consumed. The reaction mixture was filtered and the solid filter cake of sodium acetate, sodium bicarbonate and sodium carbonate was washed three times with 50 ml portions of methylene chloride. The majority of the methylene chloride was removed by distillation (Fenske column 50 x 1.5 cm, packed with 3/16" Pyrex helices). The residue in the distillation flask was then fractionally distilled in the same equipment. Again two fractions were obtained, 7 g, (0.053 mole) b.p. 129-135°/130 mm. Hg. and 7.2 g, (0.054 mole) b.p. 144-151°/130 mm. Hg. The infrared spectras of the two fractions were identical and in turn were found to be identical to the previously

prepared material. The refractive index, n_D^{20} 1.4878 of the fractions was different.

A sample of the combined fraction of the 4-chlorocyclohexene oxide was submitted for elemental analysis.

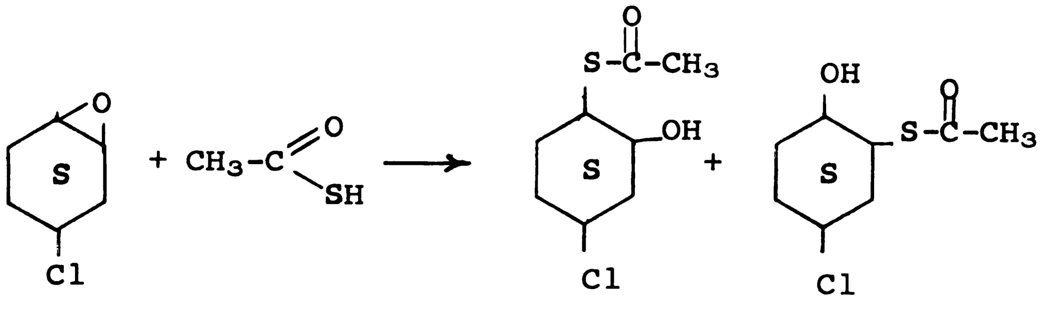
Anal. calc'd. for C_6H_9ClO: C, 54.3; H, 6.8; Cl 26.8;

Found: C, 54.28, 54.35; H, 6.68, 6.74; Cl, 26.69, 26.71 (51,63,64,65).

The peracetic acid was assayed by adding 0.5 ml of the peracid solution to 1 g. of potassium iodide dissolved in 10 ml. of water containing 3-5 drops of 5 N hydrochloric acid.

The liberated iodine was titrated with 0.1 N sodium thiosulfate. A 1 ml. volume of the thiosulfate was equal to 0.008 g. of active oxygen or 0.076 g. of peracetic acid neat. The degree of reaction was followed by acidifying 1 ml. of the reaction mixture with hydrochloric acid, adding potassium iodide and titrating the liberated iodine with 0.1 N sodium thiosulfate solution.

Reaction of 4-Chlorocyclohexene Oxide (IV) with Thioacetic Acid



IV V VI

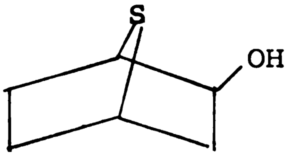
The procedure of Birch, Dean and Hunter (1), utilized for the reaction of 4-chlorocyclohexene with thioacetic acid was followed.

To 10 g. (0.075 mole) of 4-chlorocyclohexene oxide (IV) contained in a 250 ml., three necked, round bottom flask equipped with a reflux condenser, stirrer and dropping funnel, was added 8 g. of redistilled thioacetic acid (E.K. Co., b.p. 83-85.5°/742 mm., 0.105 mole, n_D^{20} 1.4645). The reaction mixture was set aside in a hood for a day, to complete the reaction. Various methods were tried to determine the amount of unreacted oxirane remaining. The attempts were unsuccessful due to the presence of excess thioacetic acid. The excess thioacetic acid was removed by vacuum distillation, leaving a brownish colored viscous oily residue with a disagreeable odor. A sample of the residue was dissolved in methylene chloride and a 5 μ l. portion was injected into a F & M gas chromatograph with a 6 ft. G. E. silicone rubber column. The chromatogram had five peaks in addition to the initial methylene chloride peak. By estimating the area under the peaks, an approximate measurement show a peak at 20 and 25 min., each 25%, a peak at 35 and 38 min., each 15%, and a single peak at 60 min., corresponding to 15%.

A portion of the residue was subjected to vacuum distillation at 130 mm. Hg. However no distillate was obtained up to a temperature of 180°. The pressure was reduced to 0.5 mm. Hg. and a viscous material distilled at 124-140° with evidence of decomposition occurring. This material gave a negative sulfur test by sodium fusion with lead acetate method.

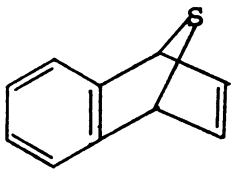
The reaction described above was repeated with 4-chlorocyclohexene oxide and thioacetic acid (1). The gas chromatogram obtained had five major peaks and one minor peak. The brown oily residue was stored for further study.

Attempted Preparation of 7-Thiobicyclo[2.2.1]heptanol



The brown oily product (2.8 g.) obtained above was added dropwise to an alcoholic solution of potassium hydroxide (8 g.), ethanol (30 ml., 95%), and water (30 ml.), heated to its reflux temperature in a similar method to that used by Birch et al. (1). The reaction mixture was maintained at reflux for an additional three hours to complete the reaction (1). It was then cooled to room temperature and extracted with n-pentane. The pentane extracts were combined and shaken with a few iodine crystals, and then with a 10% potassium hydroxide solution to remove any free thiol present. The pentane extract was washed with water until neutral, and dried over anhydrous sodium sulfate. The pentane was removed by distillation under reduced pressure to obtain a polymeric material which gave a negative test for sulfur by the sodium fusion--lead acetate procedure.

Attempted Preparation of 1,4-Thionaphthalene by Herzfelders Method (3)



Following Herzfelder's procedure (3) 150 g. of 1-nitronaphthalene (0.86 mole) was well mixed with 30 g. of flowers of sulfur (0.94 mole). The mixture was heated until an exothermic reaction commenced (300°C). The reaction was very vigorous as evidenced by foaming and evolution of sulfur dioxide and 1-nitronaphthalene vapors. After the reaction had ceased and the mixture had cooled to room temperature, the greenish black solid was pulverized to a coarse tacky powder. It was boiled with ethanol (95%, 250 ml.) to remove unreacted 1-nitronaphthalene and sulfur.

The dark green residue was then boiled (15 min.) with 10 ml. of chloroform and filtered. The filtrate was discarded as it appeared to contain mainly unreacted sulfur. The second residue was boiled with a liter of chloroform, at its reflux temperature for two hours and filtered while hot. The chloroform extraction procedure was repeated three times. The terminal extraction was light green in color. The remaining solid residue was set aside.

Following Herzfelders' procedure (3) the combined chloroform extracts were concentrated under reduced pressure to a liter in volume and a green tacky amorphous solid was precipitated by the addition of a liter of ethanol (95%). The green colored ethanol insoluble material was dissolved in a half liter of chloroform and the solution was heated to its boiling point and the green amorphous mass was again precipitated by the addition of a half liter of ethanol (95%).

This solution and reprecipitation procedure was repeated three additional times. The green amorphorus mass was again extracted by boiling with 100 ml. portions of ethanol (95%) until the extract was pale green in color. This procedure yielded a dark green intractable mass whereas Herzfelder (3) reported an amorphous green powder (m.p. 155°). The tacky mass was insoluble in diethyl ether, methyl, ethyl and isopropyl alcohol, hydrochloric acid (IN) and sodium hydroxide (IN) which were similar to the insolubilities of Herzfelder's solid. The tacky mass was soluble in chlorinated solvents, benzene, carbon disulfide and nitrobenzene. Attempts to sublime or steam distill samples failed to effect any separation or further purification.

Prolonged heating at atmospheric or pressures as low as 0.005 mm. Hg. only resulted in decomposition as evidenced by the evolution of gasseous products and charring of the sample.

Sulfur analysis of the tacky green product gave 32.1, 32.7% S (literature value 27% (3)). The calculated value for sulfur for 1,4-thionaphthalene is 20.2%.

Reacting samples of the green colored product with mercuric chloride, mercuric acetate or lead acetate failed to give a precipitate of organic sulfur compound. Some mercuric and lead sulfide was isolated from these test reaction products.

A sample of the crude green product was refluxed with alkaline potassium permanganate to obtain 3-nitrophthalic acid, m.p. 206-210° (mixed melting point with authentic sample gave no depression of the melting point). The yield of 3-nitrophthalic acid obtained was 14%.

Another sample of the green product was treated with fuming nitric acid (90%) under reflux, to obtain several products. Among these identified were the acids, 3-nitrophthalic acid and phthalic acid.

In addition several nitro aromatic compounds were isolated which contained no sulfur as determined by qualitative sulfur tests.

A sample of the green product was treated with bromine in chloroform until an excess of bromine was obtained. The excess bromine and chloroform were removed by sweeping the solution with a nitrogen gas stream and the crude product obtained was compared to 1,4-dibromonaphthalene (m.p. 81-82°C). The product from the bromination was an oil which could not be crystallized and thus was not the 1,4-dibromonaphthalene reported by Herzfelder.

Second Attempt to Prepare 1,4-Thionaphthalene

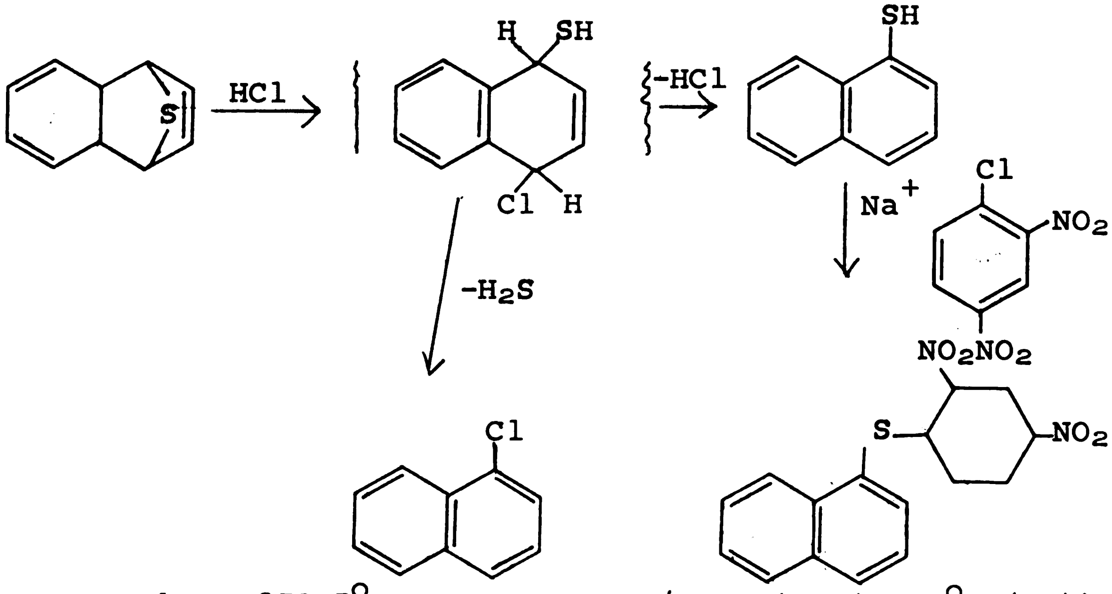
The above experimental procedure (1) was repeated. After the evolution of gaseous products had ceased and reaction mixture had cooled to room temperature, it was boiled with seven separate half liter portions of chloroform, until no additional material could be extracted. The combined chloroform extracts were concentrated under vacuum to obtain 71 g. of a tacky greenish black powder. A 7 g. quantity of this material was dissolved in carbon tetrachloride and transferred to a alumina chromatographic column (1" x 16", Al_2O_3 activity Broch I). The column was eluted with carbon tetrachloride and three bands separated, each having 0.5 g. of material and a fourth band containing sulfur (1.4 g.).

The three bands; two blue and one a reddish blue, gave negative tests for sulfur by sodium fusion and lead acetate.

The column was eluted with cyclohexane (500 ml.) and developed a light blue band (0.7 g.) which gave a negative qualitative sulfur test. The column was then eluted with benzene and four bands were obtained; yellow, red, blue and green. The yellow band material (0.2 g.) had a melting point of 55-58°C and was identified as 1-nitronaphthalene (by mixed melting point). The red band material (0.1 g) and blue band material (0.1 g.) each gave a positive qualitative test for sulfur. Infrared spectra were very complex and no identification of these materials was possible. The green band material (2.0 g.) gave a positive test for sulfur. This material had a melting point range of 43 to 68°. Sulfur analysis gave 43% S [calculated for 1,4-thionaphthalene is 20.2%]. Attempts to recrystallize this material failed to effect the melting point range. Elution of the column with diethyl ether and acetone yielded only trace quantities of a green amorphous solid. Elution of the column with chloroform gave a yellowish colored band (1.1 g.). The material had a melting point range of 146 to 152°. Sulfur analysis was 22% S.

A sample (0.1 g.) treated with nitric acid (90%) gave phthalic acid, benzoic acid and some nitro compounds. A sample treated with bromine in chloroform did not give the expected 1,4-dibromonaphthalene (m.p. 81-82°).

A sample of the yellow material was refluxed in methanolic hydrochloric acid in attempts to open the 1,4-endothiobridge if it was present and obtain α-thionaphthalene. The solid obtained did not appear to have formed the expected 2,4-dinitrophenylthio ether.

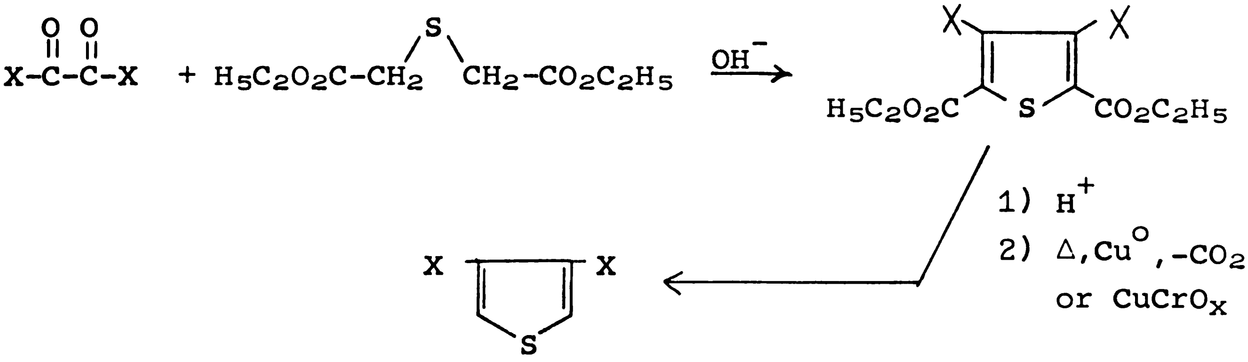


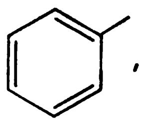
b.p. 259.3°

(m.p. 176-176.5°C (69))

The isolated solid had a melting point in the range 118-122°C. No evidence could be obtained which indicated that the reported 1,4-thionaphthalene had been prepared.

The Preparation of 3,4-Disubstituted Thiophenes



X = CH_3^-,  , CH_3O-, Cl, etc.

Preparation of Ethyl Thioglycolate (70,71)

2000 g. ethyl thioglycolate was prepared from thioglycolic acid (E. K. Co, No. 2249) and ethanol following the procedure of Fawcett (70) adapted from the methods of Rischner and Speir (71). The yields of ethyl thioglycolate were 65 to 73% b.p. 52-54°/11 mm. Hg. It had a refractive index of $n_D^{20} = 1.4570$ (literature value b.p. 156-158°/760 mm. n_D^{20} 1.4568 (70)).

Preparation of Diethyl Thiodiglycolate (70)

Diethyl thiodiglycolate, 1300 g. (18.3 moles) was prepared from the ethyl thioglycolate and ethyl chloroacetate by the procedure of Fawcett (70) and Overberger (72) in yields of 85 to 86%, b.p. 105-108°/2 mm. Hg. It has a refractive index of $n_D^{20} = 1.4644$ (literature value b.p. 105°/3 mm. Hg., 115°/5 mm., 138°/15 mm., n_D^{25} 1.4619 (70,72)).

Preparation of Disodium Salt of 2,5-Dicarbomethoxy-3,4-dihydroxythiophene (70,73)

The disodium salt of 2,5-dicarbomethoxy-3,4-dihydroxythiophene was prepared from diethyl thiodiglycolate and dimethyloxalate in absolute methanol and sodium methoxide, by the procedure of Fawcett (70) which had been adapted from the method of Fager (73), in yields comparable to other investigators (70,73).

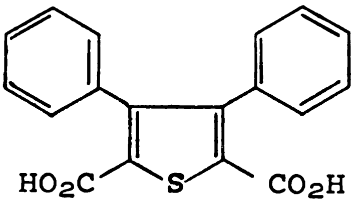
Preparation of 3,4-Dimethoxy-2,5-dicarbomethoxythiophene (70,73,74)

3,4-Dimethoxy-2,5-dicarbomethoxythiophene, 70 g. (0.269 mole), was prepared from the disodium salt of 2,5-dicarbomethoxy-3,4-dihydroxythiophene and dimethyl sulfate by the best procedure found by Fawcett (70) in yields of 32 to 51%. These yields were less than those found by other investigators (70,73,74).

Preparation of 3,4-Dimethoxythiophene (70,73,74)

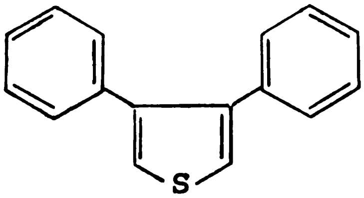
3,4-Dimethoxythiophene, 40 g. (0.312 mole), was prepared from the 3,4-dimethoxy-2,5-dicarbomethoxythiophene by decarboxylation using guinoline and copper chrominum oxide catalyst prepared by the method of Connors, Folkers and Adkins (75) and by decarboxylation using quinoline and reprecipitated copper metal as described by Overberger's method (74). Both decarboxylations gave 3,4-dimethoxythiophene in 44% to 60% yield, b.p. 106-115°/12 mm. Hg. (literature value b.p. 110°/14 mm. Hg. (74) 108-115°/12 mm. Hg. (73)).

Preparation of 3,4-Diphenyl-2,5-dicarboxythiophene



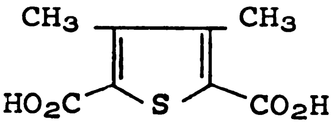
3,4-Diphenyl-2,5-dicarboxythiophene was prepared from diethylthiodiglycolate and benzil in absolute methanol containing sodium methoxide as the condensing agent by the procedures of Hinsberg (76) and Backer, Bulb and Stevens (77). These procedures in this laboratory yielded 265 g. (81% yield) of the 3,4-diphenyl-2,5-dicarboxythiophene melting at 343° with decomposition (literature value 341° (76,77)).

Preparation of 3,4-Diphenylthiophene (74,76,77,78)



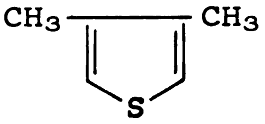
3,4-Diphenylthiophene, 60 g. (0.255 mole), was prepared from the 3,4-diphenyl-2,5-dicarboxythiophene described above by decarboxylation using quinoline and copper powder following Overberger's method (74,78). The 3,4-diphenylthiophene was obtained in a 30% yield. Its melting point was 110-112° (literature value 114° (74,78)).

Preparation of 3,4-Dimethyl-2,5-dicarboxythiophene (76,79)



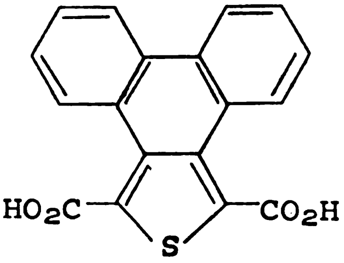
3,4-Dimethyl-2,5-dicarboxythiophene, 300 g. (1.50 moles), was prepared from the diethyl thiodiglycolate prepared above and 2,3-butanedione (diacetyl, Aldrich Chemical Co.) in absolute methanol using sodium methoxide as the condensing agent by the procedures of Seka (79) and Hinsberg (76). The 3,4-dimethyl-2,5-dicarboxythiophene was obtained in a 55% yield, and melted at 325° with decomposition (literature value m.p. 327° decomp (79)).

Preparation of 3,4-Dimethylthiophene



3,4-Dimethylthiophene, 250 g. (2.23 moles) was prepared from the 3,4-dimethyl-2,5-dicarboxythiophene described above by decarboxylation using quinoline and copper powder following Overberger's methods (72,78). 3,4-Dimethylthiophene was obtained in an 83% yield. It had a boiling point of 81-84°/100 mm. Hg., and a refractive index of $n_D^{25} = 1.5194$ (literature value b.p. 145.5-148.5°/760 mm., n_D^{25} 1.5187, n_D^{20} 1.5212 (80)).

Preparation of 4,5,6,7-Dibenzoisothianaphthalene-1,3-dicarboxylic Acid (76,9)

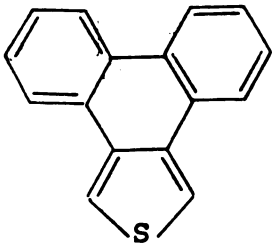


4,5,6,7-Dibenzoisothianaphthalene-1,3-dicarboxylic acid, 76 g. (0.236 mole) was prepared from diethylthiodiglycolate and phenanthraquinone in absolute methanol using sodium methoxide as the condensing agent by the methods of Hinsberg (76) and Dann et al. (9). The dibenzo-dicarboxy-isothianaphthalene was obtained in 76 to 88% yields. It melted at 253-255° with decomposition (literature value m.p. 249-251° (d) (9,76).

Anal. Calc'd for $C_{18}H_{10}O_4S$: C, 67.07%; H, 3.12%; S, 9.94%

Found: C, 67.00%; H, 3.56%; S, 9.20% (67,64).

Preparation of 4,5,6,7-Dibenzoisothianaphthalene (9,76)

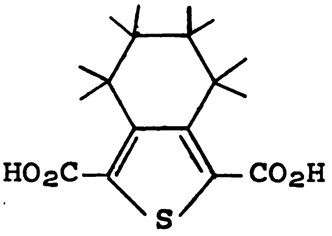


4,5,6,7-Dibenzoisothianaphthalene, 55 g. (0.235 mole), was prepared from the above preparation of 4,5,6,7-dibenzo-1,3-dicarboxy-isothianaphthalene by decarboxylation using quinoline and copper powder following Overberger's methods (72,78). The 4,5,6,7-dibenzoisothianaphthalene was obtained in a 74% yield and its melting point was 165-167° (literature value 166.5-167.0° (9)).

Anal. Calc'd for $C_{16}H_{10}S$: C, 82.01%; H, 4.30%; S, 13.68%

Found: C, 81.91%, 81.67%; H, 4.30%, 4.26%; S, 13.85%, 13.67% (67).

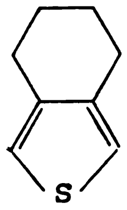
Preparation of 4,5,6,7-Tetrahydro-7,3-dicarboxy-benzo[C]thiophene (76) (3,4-tetramethylene-2,5-dicarboxy-thiophene)



4,5,6,7-Tetrahydro-1,3-dicarboxybenzo[C]thiophene, 40 g. (0.177 mole) was prepared from diethyl thiodiglycolate and 1,2-cyclohexandione (Aldrich Chemical Co.) in absolute methanol using sodium methoxide as the condensing agent by the methods of Hinsberg (76) and a more recent method reported by Meyer et al. (12). The tetrahydrodicarboxybenzo[C]thiophene was obtained in 20 to 25% yields. It melted at 343-344° with decomposition and sublimation (literature values 341° (d)(76)).

Anal. Calc'd for $C_8H_{10}O_4S$: C, 53.09%; H, 4.46%; S, 14.17% Found: C, 53.31%; H, 4.68, 4.41%; S, 13.44, 13.37% (67) 13.96, 14.01, 14.06% (63).

Preparation of 4,5,6,7-Tetrahydrobenzo[C]thiophene (4,5,6,7-tetrahydroisothianaphthalene)



The 4,5,6,7-tetrahydrobenzo[C]thiophene, was prepared by the decarboxylation of the tetrahydro-dicarboxy-benzo[C]-thiophene prepared above using quinoline and copper powder following Overberger's methods (72,78). 4,5,6,7-Tetrahydrobenzo[C]thiophene was obtained in 76-82% yields b.p. 88-90°/11 mm. Hg., 213.2°/740 mm. and its refractive index was $n_D^{25} = 1.5632$ (literature value b.p. 205-215°/760 mm. (76)).

Anal. Calc'd for $C_8H_{10}S$: C, 69.51%; H, 7.29%; S, 23.19% Found: C, 70.32%, H, 6.72%; S, 22.75, 23.01, 23.21% (67,64).

Preparation of Acetylene Dicarboxylic Acid

Acetylene dicarboxylic acid was prepared by neutralizing the acid potassium salt of acetylene dicarboxylic acid (Aldrich Chemical Co.) with sulfuric acid using the method of Abbott et al. (81). The acetylene dicarboxylic acid was obtained in a 33% yield. It melted at 173-174.5° with decomposition (literature value m.p. 175-176° (d) (81)).

Preparation of Dimethyl Acetylenedicarboxylate

The dimethyl acetylenedicarboxylate, 60 g. (0.422 mole), was prepared by esterification of the acetylene dicarboxylic acid with methanol using the method of Stark et al. (82). Dimethyl acetylenedicarboxylate was obtained in a 66% yield. It boiled in the range 93-97°/15 mm. Hg. (literature value b.p. 98°/20 mm. Hg. (82)).

This compound is a very strong lachrymator and the literature describes it as having vesicatory properties similar to that of all other esters of acetylene dicarboxylic acid.

Preparation of Dinitroacetylene

$$BrMgC{\equiv}C\text{-}MgBr + NO_2Cl \longrightarrow O_2N\text{-}C{\equiv}C\text{-}NO_2$$

Preparation of Nitryl Chloride (Nitroxyl chloride (83))

Caution. The laboratory operations were conducted in a well ventilated hood which was darkened to prevent the photochemical decomposition of the product.

The procedure used to obtain nitryl chloride was that of Kaplan and Shechter (83). Fuming nitric acid was mixed with fuming sulfuric acid at 0°. To the cold mixture at -80° was added chlorosulfonic acid (freshly distilled). As the chlorosulfonic acid was added dropwise the nitryl chloride was evolved and it was collected in a dry-ice cooled "trap". This particular preparation yielded 81 g. of nitryl chloride (literature value 95-100 g. 81-91% (83)).

Preparation of Dinitroacetylene

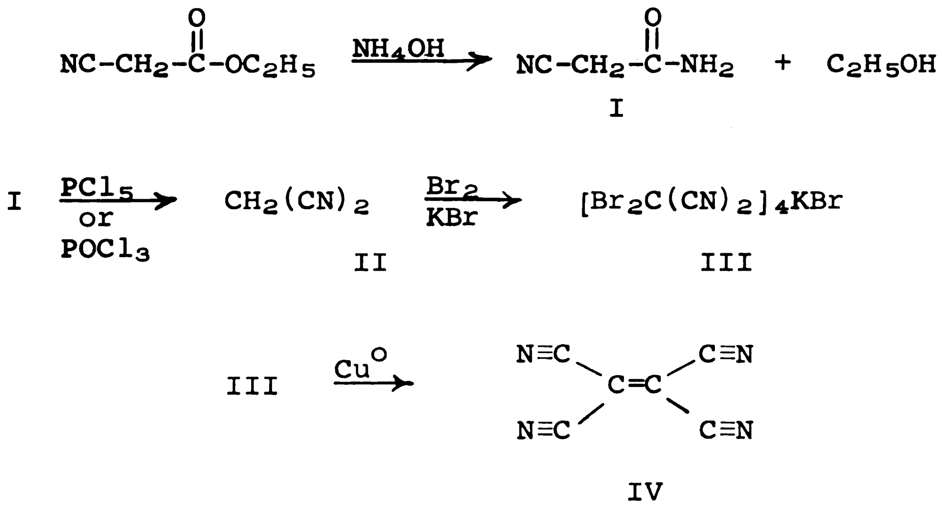
In a 2 l, three necked flask, equipped with a stirrer, reflux condenser fitted with a calcium chloride drying tube, and a dropping funnel fitted with a calcium chloride drying tube was placed 27.1 g. (1.13 g. at) of Grignard grade magnesium turnings and 100 ml. of sodium dried diethyl ether. A crystal of iodine was added to catalyse the reaction.

To this mixture was added 5 ml. of ethyl bromide and the reaction was initiated by gently heating. The remaining ethyl bromide (70 ml. total 111.6 g., 1.025 mole) dissolved in 250 ml. of sodium dried ether was added during 2.5 hours to the reaction flask using the dropping funnel at a rate sufficient to maintain the reaction mixture at its reflux temperature. When the ethyl bromide had been added, the mixture was kept at its reflux temperature until the majority of the magnesium had reacted. The solution was filtered, to remove the few pieces of magnesium that remained, into a clean two liter flask.

A liter of benzene, redistilled from phosphorous pentaoxide, was added to the solution of the ethyl magnesium bromide in ether, and the majority of the ether was removed by distillation. The ethyl magnesium bromide-benzene solution was cooled to 5° and while being vigorously stirred a rapid stream of acetylene was passed into it, using a fritted glass gas dispersing tube, for 3 hours. A pale yellowish-grey suspension was obtained. Considerable reaction heat was liberated and external cooling by immersion of the reaction flask in an ice bath was necessary to control the reaction (84). To the above suspension was added 162 g. (2.00 mole) of nitryl chloride dissolved in 400 ml. of sodium dried diethyl ether during a 4 hour period. The temperature of the reaction mixture was difficult to maintain at 4°. During the addition of the nitryl chloride, the reaction temperature rose rapidly to 10-15°. The addition of the nitryl chloride solution had to be interrupted and the reaction mixture had to be cooled again to 4°. These rapid temperature rises occurred 5-10 minutes after each addition of a portion of the nitryl chloride solution.

After 4 hours of reaction, as much ether as possible was removed with a water aspirator concentrating the reaction mixture to approximately a liter. The solution was filtered through a medium fritted glass funnel to remove the precipitated white solid and the solution was cooled to -3° at which temperature the solution started to crystalize. The dinitroacetylene solution (200 g., 2.5 moles) was stored in a dry-ice chest. It is extremely explosive at room temperature and will explode when heated above 28°.

Preparation of Tetracyanoethylene



Cyanoacetamide I

The cyanoacetamide, 245 g. (2.92 moles), was prepared from ethyl cyanoacetate (Eastman Kodak Co.) and ammonium hydroxide by the method of Corson et al. (85). An 82% yield of the cyanoacetamide was obtained melting in the range of 118.5-119.5° (literature value, m.p. 119-120° (85)).

Malononitrile II

The malononitrile, 84 g. (1.27 moles), was prepared from cyanoacetamide and phosphorous pentachloride by the method of Corson et al. (86). A 70% yield was obtained and melted in the range of 29-30.5° (literature value m.p. 28-30° (86)). Malononitrile can be vacuum distilled at 113°/30 mm.

Dibromomalononitrile-potassium bromide Complex III

$[Br_2C(CN)_2]_4KBr$

Due to the irratating effect of this complex on the eyes and nose, the amount of material prepared in this synthesis was not determined.

The dibromomalononitrile-potassium bromide complex was prepared from malononitrile, bromine and potassium bromide using the method of Carboni (87). The orange colored solid recovered from the reaction mixture liberates bromine on exposure to the air or on contact with hands or skin.

This material must be handled with rubber gloves in a good hood.

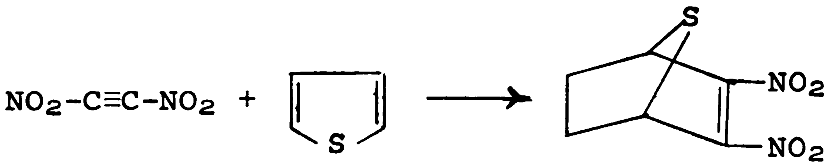
The complex had to be kept thoroughly dry or the yield of tetracyanoethylene was low.

Tetracyanoethylene IV

$(CN)_2C{=}C(CN)_2$

The tetracyanoethylene, 48 g. (0.375 mole), was prepared from the dibromomalononitrile-potassium bromide complex using Carboni's method (87). The yield of tetracyanoethylene was 53% and melted in the range of 192-197° (sealed tube) (literature value 201-202.5° (sealed tube)(87)). After vacuum sublimation through charcoal at 130-140°/1 mm. Hg. its melting point was 201-202° (sealed capillary tube).

The Reaction of Dinitroacetylene with Thiophene



To a solution of dinitroacetylene (20 g., 0.25 mole) was added a precooled (5°) solution containing 20 ml. of redistilled thiophene in 20 ml. of dried benzene during two hours. The reaction mixture was set aside for four days (5°), during which a small quantity of a white solid precipitated. The solid was recovered on a Buchner funnel using No. 1 Whatman paper. The filtrate was returned to the flask and the latter was immersed in an ice bath. The solid was transferred to a watch glass, and in the process of transferring it from the filter paper with a metal spatula the material exploded.

After the filtrate had been set aside for an additional seven days at -3°, it was allowed to warm to room temperature and left at this temperature behind a barricaded wall, for an additional three days. During this time the reaction mixture had taken on a red-brown coloration. The benzene and excess thiophene were removed in a rotary evaporator under reduced pressure yielding 84 g. quantity of a very dark reddish brown colored tarry residue.

A sodium fusion test of this material (several exploded before one was obtained) indicate the presence of nitrogen and the absence of sulfur.

The above reaction was repeated except that diethyl ether was used as the solvent in place of benzene. A 15 ml. volume of the reaction mixture was transferred to a watch glass and the ether was removed with a stream of nitrogen gas leaving a residual yellowish oil.

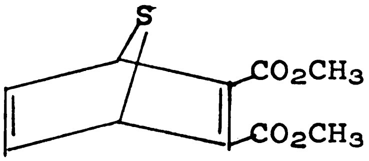
This oil exploded spontaneously at about 28°.

Dinitroacetylene appears to be quite hazardous to handle in the laboratory.

This material is mentioned in several places in the German Rocket Literature of the second world war. A literature search did not disclose any actual proof that the material had ever been prepared.

The analytical methods applied to this material gave very erratic results. The zinc reduction of the nitro groups was the primary analytical method used.

Attempted Preparation of Dimethyl-7-thiabicyclo[2.2.1]-heptadiene-2,5-dicarboxylate (2,3)



Caution: Dimethyl acetylenedicarboxylate is a very strong lachrymator. All operations should be done in a hood.

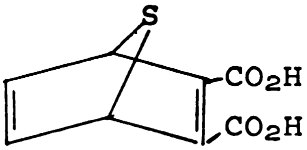
In a 250 ml., single necked, round bottom flask, was placed 5 g. (0.035 mole) of dimethylacetylenedicarboxylate, 5 ml. (5.45 g., 0.065 mole) of redistilled thiophene and 25 ml. of tetrahydrofuran redistilled from lithium aluminum hydride.

The reaction mixture was set aside for seven days at room temperature. The solvent and excess thiophene were removed in a rotary evaporator under reduced pressure. A viscous liquid, 4.65 g., was recovered which gave a negative sulfur test using the sodium fusion-lead acetate method.

The above procedure was repeated except the reaction was refluxed for 72 hrs. The flask was cooled and the solvent and excess thiophene were removed in a rotary evaporator under reduced pressure. A tar, 5.9 g., was recovered which gave a negative sulfur test using the sodium fusion-lead acetate method.

The above procedures were repeated except that diethyl ether was used as the solvent. Neither of these reactions gave a product containing sulfur.

Attempted Preparation of 7-Thiabicyclo[2.2.1]-heptadiene-2,5-dicarboxylic(2,3) acid



In a 250 ml., single necked, round bottom flask, was placed 4 g. (0.035 mole) of acetylene dicarboxylic acid, 5 ml. (5.45 g., 0.065 mole) of redistilled thiophene and 25 ml. of tetrahydrofuran redistilled from lithium aluminum hydride.

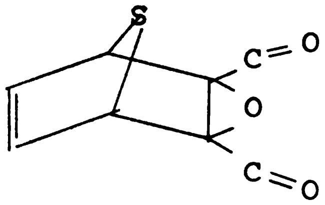
The reaction mixture was set aside for seven days at room temperature. The solvent and excess thiophene were removed in a rotary evaporator under reduced pressure. The solid recovered weighed 4.1 g., and melted in the range 172-175°, the melting point of acetylenedicarboxylic acid. The solid gave a negative sylfur test using the sodium fusion-lead acetate method.

The above procedure was repeated except the reaction was refluxed for 72 hrs. .The reaction flask was cooled and the solvent and excess thiophene were removed in a rotary evaporator under reduced pressure. A solid weighing 3.7 g., melting in the range 171-176°, was recovered. The solid gave a negative sulfur test using the sodium fusion-lead acetate method.

The above procedure was repeated except diethyl ether was used in place of tetrahydrofuran. Neither reaction, under reflux or being set aside at room temperature, gave a reaction product containing sulfur.

Attempted Preparation of 7-Thiabicyclo[2.2.1]-heptene-5-dicarboxy[2,3]anhydride (24)

(3,6-endothio-Δ^4-tetrahydrophthalic anhydride)



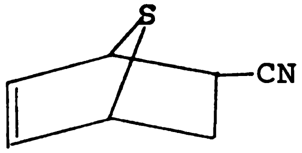
In a 500 ml. single necked, round bottom flask, was placed 50 ml. (54.5 g., 0.65 mole) of redistilled thiophene, 50 g. (0.51 mole) of maleic anhydride and 200 ml. of tetrahydrofuran redistilled from lithium aluminum hydride. The reaction mixture was set aside for seven days at room temperature with continuous stirring by a magnetic stirrer. The solvent and excess thiophene were removed in a rotary evaporator under reduced pressure. A solid weighing 49.0 g. was recovered and gave a negative sulfur test using the sodium fusion-lead acetate method.

The above reaction was repeated except the reaction mixture was heated at its reflux temperature for 24 hrs. The reaction flask was cooled and the excess solvent and thiophene were removed in a rotary evaporator under reduced pressure, yielding 48.5 g. of a solid. The solid gave a negative sulfur test using the sodium fusion-lead acetate method.

The above reaction was repeated except diethyl ether was used as the reaction solvent. Again the product obtained did not contain sulfur.

The above reaction was repeated a third time except that 200 ml. of excess thiophene was used as the reaction solvent. Neither reaction, being set aside at room temperature or heating it at its reflux temperature for 72 hrs., gave a reaction product containing sulfur.

Attempted Preparation of 2-Cyano-7-thiabicyclo[2.2.1]-heptene



In a 500 ml., single necked, round bottom flask, was placed 50 ml. (54.5 g., 0.65 mole) of redistilled thiophene, 50 ml. (70 g., 1.3 moles) of redistilled acrylonitrile and 200 ml. of tetrahydrofuran redistilled from lithium aluminum hydride. The reaction mixture was set aside for one week at room temperature, during which time it became yellow in color. The excess solvent was removed in a rotary evaporator under reduced pressure. The light yellow colored tacky residue was twice tested qualitatively for sulfur by the sodium fusion-lead acetate method. The test results were negative.

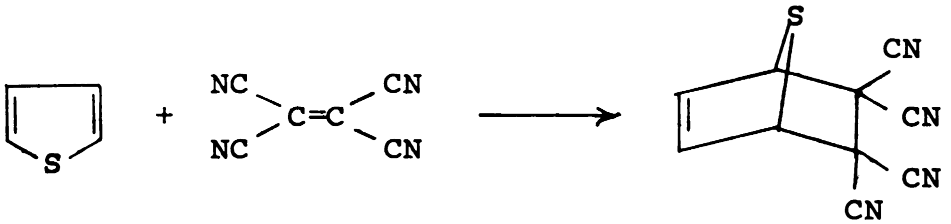
The reaction described above was repeated with the exception that it was heated at its reflux temperature for 72 hrs. on a steam bath. After cooling the reaction mixture and removing the excess solvent and reactants in a rotary evaporator, the residue was tested for sulfur using the sodium fusion-lead acetate method. The test result was negative.

The above reaction was repeated a third time substituting diethyl ether for the tetrahydrofuran and again only negative sulfur test results were obtained.

The reaction was repeated a fourth and fifth time. One was set aside at room temperature for one week and the other was heated at its reflux temperature for 72 hrs. In both reactions the only solvent used was the thiophene and acrylonitrile. Both of the residues obtained from these reactions after removing the excess reactants gave negative tests for sulfur using the sodium fusion-lead acetate method.

The above general experimental procedures were employed using acrylic acid and methyl acrylate with thiophene in place of the acrylonitrile in an effort to obtain the endo-thiobicyclo compound. Under the conditions used, only a polymeric material was obtained which gave a negative sulfur test using the sodium fusion-lead acetate method.

The Reaction of Tetracyanoethylene (43,44) with Thiophene



In a tared 300 ml., three necked, round bottom flask equipped with a stirrer, reflux condenser and a dropping funnel, was placed 85 ml. of redistilled thiophene. The flask was cooled to 4° and the stirrer was started. The cooling bath was removed and 1.28 g. (0.01 mole) of tetracyanoethylene (43,44) was added slowly to the reaction flask. There was no apparent reaction temperature rise. The stirred reaction mixture was allowed to warm to room temperature, during which time it became very dark amber-red in color. The reaction temperature was maintained at room temperature for 4 hrs., during which the reaction mixture's color changed to a light yellow. The excess thiophene was removed by distillation under reduced pressure. The recovered light yellow solid weighed 2.4 g., m.p. 138-144° (sealed tube), and the odor of cyanide ion or cyanogen was very strong.

Cairns et al. (43) recrystallized their reaction products from a benzene-cyclohexane solvent system. On attempts to recrystallize the above material, the solid turned dark brown in color and the crystals remaining weighed 0.8 g. and melted at 192-194° (sealed tube). This corresponds to the melting point of tetracyanoethylene. No additional solid was recovered from the solvent when it was removed by distillation under reduced pressure.

The Second Attempt to React Tetracyanoethylene with Thiophene

In the same apparatus as described above was placed 1.86 g. (0.014 mole) of tetracyanoethylene in 15 ml. of tetrahydrofuran redistilled from lithium aluminum hydride. The solution was cooled to 4° by immersion in an ice bath and

10 ml. (11.98 g., 0.13 mole) of thiophene, in 25 ml. of redistilled tetrahydrofuran, was added to the stirred tetracyanoethylene solution during a 30 min. period. The reaction mixture was warmed to room temperature and kept at this temperature for 4 hrs. with constant stirring. The color of the reaction mixture changed from a dark red-yellow to a light amber color. At this point the contents of the flask were transferred to a tared flask using tetrahydrofuran. The solvent and thiophene were removed in a rotary evaporator under reduced pressure. The light yellow solid recovered, weighed 2.96 g. and had a strong odor of cyanide or cyanogen. The flask was swept with dry nitrogen gas for 2 hrs. carrying the exiting gases into a flask containing potassium iodide. Iodine was liberated by the appearance of a brownish-red color in the aqueous solution. The appearance of free iodine indicated that cyanogen was being produced.

In a 50 ml. burette was placed 35 ml. of chromatographic grade alumina. The light yellow reaction solid was dissolved in benzene. The solution, which became dark amber in color, was poured onto the chromatographic column. The section of the column, where the sample was, turned black immediately, began to evolve a gas. The glass chromatographic column became extremely hot and broke.

A Third Attempt to React Tetracyanoethylene with Thiophene

The experimental procedure described above was repeated. After removal of the solvents and thiophene, the solids were transferred to a large sublimator. The sublimator was evacuated to 0.5 mm. Hg. and was heated by immersion in an oil bath. The solid darkened and began to evolve a gas. No product was collected on the water condenser of the sublimator until the temperature of the oil bath reached 110-120°. A solid was then deposited. This solid melted at 195-196° (sealed tube). This was tetracyanoethylene since a mixed melting point with an authentic sample was not depressed. The cold trap had the odor of hydrogen sulfide. The black residue from the sublimator was taken up in diethyl ether. The solution was filtered to remove insoluble materials and then cautiously warmed with hydrochloric acid (IN) on a steam bath for 2 hrs. No reaction had apparently taken place. The reaction mixture was filtered and the black residue which remained failed to melt below 250°. Its infrared spectrum was too complex for structural information to be obtained from it.

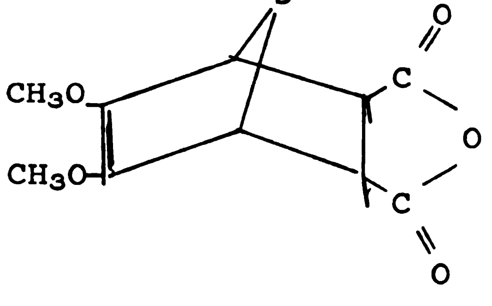
A Fourth Attempt to React Tetracyanoethylene with Thiophene

The experimental procedure used was the same as that employed in the second attempt to conduct this reaction. Attempts to recrystallize the reaction solids from diethyl ether failed. Upon heating the ether solution, it became very dark in color. The dark solid recovered from the ether solution was sealed in a melting point tube and the melting point determined. A glass like solid sublimed and this melted at 192-194° (tetracyanoethylene) leaving in the bottom of the tube a black charred like residue.

The Fifth Attempt to React Tetracyanoethylene with Thiophene

The experimental procedure used was the same as that employed in the second attempt to conduct this reaction. The solid product was heated with 50 ml. of hydrochloric acid (IN). Hydrogen sulfide gas was evolved as well as a gas which had an odor like cyanide. A black polymeric residue remained in the reaction flask. No further attempts to react tetracyanoethylene with thiophene were undertaken because no reaction product, or proof of a reaction, having taken place yielding the endothiobicyclo bridged compound, could be obtained.

The Attempted Preparation of 1,2,3,4-Tetrahydro-5,6-dimethoxy-1,4-endothiophthalic anhydride (2,3)

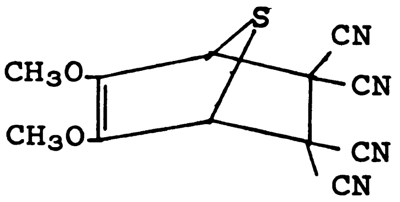


In a 100 ml., single necked, round bottom flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.0 g. (0.014 mole) of 3,4-dimethoxythiophene and 2.0 g. (0.020 mole) of maleic anhydride in 20 ml. of dioxane redistilled from sodium metal.

The reaction mixture was heated at its reflux temperature for 4 hrs. and then it was cooled to room temperature by immersion in an ice bath. The dioxane and other volitile materials were removed by vacuum distillation. The recovered residue was recrystallized twice from cyclohexane to obtain 1.67 g. of maleic anhydride (m.p. 49.5-50.5°). A mixed melting point of this material with an authentic sample of the anhydride was not depressed.

The cyclohexane mother liquor used for the recrystallization was evaporated on a steam bath to obtain 1.1 g. of a liquid residue whose infrared spectrum was found to be identical to the infrared spectrum of 3,4-dimethoxythiophene, indicating that the expected 1,2,3,4-tetrahydro-5,6-dimethoxy-1,4-endothiophthalic anhydride (2,3) had not been obtained.

The Attempted Preparation of 2,2,3,3-Tetracyano-5,6-dimethoxy-1,4-dihydro-1,4-endothiobenzene



In a 100 ml., single necked, round bottom flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.0 g. (0.014 mole) of 3,4-dimethoxythiophene, 2.0 g. (0.016 mole) of tetracyanoethylene in 50 ml. of dioxane redistilled from sodium metal. The reaction mixture was heated at its reflux temperature for 4 hrs. The color of the reaction mixture became a dark blood red during the heating and on cooling to room temperature, a solid crystallized from the reaction mixture. The reaction mixture was set aside for 16 hrs. in a refrigerator at 10°.

The crude solid (3.7 g.) was collected on a Buckner funnel. It was in the form of light pinkish colored platelets and melted in the range of 78-130°. The solid was recrystallized from 10 ml. of a 1:1 benzene:cyclohexane mixture to obtain 0.7 g. of tetracyanoethylene. The "mother liquor" was reduced to 5 ml. in volume by a nitrogen gas stream. On cooling this concentrated solution to 10° for 60 min. an additional quantity of solid was obtained melting in the range 72-114°. During the melting, tetracyanoethylene sublimed onto the cooler portions of the sealed capillary tube.

The solid appeared to be a molecular complex, discussed by Cairns et al. (43) rather than a chemical compound.

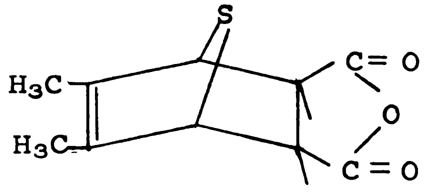
Elemental analysis for C, H, N and S gave very erratic results.

Elemental analysis calc'd for $C_{12}H_8N_4SO_2$: C, 52.9; H, 2.94; N, 20.6; S, 11.76;

Found: C, 60.71, 63.14; H, 1.91, 1.43; N, 24.06, 27.54; S, 8.57, 6.63 (64,65).

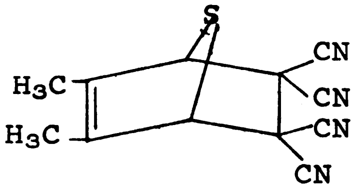
The solid obtained on being set aside for 72 hrs. became wet in appearance and turned brown in color. Based on the analytical results the expected 2,2,3,3-tetracyano-5,6-dimethoxy-1,4-dihydro-1,4-endothiobenzene had not been obtained.

The Attempted Preparation of 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-endothiophthalic anhydride (2,3)



In a 100 ml., single necked, pear-shaped flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.00 g. (0.018 mole) of 3,4-dimethylthiophene, 2.0 g. (0.020 mole) of maleic anhydride in 50 ml. of dioxane redistilled from sodium metal. The reaction mixture was heated at its reflux temperature for 4 hrs. The dioxane and other volatile materials were removed by vacuum distillation, leaving a solid residue of 1.97 g. The residue after recrystallization from cyclohexane melted in the range 49.5-51.0. The material was identified as maleic anhydride by a mixed melting point determination with an authentic sample of maleic anhydride and by its infrared spectrum, which showed that the expected 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-endothiophthalic anhydride (2,3) had not been obtained.

The Attempted Preparation of 2,2,3,3-Tetracyano-1,4-dihydro-5,6-dimethyl-1,4-endothiobenzene



In a 100 ml., single necked, pear-shaped flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 3.6 g. (0.032 mole) of 3,4-dimethylthiophene, 4.1 g. (0.032 mole) of tetracyanoethylene and 50 ml. of dioxane redistilled from sodium metal.

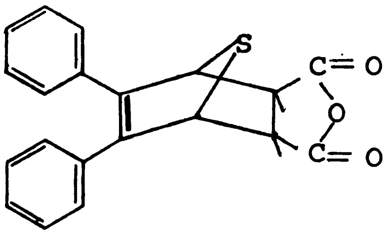
The reaction mixture was heated at its reflux temperature for 4 hrs. The color of the reaction mixture changed to a dark "blood" red coloration during heating. The reaction mixture was cooled to room temperature and a solid crystallized from solution in the form of large platelets. The reaction mixture was set aside in a refrigerator for 16 hrs. at 10°.

The solid was collected on a Buchner funnel. It weighed 6.7 g. and was in the form of light tan crystalline, platelets melting in the range 68 to 120°. Attempts to recrystallize the solid from 60 ml. of 1:1 benzene:cyclohexane mixture yielded a solid melting at 194-196° (sealed tube). This was identified as tetracyanoethylene by a mixed melting point with an authentic sample of tetracyanoethylene and by its identical infrared spectrum to that of tetracyanoethylene.

The filtrate from the above recrystallization was concentrated to 10 ml. in volume under reduced pressure and set aside in a refrigerator for 16 hrs. at 10°. There was obtained a second quantity of light tan colored platelets which melted at 194-196° (sealed tube). Thus, the expected 2,2,3,3-tetracyano-5,6-dimethyl-1,4-dihydro-1,4-endothiobenzene had not been obtained.

The blood red colored solution did indicate that a reaction had occurred and further the 6.7 g. of solid which were obtained would indicate a reaction had taken place. This solid could be the molecular complex discussed by Cairns et al. (43) which on attempts to recrystallize reverts back to the aromatic compound and tetracyanoethylene.

The Attempted Preparation of 1,2,3,4-Tetrahydro-5,6-diphenyl-1,4-endothiophthalic anhydride (2,3)



(Reaction of 3,4-diphenylthiophene with maleic anhydride)

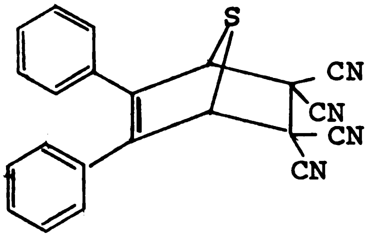
In a 100 ml. single necked, round bottom flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.0 g. (0.0085 mole) of 3,4-diphenylthiophene, 1.0 g. (0.010 mole) of maleic anhydride and 30 ml. of dioxane redistilled from sodium metal.

The reaction mixture was heated at its reflux temperature for 4 hrs. The volume of the reaction mixture was then reduced to 10 ml. and it was set aside in a refrigerator for 16 hrs. at 5°. A solid crystallized from the reaction mixture and was collected on a Buchner funnel. It was recrystallized from cyclohexane to obtain 1.7 g. of 3,4-diphenylthiophene (m.p. 112-113.5°).

The original dioxane mother liquor and cyclohexane mother liquor were combined and the solvents were removed by evaporation on a steam bath. The solid residue was recrystallized from diethyl ether to obtain 0.85 g. of maleic anhydride (m.p. 50.0-52.5°). A mixed melting point of this material with an authentic sample of the anhydride was not depressed.

Thus, the expected 1,2,3,4-tetrahydro-5,6-diphenyl-1,4-endothiophthalic anhydride (2,3) had not been obtained.

The Attempted Preparation of 2,2,3,3-Tetracyano-5,6-diphenyl-1,4-dihydro-1,4-endothiobenzene



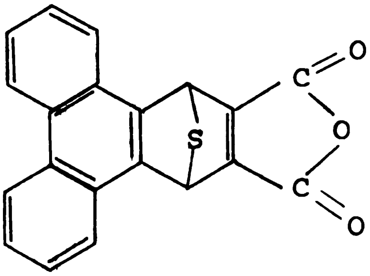
(Reaction of 3,4-Diphenylthiophene with Tetracyanoethylene)

In a 100 ml. single necked, round bottom flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.2 g. (0.0093 mole) of 3,4-diphenylthiophene, 1.4 g. (0.011 mole) of tetracyanoethylene in 50 ml. of dioxane redistilled from sodium metal.

The reaction mixture was heated at its reflux temperature for 4 hrs. The color of the reaction changed from a dark red brown to a light red during the reaction. The reaction mixture was cooled to room temperature and the dioxane was removed by distillation under reduced pressure yielding 3.3 g. of a light yellow crystalline solid (m.p. 108-109.5^{o}). The crude product was recrystallized from a 1:1 benzene:cyclohexane mixture. There was obtained 1.1 g. of tetracyanoethylene (m.p. 197-199^{o} sealed tube) which did not give a mixed melting point depression with an authentic sample of the tetracyanoethylene. Further the infrared spectrum of the material isolated was identical to that of an authentic sample of tetracyanoethylene.

The benzene:cyclohexane mother liquor from the recrystallization was evaporated to dryness on a steam bath. The solid residue was recrystallized from diethyl ether, yielding 2.1 g. of 3,4-diphenylthiophene. A mixed melting point of this material with an authentic sample of 3,4-diphenylthiophene, was not depressed. Thus, the expected 2,2,3,3-tetracyano-5,6-diphenyl-1,4-dihydro-1,4-endothiobenzene had not been obtained.

The Preparation of 5,6,7,8-Dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalene(2,3) anhydride (9) by the Reaction of 4,5,6,7-Dibenzoisothionaphthalene with Maleic Anhydride



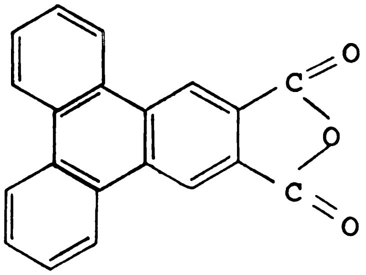
In a 100 ml. single necked, pear-shaped flask, equipped with a reflux condenser fitted with a calcium chloride drying tube was placed 2.34 g. (0.010 mole) of 4,5,6,7-dibenzoisothionaphthalene, 1.47 g. (0.015 mole) of maleic anhydride and 25 ml. of dioxane redistilled from sodium metal.

The reaction mixture was heated at its reflux temperature for 4 hrs. and allowed to cool to room temperature by immersion in an ice bath. It was then concentrated to 10 ml. and an insoluble product separated from solution. The crude product was recrystallized twice from hexane to obtain 2.5 g. (0.0075 mole, 75% yield) of 5,6,7,8-dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalic(2,3)anhydride melting in the range 216-219° (literature value m.p. 219-220° (9)).

Anal. Calc'd for $C_{20}H_{12}O_3S$: C, 72.40; H, 3.62; S, 9.65; Found: C, 72.37, 72.44; H, 3.67, 3.58; S, 9.59, 9.63% (64).

A 0.5 g. sample of the product was refluxed for 4 hrs. with 5 ml. of methanol containing 0.5 ml. of concentrated hydrochloric acid. The solid isolated from this reaction was only the starting material as was evidenced by comparison of its infrared spectrum with that of the original sample and by a mixed melting point with the original sample which was not depressed (m.p. 218-220°).

A 0.5 g. (0.0015 mole) sample of the dibenzoendothionaphthalene was fused with 2 g. of sodium hydroxide at 300° for 15 min. The reaction product was dissolved in water, neutralized with hydrochloric acid and the solid collected, was recrystallized twice from benzene to obtain 0.31 g. (0.001 mole, 66.7% yield) of 5,6,7,8-dibenzonaphthalic(2,3) anhydride melting in the range 246-252° (d) (literature value m.p. 248-250° (d)(9))

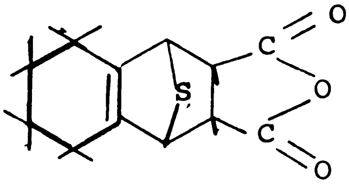


Anal. Calc'd for $C_{20}H_{10}O_3$: C, 80.53; H, 3.35;

Found: C, 76.63, 79.77; H, 3.61, 3.58 (64).

This product may have some acid present in it. The elemental analysis calculated for $C_{20}H_{12}O_4$ is C, 75.93; H, 3.79. Apparently some saponification-hydrolysis of the anhydride has occurred during the fusion with sodium hydroxide and in the subsequent isolation.

The Preparation of 1,2,3,4,5,6,7,8-Octahydro-1,4-endothionaphthalene(2,3)anhydride by the Reaction of 4,5,6,7-Tetrahydrobenzo[C]thiophene with Maleic Anhydride



In a 100 ml. single necked, pear-shaped flask, equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.00 g. (0.014 mole) of 4,5,6,7-tetrahydrobenzo[C]thiophene, 1.50 g. (0.015 mole) of maleic anhydride and 25 ml. of dioxane redistilled from sodium metal.

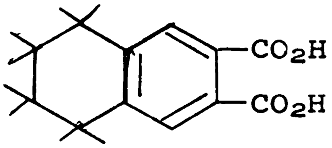
The reaction mixture was heated at its reflux temperature for 4 hrs. and then set aside for 16 hrs. at 5° in a refrigerator. The product was recrystallized twice from hexane to obtain 1.63 g. (0.078 mole, 54.3%) of 1,2,3,4,5,6,7,8-octahydro-1,4-endothionaphthalene(2,3)anhydride melting in the range 83-85° (d).

Anal. Calc'd for $C_{12}H_{12}O_3S$: C, 60.99; H, 5.12; S, 13.57; Found: C, 60.15, 60.43 (64,65); H, 4.97, 5.04 (63,64); S, 13.11, 13.54 (63,64).

A 0.5 g. sample of the octahydroendothionaphthalene was refluxed for 4 hrs. with 5 ml. of methanol containing 0.5 ml. of concentrated hydrochloric acid. During the reaction time hydrogen sulfide was evolved as evidenced by its odor and by blackening of lead acetate test paper. The crude product (0.3 g.) isolated from the reaction was recrystallized twice from hexane and melted at 212-214°. Its infrared spectrum indicated that the anhydride functional group was absent and the carboxyl group absorption was present. The qualitative test for sulfur by the sodium fusion-lead acetate method indicated that sulfur was absent in the product.

A 0.5 g. sample of the 1,2,3,4,5,6,7,8-octahydro-1,4-endothionaphthalic anhydride, was fused with 2 g. of sodium hydroxide at 300° for 15 min. The reaction product was dissolved in water, neutralized with hydrochloric acid (6N) and the solid obtained was recrystallized twice from benzene to obtain 0.27 g. of a solid, melting at 211-214°. This was identical to the solid obtained from the reaction of methanolic hydrochloride and octahydroendothionaphthalic anhydride, as was evidenced by no mixed melting point depression and both infrared spectra were identical.

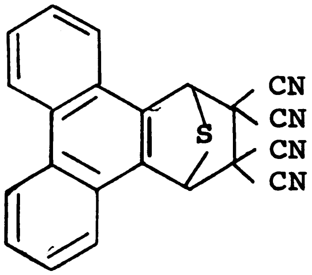
It is very probable that the solid product was 5,6,7,8-tetrahydronaphthalic(2,3)acid.



Anal. Calc'd for $C_{12}H_{12}O_4$: C, 65.50; H, 5.50;

Found: C, 64.97, 65.15; H, 5.93, 5.61 (64).

The Preparation of 5,6,7,8-Dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene by the Reaction of 4,5,6,7-Dibenzoisothionaphthalene with Tetracyanoethylene



In a 100 ml. single necked, pear-shaped flask equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.5 g. (0.011 mole) of 4,5,6,7-dibenzoisothionaphthalene, 1.8 g. (0.014 mole) of tetracyanoethylene and 25 ml. of dioxane redistilled from sodium metal.

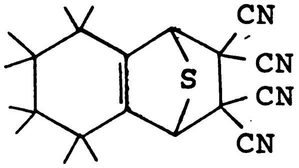
The reaction mixture was heated at its reflux temperature for 4 hrs. and cooled to room temperature. The blood red colored reaction solution was then concentrated to 10 ml. and chilled to 5°. The reddish colored solid which precipitated was collected on a Buchner funnel and recrystallized three times from a 1:1 benzene-cyclohexane solvent to obtain 2.1 g. (0.0059 mole, 53.5% yield) of a solid melting in the range 262-271° (d) which was tentatively identified as 5,6,7,8-dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene.

Anal. Calc'd. for $C_{22}H_{10}N_4S$: C, 72.90; H, 2.76; N, 15.45; S, 8.83;

Found: C, 72.35 (63); H, 2.71 (63); N, 15.61, 15.87 (63,64); S, 8.73, 8.78 (64).

A 0.5 g. sample of the product was refluxed for 4 hrs. with 5 ml. of methanol containing 0.5 ml. of concentrated hydrochloric acid. The reaction mixture turned a dark brown and a gas evolved during the reaction. The product isolated from this reaction was recrystallized three times from hexane to obtain 0.2 g. of a solid melting in the range 218-220°. Its infrared spectrum was identical to the infrared spectrum of the 5,6,7,8-dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalene(2,3)anhydride. A mixed melting point of the two compounds was not depressed.

The Preparation of 1,4,5,6,7,8-Hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene by the Reaction of 4,5,6,7-Tetrahydrobenzo [C] thiophene with Tetracyanoethylene



In a 100 ml. single necked, pear-shaped flask equipped with a reflux condenser fitted with a calcium chloride drying tube, was placed 2.00 g. (0.014 mole) of 4,5,6,7-tetrahydrobenzo [C]thiophene, 2.0 g. (0.16 mole) of tetracyanoethylene and 25 ml. of dioxane redistilled from sodium metal.

The reaction mixture was heated at its reflux temperature for 4 hrs. and cooled to room temperature. The orange red colored reaction solution was concentrated to 10 ml. and chilled at 5°. The reddish colored solid which precipitated was collected on a Buchner funnel and recrystallized twice from a 1:1 benzene-cyclohexane mixture to obtain 2.4 g. (0.009 mole, 62.5% yield) of 1,4,5,6,7,8-hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene melting in the range 154-162° (d). This material was tentatively identified by elemental analysis.

Anal. Calc'd for $C_{14}H_{10}N_4S$: C, 63.15; H, 3.75;

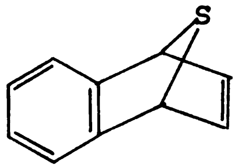
N, 21.06; S, 12.03;

Found: C, 61.21 (63); H, 4.14 (63); N, 19.06 (63); S, 12.70, 12.13 (64).

This material decomposed on being set aside at ambient conditions for two weeks. It was stable for months when stored under nitrogen atmosphere at 0°.

Attempts to make derivatives of this material by treating with methanolic hydrogen chloride or sodium hydroxide fusion or hydrolysis of the nitrile groups with dilute hydrochloric acid led to extensive decomposition and only unidentifiable tarry materials were recovered.

The Attempt to Prepare 1,4-Dihydro-1,4-endothionaphthalene(The Reaction of Thiophene with Benzyne) I



By a procedure similar to that of Wittig and Pohmer (36), thiophene was caused to react with benzyne in the following manner.

In a 300 ml. three necked, round bottom flask, equipped with a stirrer, condenser fitted with a calcium chloride drying tube, and a parallel adapter fitted with a gas inlet tube and a dropping funnel; was placed 1.5 g. (0.062 g. at.) of Grignard grade magnesium turnings. The apparatus was swept with oxygen free dry nitrogen gas, while the magnesium turnings and reaction flask were heated by a "hot air gun" to remove moisture from the system.

When the system was dry and had cooled to room temperature, the magnesium turnings were covered with 12 ml. of tetrahydrofuran redistilled from calcium hydride and then 4.2 g. (0.05 mole) of redistilled thiophene was added. The stirrer was started and a small crystal of iodine was added. The reaction flask and contents were heated at 50° until the iodine color disappeared, and then a solution of 8.7 g. (6 ml. 0.05 mole) of o-fluorobromobenzene (Beckwith Chemical Co.) in 12 ml. of tetrahydrofuran, redistilled from calcium hydride, was added. The reaction was initiated by heating the reaction flask with a hot air gun until the tetrahydrofuran commenced to reflux.

The reaction mixture was stirred for 96 hrs. under a nitrogen atmosphere, cooled, and filtered to remove the excess magnesium. The magnesium residue in the reaction flask was extracted with three 50 ml. portions of diethyl ether.

The combined reaction mixture and ether extracts were treated first with 150 ml. of 5% hydrochloric acid and then washed with two 50 ml. portions of water. The organic layer was dried over anhydrous magnesium sulfate and the volatile materials were removed by distillation under reduced pressure. The remaining brown viscous residue weighed 6.0 g. and had an odor similar to an ester or flavone.

The residue was dissolved in 20 g. of methylene chloride. Two, 20 μl. aliquots of this solution were injected into a Perkin-Elmer gas chromatograph having a G. E. silicone rubber column at 150° (helium as a carrier, 15 ml./min.).

The chromatograms gave 14 and 20 peaks of which 8 and 11, respectively, were of about the same proportions. Two, 10 μl. aliquots of this solution were injected into a F & M gas chromatograph using a G. E. silicone rubber column and temperature programmed from 150 to 300° (helium as carrier, 25 ml./min). The temperature of the injection port was 250° and the temperature of the flame ionization detector was 300°. The two chromatograms gave 54 and 76 peaks, respectively. Many of the peaks were broad indicating very probably that appreciable thermal decomposition had occurred in the chromatograming.

The infrared spectrum of a solvent freed residue of the above solution was extremely complex and indicated clearly that more than a single component was present.

Qualitative tests using the sodium fusion-lead acetate method indicated that sulfur was present in fairly large amounts in the crude reaction products.

Second Reaction of Thiophene with Benzyne

In a dry 300 ml. three necked flask, equipped with a stirrer, reflux condenser fitted with a calcium chloride drying tube, adapter fitted with a gas inlet tube and a dropping funnel; was placed 4.0 g. (0.16 g. at.) of Grignard grade magnesium turnings, 17.6 g. (0.21 mole) of redistilled thiophene and 20 ml. of tetrahydrofuran redistilled from calcium hydride.

The system was flushed with dry oxygen free nitrogen gas and the reaction mixture was kept under a nitrogen atmosphere for the duration of the reaction. To the stirred thiophene magnesium suspension was added dropwise, a solution containing 18.1 g. (0.11 mole) of o-fluorobromobenzene and 20 ml. of tetrahydrofuran redistilled from calcium hydride.

At the end of four days no apparent reaction had taken place. The reaction mixture was then heated by a "hot air gun" until the solvents commenced to reflux. The reaction initiation was evidenced by a cloudy appearance in the reaction mixture. The reaction mixture was maintained at the reflux temperature for 24 hrs.

The contents in the reaction flask at this point had become a dark brown viscous liquid with a sweet ester odor. The reaction product was dissolved in 50 ml. of diethyl ether, and the unreacted magnesium was removed by filtration.

The filtrate was hydrolized with three, 100 ml. portions of saturated ammonium chloride to decompose any unreacted Grignard reagent and complex magnesium salts. The organic layer was then washed with 20 ml. of hydrochloric acid solution (5%) and finally with two, 25 ml. portions of water.

Hydrogen sulfide was evolved during these washings as evidenced by its odor and a lead acetate test paper test.

The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered into a tared 500 ml. single necked flask. The solvents and excess thiophene were removed in a rotary evaporator under reduced pressure. A light brown viscous residue, weighing 12.0 g., was obtained. This material had a sweet ester odor.

The crude product was fractionally distilled, to obtain two fractions; 2.7 g., b.p., $105-111^{o}/0.15$ mm. Hg., 2.1 g., b.p., $140-145^{o}/0.15$ mm. Hg. There was evidence of some decomposition having occurred during the distillation by the burnt odor and the dark brown color of the distillation residue. A light yellow colored solid was recovered from the dry ice trap used in the distillation apparatus and hydrogen sulfide was also present in the trap as evidenced by its odor and a lead acetate test paper test.

The distillation residue was dissolved in chloroform, decolorized with Norite, filtered and set aside in a refrigerator for 16 hrs. at 5^{o} in an effort to obtain a crystalline product, but without success. On removal of the chloroform, a viscous tarry residue remained which weighed 6.8 g.

The preceding vacuum distillates were combined and chromatographed on an aluminum oxide column (Brock Activity I) using ligroin ($60-90^{o}$) as the eluent. The eluent was collected in 50 ml. fractions, and the solvent was removed from the fractions by an air sparge.

The first solid fraction obtained weighed 2.3 g. and melted in the range 35.0-36.5°. This was identified as 2-phenylthiophene by comparison of its infrared spectrum with a spectrum of an authentic sample of 2-phenylthiophene and by a mixed melting point, with an authentic sample of 2-phenylthiophene, which was not depressed.

The amount of this material obtained was 2.3 g. represents 0.014 mole, or a 13% yield of 2-phenylthiophene. After recrystallization from ethanol (95%), this material melted in the range 41.0-42.5° (literature values m.p. 35-36° (88) and 40-41° (89)).

The second solid fraction obtained weighed 0.8 g. and had a melting range of 88.5-90.2°. After recrystallization from methanol, it melted in the range 90.5-91.5°. The solid was identified as 3-phenylthiophene by comparison of its infrared spectrum with the spectrum of an authentic sample of 3-phenylthiophene and by a mixed melting point of this material with an authentic sample of 3-phenylthiophene which was not depressed. The 0.8 g. of pure product obtained represents 0.005 mole, or a 4.5% yield of 3-phenylthiophene.

A third solid was obtained and melted in the range 191-194° (36). This gave a negative qualitative sulfur test using the sodium fusion-lead acetate method. This was 0.8 g. of triphenylene (0.0035 mole, 3.2%) and was identified by a mixed melting point with an authentic sample of triphenylene which was not depressed and by the comparison of its infrared spectrum with the spectrum of triphenylene.

Further elution of the column with benzene yielded 0.6 g. of a colorless oil which gave a negative qualitative sulfur test. Microdistillation of this oil gave a product with a boiling range unsuitable for identification purposes. Its infrared spectrum indicated the presence of an aromatic group and additional unsaturation. This infrared spectrum appeared to be similar to the spectrum of dihydronaphthalene.

The distillation residue was treated with various organic solvents in efforts to obtain a crystalline material, but were unsuccessful. The residue was then chromatographed on an aluminum oxide column (Brock's Activity I) and eluted with ligroin (60-90°). The first solid obtained weighed 0.1 g. and melted in the range 83-84°. This material was identified as 2,3-diphenylthiophene by its infrared spectrum and its melting point (57). The second solid obtained weighed 0.3 g. and melted in the range 107-111°. On recrystallization from ethanol, it had a melting point of 112-114° (74,78). A mixed melting point of this material with an authentic sample of 3,4-diphenylthiophene was not depressed.

Further elution using a 2:1 ligroin:benzene mixture gave a third solid, weighing 0.3 g., which melted in the range 151-153° (57). This material was identified as 2,5-diphenylthiophene by a mixed melting point with an authentic sample of 2,5-diphenylthiophene which was not depressed (m.p. 146-147.5° (90,91)) and by comparison of its infrared spectrum to the spectrum of an authentic sample of the 2,5-diphenylthiophene.

A fourth solid, weighing 0.3 g., was obtained which melted in the range 142-144°. The solid contained sulfur as shown by the sodium fusion-lead acetate test method and by its infrared spectrum did not appear to be a phenylthiophene.

Continued elution with a 1:1 ligroin:benzene mixture and finally by benzene gave four additional solids in trace quantities (<0.1 g.) with melting point ranges of 213-216°, 230-232°, 276-280° and 314-320°, respectively. All of these solids contained sulfur as shown by qualitative tests. Infrared spectra of the solids were not sufficiently informative for their identification.

During the elution some oily fractions, weighing 3.0 g., were obtained, which did not contain sulfur and these were discarded.

Elution with chloroform after the benzene elution yielded a solid (0.8 g.) melting in the range 195-198°, and identified as triphenylene.

The Third Attempt to Prepare 1,4-Dihydro-1,4-endothionaphthalene

A 300 ml., three necked, round bottom flask was equipped with a stirrer, and two parallel adapters; one adapter fitted with a gas inlet tube, and a 100 ml. dropping funnel, the other fitted with a reflux condenser protected by a calcium chloride drying tube, and a 100 ml. dropping funnel.

The reaction flask was charged with 4.0 g. (0.17 g. at.) of Grignard grade magnesium turnings. The apparatus was then heated by a "hot air gun" while dry oxygen free nitrogen gas was passed through the system to remove all moisture. After the apparatus and magnesium had been dried, 20 ml. of tetrahydrofuran redistilled from calcium hydride and a small crystal of iodine were added to the reaction flask. The stirred reaction mixture was heated by the "hot air gun" until the tetrahydrofuran was gently refluxing. The heating was continued until the iodine color had disappeared to activate the magnesium. The reaction flask and its contents were cooled to room temperature by an ice bath.

In the first dropping funnel was placed 19.2 g. (0.228 mole) of redistilled thiophene in 25 ml. of tetrahydrofuran redistilled from calcium hydride. In the second dropping funnel was placed 18.7 g. (0.107 mole) of o-fluorobromobenzene in 25 ml. of tetrahydrofuran redistilled from calcium hydride. A few drops of the o-fluorobromobenzene solution were added to the stirred reaction mixture and was heated by the hot air gun until the tetrahydrofuran began to reflux and a cloudiness appeared in the reaction mixture. The remaining o-fluorobromobenzene solution was added dropwise (60 min.) simultaneously with the thiophene solution at a rate such that the thiophene was in excess and that the reaction was not abated. The reaction was slow to initiate and it was necessary to heat the mixture to sustain the initial reaction. After 15 mins. the reaction was exothermic enough to maintain the solvent at its reflux temperature during the remaining addition of the o-fluorobromobenzene (45 min.). During this time the color of the reaction mixture changed from colorless to dark brown and the magnesium had nearly all reacted.

The stirred reaction mixture was heated at its reflux temperature for an additional 16 hrs. and then cooled to room temperature. It was filtered to remove the unreacted magnesium using 25 ml. of tetrahydrofuran as a transfer agent. The filtrate was diluted with 100 ml. of diethyl ether and the complex magnesium salts were hydrolyzed with three, 100 ml. portions of a saturated ammonium chloride solution. Some gas evolution occurred and a strong odor of hydrogen sulfide was in evidence. The organic layer was washed with two, 100 ml. portions of water and dried over anhydrous magnesium sulfate.

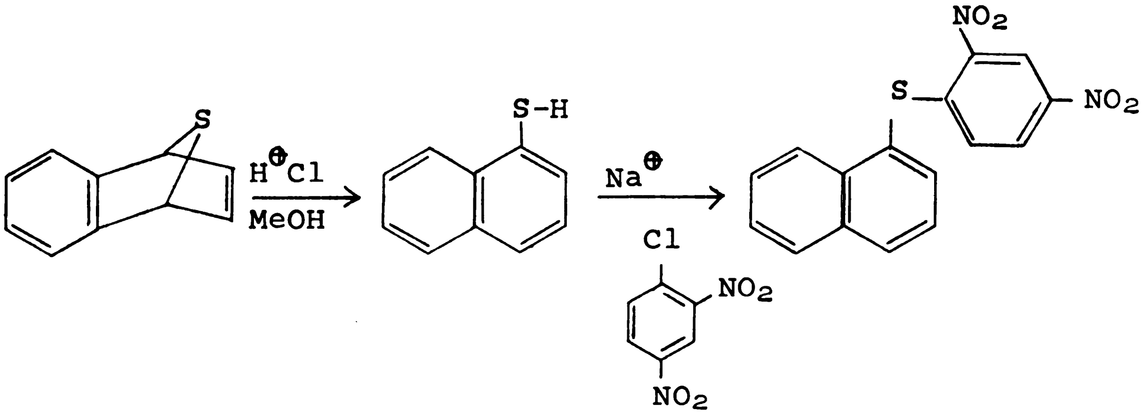
The dried organic layer was transferred to a tared flask and the volatile solvents were removed by vacuum distillation, to obtain 12.4 g. of a brown viscous material which had a sweet ester like odor. Elemental analysis for sulfur gave 12.23% (64) (calculated for 1,4-dihydro-1,4-endothionaphthalene, $C_{10}H_8S$, S = 20.0%).

The reaction product (11.0 g.) was vacuum distilled and the fraction (4.1 g.) distilling from 50-105°/0.05 mm. Hg. was collected. This material was redistilled in a micro vacuum distillation apparatus with four receivers. The following fractions were collected; 0.8 g. b.p. 60-85°/0.05 mm. Hg., (S = 10.96, 12.06% (64.66)); 1.8 g., b.p. 85-95°/0.05 mm. Hg., (S = 19.80, 19.94% (64,66)); 0.6 g., b.p. 95-105°/0.05 mm. Hg., (S = 1.42, 1.26% (64,66)); 0.4 g., b.p. 105-125°/0.05 mm. Hg., (S = 1.54, 2.29% (64,66)).

The second fraction, b.p. 85-95°/0.05 mm. Hg. having 19.80 and 19.94% sulfur was set aside in a refrigerator for 16 hrs. at 0°, to obtain 1.4 g. of a crystalline solid melting in the range 53-56°. This material was recrystallized three times from pentane yielding 1.1 g. (0.0089 mole, 6.4%) of 1,4-dihydro-1,4-endothionaphthalene, a clear crystalline solid melting in the range 78.5-80.0°. This solid slowly turns greenish on standing at room temperature, but remains colorless and stable when maintained at 0°. The above preparation and isolation procedure was repeated three additional times yielding 5.5 g. of the above 1,4-dihydro-1,4-endothionaphthalene.

For structure proof 0.5 g. (3.1 mmoles) of this solid was refluxed for 4 hrs. with 5 ml. of methanol containing 1 ml. of concentrated hydrochloric acid. Some hydrogen sulfide was evolved as evidenced by its odor. After the solution was refluxed, it was cooled, diluted with 10 ml. of water, and made basic (pH 10) with sodium hydroxide. To this basic solution was added 600 mg. of 2,4-dinitrochlorobenzene in 4 ml. of methanol. This solution was refluxed for 10 minutes and then filtered while hot. The solution was cooled (5°) and the thioether allowed to crystallize from solution. The solid thioether was recrystallized twice from methanol, to obtain 0.38 g. (1.16 mmole, 37%) of 2,4-dinitrophenyl-1-naphthylthioether melting at 172.0-173.5° (literature value 174-176° (69)). A mixed melting point with an authentic sample of 2,4-dinitrophenyl-1-naphthylthioether was not depressed. The infrared spectras (65) of both thioethers were identical.

Anal. Calc'd. for $C_{16}H_{10}O_4N_2S$:



C, 58.88; H, 3.10; S, 9.81;

Found: C, 58.1 (64); H, 2.97 (64); S, 9.63, 9.47, 9.76, 9.58 (64,68).

The basic solution from the thiobridge opening reaction was extracted with methylene chloride. On evaporation of the methylene chloride, there was obtained some crystals of an off white colored solid. The solid was recrystallized from n-pentane twice to obtain a solid melting at 80-81°. This solid was identified as naphthalene by comparison of its infrared spectrum with the spectrum of an authentic sample of naphthalene and by a mixed melting point with an authentic sample of naphthalene which was not depressed.

The 1,4-dihydro-1,4-endothionaphthalene was submitted for elemental analysis.

Anal. Calc'd for $C_{10}H_8S$: C, 74.96; H, 5.03; S, 20.01;
Found: C, 71.19, 73.93 (63,64)); H, 5.66, 5.41 (63,64));
S, 19.80, 19.94 (63,64)).

The reaction of thiophene with benzyne has been tried in several solvents; diethyl ether, tetrahydrofuran, dioxane, dimethylether of ethylene glycol and dimethyl sulfoxide.

Diethyl ether was the first solvent tried, the reaction did not appear to occur because the products formed made a tacky ball picking up the magnesium turnings causing the reaction to cease. Dimethyl sulfoxide appeared to have many side reactions and it appeared that the Grignard reagent or the benzyne had added across the sulfur oxygen bond. Tetrahydrofuran was chosen as the best solvent because of the ease in drying it, fewer side reactions, solvates the Grignard complexes and has a low boiling point which was helpful in product isolation.

There were solids and oils isolated from this reaction which did not contain sulfur. These were not investigated because of the number of sulfur containing compounds that were separated and studied. If these other compounds had been identified, they might have added further proof of the formation of the 1,4-endothiobridge.

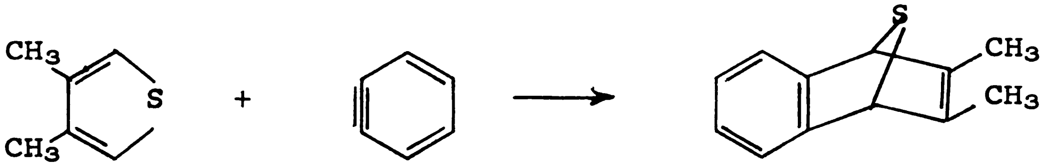
Following the procedures described by Chernois, Entrikin and Hodnett (98) a 0.5 g. (0.003 mole) sample of 1,4-dihydro-1,4-endothionaphthalene was heated under reflux, with 1.5 g. (0.0095 mole) of potassium permanganate, 25 ml. of water, 0.5 ml. of 6 N sodium hydroxide, until the purple color had nearly disappeared. The cooled reaction mixture was neutralized with dilute sulfuric acid, and then heated to boiling. The mixture was cooled and the precipitated acid collected and recrystallized three times from a (1:1) ethanol water mixture to obtain 0.18 g. (0.0013 mole, 98% yield) of phthalic acid melting at 204-207° (literature value 205-208° (98)).

A 0.10 g. (0.0007 mole) of the phthalic acid was heated with aniline and then recrystallized three times from methanol to obtain 0.16 g. (0.00052 mole, 75% yield) of the dianilide of phthalic acid melting at 253-254° (literature value 253-255° (98)). This indicated that the above was phthalic acid. Mixed melting points with an authentic sample of the dianilide of phthalic acid was not depressed.

A 0.3 g. (0.0019 mole) sample of the 1,4-dihydro-1,4-endothionaphthalene was refluxed with 0.5 ml. of hydrobromic acid for 10 min. The solid was collected and recrystallized three times from hot ethanol. A sodium fusion-silver nitrate test indicated the absence of bromide ion. The solid melted at 80.5-81.5° and a mixed melting point with an authentic sample of naphthalene was not depressed. Comparison of its infrared spectrum with an authentic sample of naphthalene also indicated that this solid was naphthalene.

A 0.3 g. (0.0019 mole) sample of the 1,4-dihydro-1,4-endothionaphthalene was reacted with three drops of bromine in chloroform. Two materials were isolated, α-bromonaphthalene and 1,4-dibromonaphthalene (m.p. 81.5-83.0°). Their infrared spectra were identical to the spectra of these materials which had been prepared previously in this study in preparing, α-thionaphthalene.

The Reaction of 3,4-Dimethylthiophene with "Benzyne" (An Attempt to Prepare 2,3-Dimethyl-1,4-dihydro-1,4-endothionaphthalene)



A 300 ml. three necked, round bottom flask was equipped with a stirrer and two parallel adapters; one of the adapters was fitted with a gas inlet tube and a 50 ml. dropping funnel, the other with a reflux condenser, protected by a calcium chloride drying tube, and a 50 ml. dropping funnel.

The reaction flask was charged with 2.9 g. (0.12 g. at.) of Grignard grade magnesium turnings. The apparatus was heated with a "hot air gun" while dry oxygen free nitrogen gas was passed through the system to remove moisture. Following the drying operation 20 ml. of tetrahydrofuran redistilled from calcium hydride and a small crystall of iodine was added to the magnesium.. The stirrer magnesium suspension was heated until the iodine color had disappeared. The reaction flask and contents were cooled to room temperature by an ice water bath.

In one dropping funnel was placed a solution containing 18.7 g. (0.101 mole) of o-fluorobromobenzene in 25 ml. of tetrahydrofuran redistilled from calcium hydride. In the other dropping funnel was placed a solution containing 12.5 g. (0.111 mole) of 3,4-dimethylthiophene in 25 ml. of tetrahydrofuran redistilled from calcium hydride.

A few drops of the o-fluorobromobenzene solution were added to the stirred reaction mixture and it was heated with a "hot air gun" until the tetrahydrofuran commenced to reflux gently and a white cloudiness appeared in the reaction mixture.

The remaining o-fluorobromobenzene and 3,4-dimethylthiophene solutions were then simultaneously added dropwise during 90 min. The reaction was slow to initiate and it was necessary to heat the reaction mixture to sustain the initial reaction. After approximately a quarter of the reactants had been added the exothermic reaction was sufficient to maintain the tetrahydrofuran at its reflux temperature. During the addition of the reactants the color of the reaction mixture changed from a milky white to a reddish-brown.

Following the addition of the reactants the mixture was heated at its reflux temperature for an additional hour and then stirred at room temperature for 16 hrs. It was filtered to remove unreacted magnesium using 25 ml. of tetrahydrofuran as a transfer agent.

Diethyl ether (100 ml.) was added and the complex magnesium salts were hydrolyzed with three, 100 ml. portions of saturated ammonium chloride. Some gas evolution occurred and the odor of hydrogen sulfide was detected. The organic layer was separated, washed with 100 ml. of water and dried with anhydrous magnesium sulfate.

The solvents were removed by distillation under reduced pressure to obtain 13.7 g. of a light brown oil with a sweet ester like odor. (Anticipated obtaining 20 g. of 2,3-dimethyl-1,4-dihydro-1,4-endothionaphthalene.)

To the reaction product was added 10 ml. of diethyl ether and this mixture was set aside in a refrigerator at 5° for 16 hrs. The precipitated solid was collected on a Buchner funnel to obtain 0.7 g. of terphenylene (m.p. 195.0-196.5°) identified by no depression of a mixed melting point (m.p. 194-197°) with an authentic sample of terphenylene and by comparison of the infrared spectrum of this solid with a spectrum of an authentic sample of terphenylene which were identical.

A thin layer chromatographic analysis of 20 μg. samples of the original reaction product using ethyl acetate-chloroform and benzene-chloroform eluents indicated that only a single component was present.

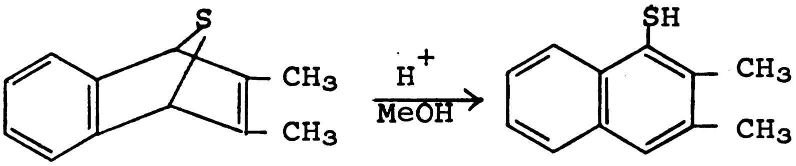
Gas chromatographic analysis of a 0.01 mg. sample on a temperature programmed apparatus (130-250°, 10°/min.) using a Versamide column (3') and a flame detector (He 8.3, Air 120,

H_2 5.0 ml./min.) gave six major peaks (133, 137, 166, 210, 225, 245°) and four minor peaks (157, 176, 255, 260°).

A 1.0 g. sample of the original product was distilled in a micro distillation apparatus. Two drops of a distillate, b.p. 60-70°/0.07 mm. Hg. were collected and on continued heating some liquid appeared to be refluxing in the column at 110-120°/0.07 mm. Hg. The column was rapidly cooled in an attempt to collect a sample of the liquid. The infrared spectrum of the distillate, liquid in the column and the distillation residue appeared to be identical and no separation had occurred. The infrared spectrum of the distillation residue was identical to the original reaction produced even though it had been heated to 230° with the exception of an absorption band at 5.6μ which had disappeared during the heating period.

Elemental analysis for sulfur on a sample of the reaction product after removing the terphenylene gave 5.70 and 5.76% sulfur. Sulfur calculated for $C_{12}H_{12}S$ is 17%.

A 1.0 g. sample of the reaction product, was chromatographed on a 1/2"-8" alumina column (Broch Activity I) eluting with cyclohexane, to obtain ten, 50 ml. fractions. On removing the cyclohexane, fractions 4-9 (light yellow oils, combined weight -0.8 g.) appeared to have identical infrared spectra and these appeared identical to the spectrum of the starting material, which indicated that the expected separation had not been obtained.

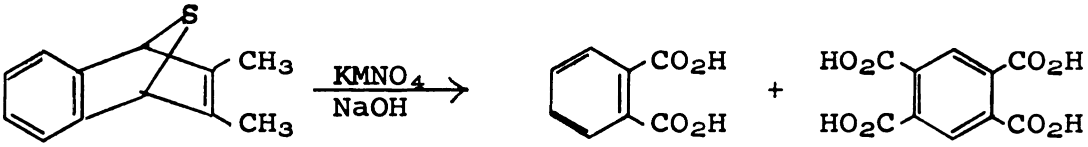


A 1.0 g. sample of the original reaction product was refluxed for 4 hrs. in 10 ml. of methanol containing 2 ml. of concentrated hydrochloric acid. Hydrogen sulfide was evolved as was evidenced by its odor and by a lead acetate paper test.

The solution was diluted with 10 ml. of water and made basic (pH 10) with sodium hydroxide. This solution was extracted with three, 10 ml. portions of methylene chloride to remove all organic substances except the sodium salt of the mercaptan (sodium thionaphthanate). The infrared spectrum of the residue after removal of the methylene chloride from the extract (0.9 g.) appeared to be identical to the spectrum of the original reaction product except for the appearance of an absorption band at 5.86 μ.

The basic solution obtained above possibly containing the sodium thionaphthanate was acidified with hydrochloric acid (5%) and the acid solution was extracted with three, 10 ml. portions of methylene chloride. On removal of the methylene chloride there was obtained 0.05 g. of a yellow waxy material having a "sour odor". (The infrared spectrum was different from the starting material; the 11.65 μ absorption band had disappeared; the 5.60 μ band had disappeared and new adsorption bands at 7.9 μ, 8.4 μ, 10.3 μ were found.)

The waxy solid was dissolved in 2 ml. of methanol and made basic with sodium hydroxide (3 drops 6N) and then 0.1 g. of 2,4-dinitrochlorobenzene was added to the solution. The mixture was heated at its reflux temperature for a half hour and set aside at 5° for 2 hrs. The solid isolated was 2,4-dinitrochlorobenzene (m.p. 49.5-51.0°). The expected 2,4-dinitrophenylthioether was not found.



A 1.0 g. sample of the original reaction product was refluxed for 2 hrs. with 3.0 g. of potassium permanganate, 35 ml. of water and 0.5 g. of sodium carbonate (98). The reaction mixture was cooled and acidified carefully with dilute sulfuric acid (6N). The manganese dioxide and excess permanganate were destroyed with solid sodium bisulfite.

The solution was cooled to 5° and filtered to remove the precipitated acidic material. The crude acid melted in the range 92-181°.

The acidic solution obtained above was extracted with three, 10 ml. portions of methylene chloride. On removal of the methylene chloride a light tan crystalline solid residue was obtained melting in the range 55-104°.

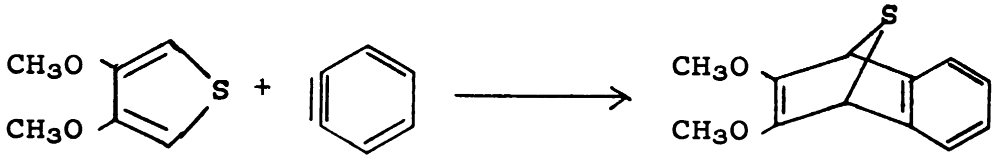
The two acidic solids were combined (0.61 g.) and chromatographed on a 1/3"-6" alumina column (Broch Activity I) eluting with cyclohexane. Traces of benzoic acid were found (identified by infrared spectrum comparison and mixed melting point tests) as well as phthalic acid. In addition an acidic material (m.p. 56-59°) and traces of other acidic material not in sufficient quantity to determine their melting point or structure were also found.

A sample of the original reaction product, dimethylthiophene and benzyne, was submitted for elemental analysis.

Anal. Calc'd. for $C_{12}H_{12}S$: C, 76.7; H, 6.37; S, 17.0; Found: C, 79.1; H, 10.97; S, 5.70, 5.76; Halogen as Cl, 3.54.

The reaction between 3,4-dimethylthiophene and benzyne did not yield the expected product 2,3-dimethyl-1,4-dihydro-1,4-endothionaphthalene. The product appeared to be a complex mixture which was very stable. On standing at room temperature for 6-7 weeks, no apparent decomposition had occurred.

The Reaction of 3,4-Dimethoxythiophene with "Benzyne" in an Attempt to Prepare 2,3-Dimethoxy-1,4-dihydro-1,4-endothionaphthalene



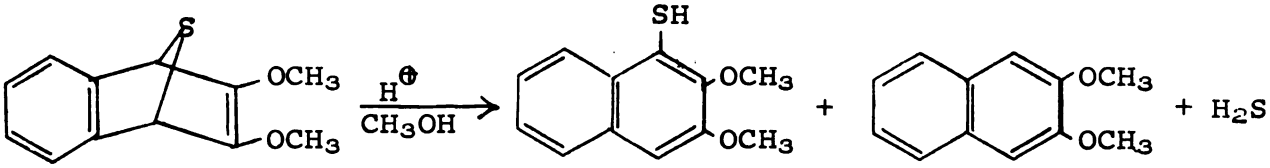
This preparation was carried out in the same apparatus described above for the reaction of 3,4-dimethylthiophene with benzyne, using 2.8 g. (0.11 g. at.) of Grignard grade magnesium turnings, 15.0 g. (0.104 mole) of 3,4-dimethoxythiophene and 20.0 g. (0.114 mole) of o-fluorobromobenzene. The reaction product was isolated as previously described and after the solvents were removed by distillation under reduced pressure, there was obtained 19.6 g. of a brown oily product which had a sweet ester-like odor. Elemental analysis for sulfur gave 12.3% S (64).

A thin layer chromatographic separation of a 0.8 g. sample of the product in 25 ml. of ethyl acetate, using ethyl acetate and chloroform elution gave a major spot, a minor spot and two trace spots. The major and minor spots fluoresced under ultraviolet light and both turned brown after a 10 min. exposure to iodine vapors.

The original product (18.5 g.) was dissolved in 20 ml. of diethyl ether and set aside in a refrigerator for 16 hrs. at -5°. A crystalline solid separated from solution and was collected by filtration on a Buchner funnel, to obtain 0.7 g. (0.003 mole) of terphenylene melting at 194-196°. Its infrared spectrum was identical with a spectrum of an authentic sample of terphenylene and a mixed melting point with an authentic sample of terphenylene showed no depression (m.p. 193-195°).

A 1.0 g. sample of the original reaction product was distilled in a short path high vacuum distillation apparatus.

Two fractions were collected; 0.2 g., b.p. 60-90°/0.005 mm. Hg., and 0.2 g., 90-110°/0.005 mm. Hg. The infrared spectras of the two fractions appeared to be identical to the starting material. No additional distillate was obtained by heating the sample to 200° (still temperature) but decomposition occurred in the still as evidenced by the residue turning black and by the burnt odor.



A 0.5 g. sample of the reaction product was refluxed for 4 hrs. with 5 ml. of methanol containing 1 ml. of concentrated hydrochloric acid. Hydrogen sulfide was evolved as evidenced by its odor and by a lead acetate paper test. The solution was diluted with 10 ml. of water, made basic (pH 10) with sodium hydroxide and extracted with three, 15 ml. portions of methylene chloride. The basic solution was labeled, B-1, and set aside. The infrared spectrum of the residue after removal of the methylene chloride was different from the original starting material. The spectrum did not have 3,4μ absorption band (-S-) and the methoxyl group absorption could not be observed. Attempts to identify the oily material as 2,3-dimethoxy-1,4-dihydronaphthalene or 2,3-dimethoxynaphthalene were unsuccessful.

The oily residue was refluxed with basic potassium permanganate for 4 hrs. The excess permanganate was destroyed with sodium bisulfite. The solution was made acid with 5% hydrochloric acid and extracted with methylene chloride. The infrared spectrum of the residue after removal of the methylene chloride indicated the presence of a carboxyl group but that a methoxyl group was absent. The oxidized material was chromatographed on a 1/2"-6" alumina column and yielded traces of benzoic acid (mixed m.p. not depressed), phthalic acid (mixed m.p. not depressed) and other additional acidic materials.

The basic solution, B-1, obtained by refluxing the reaction product with methanolic hydrogen chloride, was acidified with 5% hydrochloric acid and extracted with methylene chloride. The methylene chloride was removed by a nitrogen sparge to obtain 0.2 g. of a light yellow waxy solid which had no definite melting point.

A 50 mg. sample of this material was dissolved in methanol, made basic with sodium hydroxide, and then reacted with 100 mg. of 2,4-dinitrochlorobenzene in an unsuccessful attempt to prepare a thioether.

A 0.2 g. sample of the original reaction product was fused for 15 min. with 1 g. of sodium hydroxide at 315°. The residue was dissolved in water and neutralized with 5% hydrochloric acid, but no material separated from solution. The acid solution was extracted with three, 15 ml. portions of methylene chloride. On removal of the methylene chloride, there was obtained a light yellow solid melting in the range

164-182° (d) whose infrared spectrum was very complex. Recrystallization of the solid from ethanol, benzene and then chloroform failed to alter its infrared spectrum. The melting range after several recrystallizations was 186.5-188.5° (d). A sodium fusion and lead acetate test indicated the absence of sulfur.

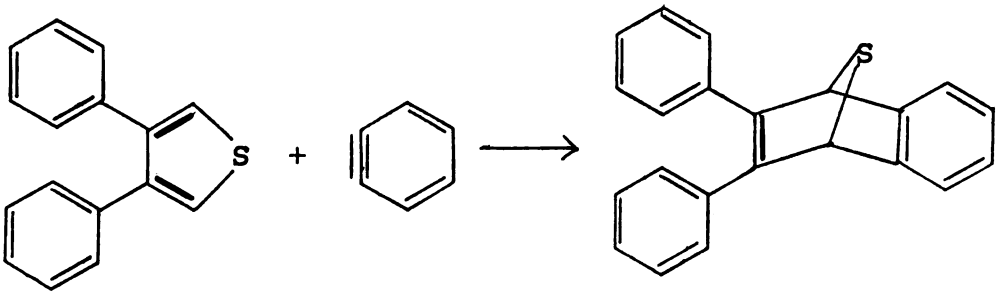
A 5 g. sample of the original reaction product was chromatographed on a 1"-12" alumina column using cyclohexane as the eluent, to obtain eighteen 100 ml. fractions. The infrared spectra's of fractions 4 through 10 were identical. These seven fractions were combined and on removal of the solvent yielded a pale yellow oil (3.1 g.). A sample of the oil was submitted for elemental analysis.

Anal. Calc'd. for $C_{12}H_{12}O_2S$: C, 65.45; H, 5.45; O, 14.54; S, 14.54.

Found: C, 62.71, 63.11; H, 7.34, 6.84; O, {16.3, 17.1}; S, 13.62, 13.96 (64).

The reaction product from the reaction product of 3,4-dimethoxythiophene with "benzyne" could not be identified as the expected 2,3-dimethoxy-1,4-dihydro-1,4-endothionaphthalene. The reaction product on being set aside for a few weeks changed from a light yellow colored material to orange-brown in color and had a very disagreeable odor. The distilled fractions on being set aside for a few weeks also underwent a color change from a bright green (2 weeks) to almost black (4-5 weeks).

The Reaction of 3,4-Diphenylthiophene with "Benzyne" in an Attempt to Prepare 2,3-Diphenyl-1,4-dihydro-1,4-endothionaphthalene

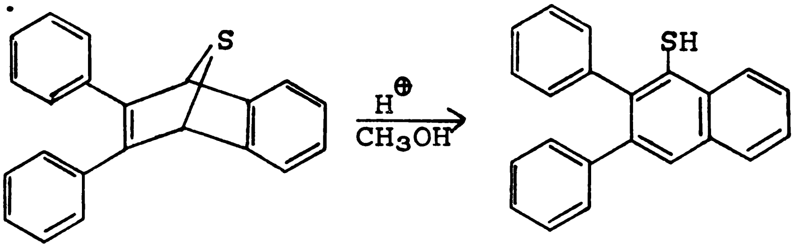


This preparation was carried out in the apparatus described above for the reaction of 3,4-dimethylthiophene with benzyne using 2.8 g. (0.11 g. at.) of Grignard grade magnesium turnings, 17.6 g. (0.071 mole) of 3,4-diphenylthiophene and 14.6 g. (0.083 mole) of o-fluorobromobenzene. The reaction product was worked up as previously described and after the solvents were removed by distillation under reduced pressure, there was obtained 22.8 g. of a brown viscous oil with an ester odor. The oil was dissolved in 50 ml. of diethyl ether and set aside in a refrigerator (0°) for 2 hrs. A solid separated from solution and was collected by filtration on a Buchner funnel. 3,4-Diphenylthiophene, 10.6 g. (0.045 mole), was recovered and identified by a mixed melting point (m.p. 110.0-112.5°) with an authentic sample of 3,4-diphenylthiophene which was not depressed. Comparison of the infrared spectrum of the isolated 3,4-diphenylthiophene with that of an authentic sample indicated the two were identical.

The filtrate from the treatment of the reaction product with diethyl ether was concentrated to 30 ml. and set aside in a refrigerator for 16 hrs. at -5°. No additional 3,4-diphenylthiophene was recovered. The ether solution was heated (40°) to remove the ether and the recovered light orange viscous residue was chromatographed on an alumina column using cyclohexane as the eluent. The eluting solvent was collected in 100 ml. fractions. The fractions 3 through 7 appeared to be identical as indicated by their infrared spectra. These fractions were combined and gave 8.6 g. of a light orange viscous oil on removal of the solvent. The oil was submitted for elemental analysis.

Anal. Calc'd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16; S, 10.27; Found: C, 82.40, 81.14; H, 4.97, 4.89; S, 10.96, 11.31 (64).

The oily product was tested for the expected endothiobridge.



A 0.1 g. sample of the oil was refluxed for 4 hrs. with 5 ml. of methanol containing 1 ml. of concentrated hydrochloric acid. Hydrogen sulfide was evolved as evidenced by its odor. The solution after refluxing was diluted with 10 ml. of water, made basic (pH 10) with sodium hydroxide and extracted with three, 10 ml. portions of methylene chloride. The infrared spectrum of the residue after removal of the methylene chloride appeared to be identical to the original product.

The basic solution was acidified with 5% hydrochloric acid and extracted with three, 10 ml. portions of methylene chloride. On removal of the methylene chloride a white solid was obtained melting in the range 202-211°. The infrared spectrum of this solid indicated the presence of a carbonyl group. Attempts to prepare a 2,4-dinitrophenylthioether derivative of this solid were unsuccessful.

A 0.3 g. sample of the original oily product was refluxed with 2 g. of Raney nickel in 25 ml. of absolute ethanol for 24 hrs. The reaction mixture was filtered to remove the nickel residue and the ethanol was removed by distillation under reduced pressure. Qualitative tests on the residue for sulfur by the sodium fusion and lead acetate method indicated that sulfur was absent. The infrared spectrum, of the Raney nickel treated material, indicated the 3.4 μ sulfur band had been removed. The material unfortunately could not be crystallized. Attempts to identify this residue failed to give any information other than it was a compound containing both aromatic and aliphatic groups.

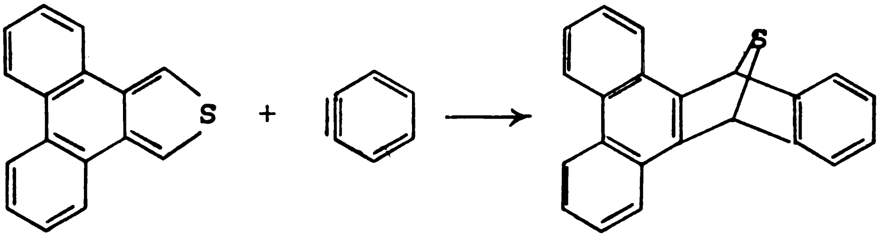
A 0.3 g. sample of the original oily product was refluxed with basic potassium permanganate solution (98). The excess permanganate was destroyed with sodium bisulfite. The reaction mixture was made acid with 5% hydrochloric acid and extracted with three, 20 ml. portions of methylene chloride. The infrared spectrum of the "paste" residue after removal of the methylene chloride indicated the presence of a carboxyl group. Further identification was not undertaken.

A 0.5 g. sample of the original oily product was heated 15 min. with 2 g. of sodium hydroxide at 315°. The residue was dissolved in 25 ml. of water and neutralized with 5% hydrochloric acid.

No crystalline material separated from the acidified solution. The acidic solution was extracted with methylene chloride and on removal of the methylene chloride a "pasty residue" was obtained which melted in the range 62-138°. The infrared spectrum of this was extremely complex and further identification work was not undertaken.

The reaction between 3,4-diphenylthiophene and benzyne appeared to have taken place. A light yellow viscous oil was isolated but could not be identified as the expected product; 2,3-diphenyl-1,4-dihydro-1,4-endothionaphthalene.

The Preparation of 6,7,8,9-Dibenzo-5,10-dihydro-5,10-endothioanthracene by the Reaction of 4,5,6,7-Dibenzoisothionaphthalene with "Benzyne"



In a 250 ml. three necked, round bottom flask, equipped with a stirrer and two parallel adapters; one equipped with a gas inlet tube and a 50 ml. dropping funnel, the other with a reflux condenser protected by a calcium chloride drying tube and a 50 ml. dropping funnel; was placed 0.3 g. (0.013 g. at.) of Grignard grade magnesium turnings.

The apparatus was heated with a "hot air gun" to remove moisture while dry oxygen free nitrogen gas was flowing through the apparatus.

Tetrahydrofuran, 10 ml. redistilled from calcium hydride, was added to the reaction flask and a small crystal of iodine was added to catalyze the reaction. While stirring the magnesium suspension, the flask was heated until the iodine color disappeared. The reaction flask was then cooled to room temperature by immersion in an ice water bath.

In one dropping funnel was placed 1.8 g. (0.013 mole) of o-fluorobromobenzene in 5 ml. of tetrahydrofuran redistilled from calcium hydride, and in the other dropping funnel was placed 2.2 g. (0.0094 mole) of 4,5,6,7-dibenzcisothionaphthalene in 20 ml. of tetrahydrofuran redistilled from calcium hydride. While stirring the magnesium suspension, a few drops of the o-fluorobromobenzene solution were added and the reaction mixture was heated at its reflux temperature by a "hot air gun" until a white cloudiness appeared in the reaction mixture.

The remaining o-fluorobromobenzene solution and the dibenzoisothionaphthalene solution were simultaneously added dropwise. The reaction flask was heated occasionally to maintain the reaction temperature at 40-45°.

The reaction appeared to be complete in 2 hrs. after which the reaction mixture was heated to its reflux temperature for 10 min. and cooled to room temperature. The mixture was filtered to remove the unreacted magnesium and then diluted with an equal volume of diethyl ether.

The magnesium complex was hydrolyzed with three, 10 ml. portions of saturated ammonium chloride solution. Hydrogen sulfide gas was evolved as evidenced by its odor. The organic layer was separated, dried with anhydrous magnesium sulfate and the solvents and other volatiles were removed under reduced pressure in a rotary evaporator. The tan colored product, 2.68 g., was dissolved in methylene chloride (10 ml.) and decolorized with activated charcoal.

After filtering, the methylene chloride was removed by a nitrogen gas stream and the off-white product was recrystallized three times from cyclohexane to obtain 1.96 g. (0.0063 mole, 68.2% yield) of 6,7,8,9-dibenzo-5,10-dihydro-5,10-endothionaphthalene melting at 186-188°.

Anal. Calc'd. for $C_{22}H_{14}S$: C, 85.12; H, 4.54; S, 10.32.

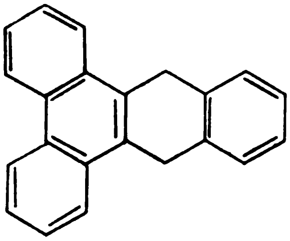
Found: C, 84.96, 85.27 (64); H, 4.31, 4.07 (64);

S. 10.06, 10.18 (64).

A 0.5 g. sample of the 6,7,8,9-dibenzo-5,10-dihydro-5,10-endothionaphthalene was refluxed for 4 hrs. with 5 ml. of methanol containing 0.5 ml. of concentrated hydrochloric acid. A solid reaction product was recovered melting at 176.0-177.5°.

Qualitative sulfur tests on this material by the sodium fusion-lead acetate method were negative.

Elemental analysis gave C, 94.55 and H, 5.44. It is very probable that the solid was dihydrodibenzoanthracene as suggested by the carbon and hydrogen calculations.



Anal. Calc'd for dihydrodibenzoanthracene,

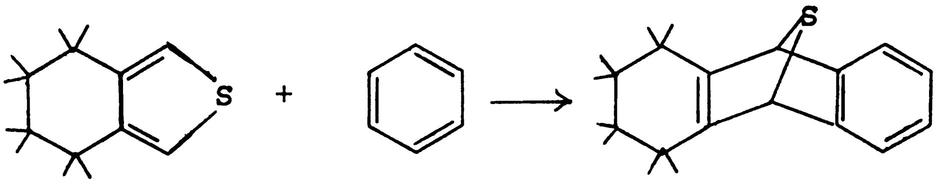
$C_{22}H_{16}$: C, 94.28; H, 5.72.

Anal. Calc'd for dibenzanthracene (α,γ) or dibenz(a,c)-anthracene,

$C_{22}H_{14}$: C, 94.92; H, 5.08.

A 0.5 g. sample of the 6,7,8,9-dibenzo-5,10-dihydro-5,10-endothionaphthalene was fused with 2 g. of sodium hydroxide at 300° for 15 min. The reaction mixture was cooled to room temperature, dissolved in 10 ml. of water and neutralized with (6N) hydrochloric acid. The solid product was collected on a Buchner funnel and recrystallized from benzene. The solid reaction product melted at 199.5-202.5°. Qualitative sulfur test on this material by the sodium fusion-lead acetate method were negative. This solid probably was dibenzanthracene (92,93). A mixed melting point determination with an authentic sample of dibenzanthracene was not depressed and comparison of its infrared spectrum with the spectrum of an authentic sample of dibenzanthracene indicated they were identical.

Preparation of 5,6,7,8,9,10-Hexahydro-9,10-endothionaphthalene by the Reaction of 4,5,6,7-Tetrahydrobenzo[C]thiophene with "Benzyne"



In a 250 ml. three necked, round bottom flask, equipped with a stirrer and two parallel adapters; one equipped with a gas inlet tube and a 50 ml. dropping funnel, the other with a reflux condenser protected by a calcium chloride drying tube and a 50 ml. dropping funnel; was placed 0.40 g. (0.016 g. at.) of Grignard grade magnesium turnings. The apparatus was heated with a "hot air gun" to remove moisture while dry oxygen free nitrogen gas was flowing through the apparatus.

After the apparatus was dry and cooled, a 10 ml. volume of tetrahydrofuran redistilled from calcium hydride was added to the flask. A small crystal of iodine was then added and the flask was heated at the reflux temperature of the tetrahydrofuran until the iodine color had disappeared to initiate the reaction. The reaction flask was cooled to room temperature by immersion in an ice water bath.

In one dropping funnel was placed 2.6 g. (0.015 mole) of o-fluorobromobenzene in 5 ml. of tetrahydrofuran redistilled from calcium hydride and in the other dropping funnel was placed 2.0 g. (0.015 mole) of 4,5,6,7-tetrahydrobenzo[C]-thiophene in 10 ml. of tetrahydrofuran redistilled from calcium hydride. While stirring the magnesium suspension, a few drops of the o-fluorobromobenzene solution were added and the reaction flask was heated by a "hot air gun" at the reflux temperature of the tetrahydrofuran and a white cloudiness appeared in the reaction mixture.

The remaining o-fluorobromobenzene solution and tetrahydrobenzo[C]thiophene solution were simultaneously added dropwise. The reaction mixture was occasionally heated to maintain the reaction temperature between 40-45°. The reaction appeared to be complete after 2 hrs.

The reaction mixture was then heated to its reflux temperature for 10 min., cooled to room temperature and it was filtered to remove the unreacted magnesium. The filtrate was diluted with an equal volume of diethyl ether.

The reaction mixture was treated with three, 10 ml. portions of saturated ammonium chloride to decompose any complex magnesium salts. Some hydrogen sulfide was evolved during this treatment as evidenced by its odor.

The organic layer was separated, dried with anhydrous magnesium sulfate and the solvents and other volatiles were removed under reduced pressure in a rotary evaporator.

The light brown crystalline solid, 2.1 g., was dissolved in methylene chloride and decolorized with activated charcoal. The methylene chloride was removed by a nitrogen gas stream. The yellowish colored solid was recrystallized three times from cyclohexane to obtain 1.64 g. (0.0076 mole, 52.8% yield) of 5,6,7,8,9,10-hexahydro-9,10-endothioanthracene melting at 67.0-68.5°.

Anal. Calc'd. for $C_{14}H_{14}S$: C, 78.51; H, 6.54; S, 14.95; Found: C, 78.46, 78.52 (64); H, 6.41, 6.48 (64); S, 14.87, 14.81 (64).

Reaction of Methanolic Hydrochloric Acid with 5,6,7,8,9,10-Hexahydro-9,10-endothioanthracene

A 0.5 g. sample of the hexahydroendothioanthracene was refluxed for 4 hrs. with 5 ml. of methanol containing 0.5 ml. of concentrated hydrochloric acid. The solid reaction product was recovered and melted at 74.0-76.5°. Qualitative sulfur tests on the solid by the sodium fusion and lead acetate method were negative. It is very probable that the solid was 1,2,3,4-tetrahydroanthracene.

Anal. Calc'd. for $C_{14}H_{14}$: C, 92.26; H, 7.74; Found: C, 91.71, 91.54 (64); H, 8.04, 8.26 (64). However the analysis would indicate that it was a hexahydroanthracene, $C_{14}H_{16}$: C, 91.19; H, 8.75.

Reaction of 5,6,7,8,9,10-Hexahydro-9,10-endothioanthracene with Sodium Hydroxide

A 0.5 g. sample of the hexahydroendothioanthracene was fused with 2 g. of sodium hydroxide at 300° for 15 min.

The reaction product was dissolved in water and neutralized with hydrochloric acid (6N). The solid which separated was collected on a Buchner funnel and recrystallized three times from cyclohexane to obtain 0.31 g. of a solid melting in the range 73-104°. Repeated recrystallization from methanol gave a solid melting at 76.0-78.5°. A qualitative test for sulfur on the product was negative. The mixed melting point of this product with the product from the reaction of methanolic hydrogen chloride with hexahydroendothioanthracene was depressed (m.p. 64-67°). The infrared spectras of the two products appeared to be identical, and were assumed to be 5,6,7,8,9,10-hexahydroanthracene.

SUMMARY

1. The compound, 4-chlorocyclohexene oxide, an intermediate in the attempted preparation of 1-hydroxy-7-thiobicyclo[2.2.1]heptane, was synthesized for the first time by the epoxidation of 4-chlorocyclohexene with peracetic acid.

2. The Diels-Alder adduct of 1,2,3,4,5,6,7,8-octahydro-1,4-endothionaphthalene(2,3)anhydride was synthesized for the first time from 4,5,6,7-tetrahydrobenzo[C]thiophene.

3. Thiophene, 3,4-dimethyl-, 3,4-dimethoxy-, or 3,4-diphenylthiophene failed to undergo a Diels-Alder reaction with maleic anhydride or tetracyanoethylene.

4. 4,5,6,7-Tetrahydrobenzo[c]thiophene and 4,5,6,7-dibenzoisothionaphthalene both reacted with tetracyanoethylene to give Diels-Alder adducts, reported here for the first time. These adducts are 1,4,5,6,7,8-hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene and 5,6,7,8-dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene respectively.

5. 3,4-Dimethyl-, 3,4-dimethoxy-, and 3,4-diphenylthiophene did react with benzyne but attempts to isolate the respective Diels-Alder adducts were unsuccessful.

6. Thiophene did react with benzyne to give the Diels-Alder adduct in low yields. This is the first reported synthesis of 1,4-dihydro-1,4-endothionaphthalene at moderate conditions.

7. 4,5,6,7-Dibenzoisothionaphthalene and 4,5,6,7-tetrahydrobenzo[C]thiophene did react with benzyne to give the respective Diels-Alder adducts, reported here for the first time. They are 6,7,8,9-dibenzo-5,10-dihydro-5,10-endothioanthracene and 5,6,7,8,9,10-hexahydro-9,10-endothioanthracene.

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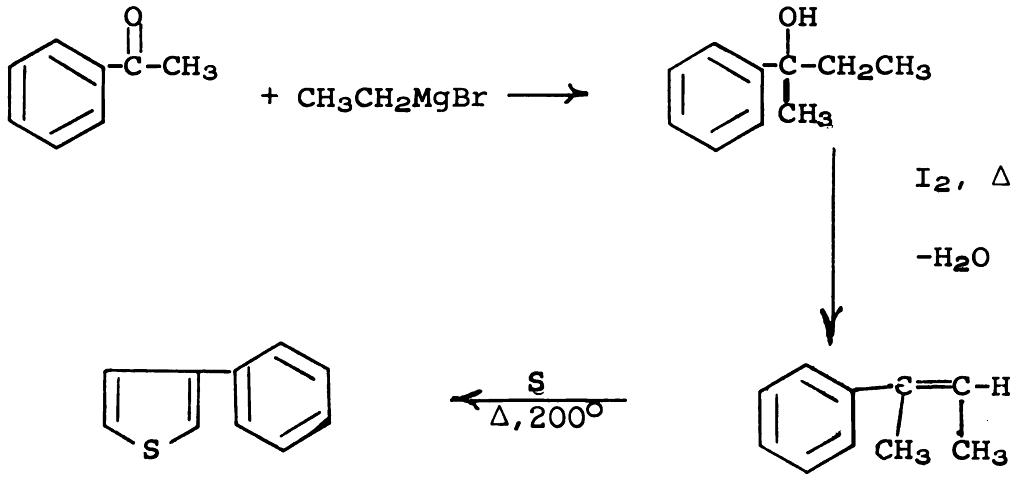
APPENDIX

APPENDIX

EXPERIMENTAL

Preparation of 3-Phenylthiopene



m.p. 91.5-92.0°

Preparation of Methyethyl Phenyl Carbinol

Using the method of Brown and Voronkov (94) acetophenone, 132 g. (1.1 moles), was reacted with 133 g. (1.0 mole) of ethyl magnesium bromide. From product isolation procedures, there was obtained 147 g. (0.99 mole) of crude methylethyl phenyl carbinol (90% yield).

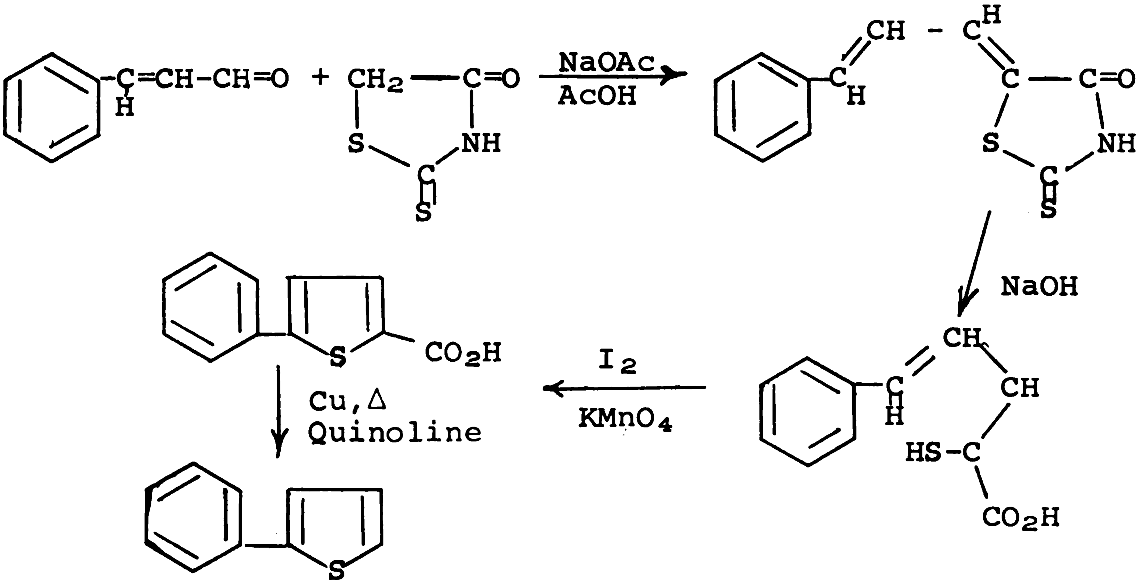
Preparation of α,β-Dimethyl Styrene

Again using the method of Brown and Voronkov (94), the methylethyl phenyl carbinol, 147 g. (0.99 mole) described above was reacted with iodine (0.5 g.) at 200°. The reaction mixture was distilled to obtain α,β-dimethylstyrene, 111 g. (0.84 mole, 85% yield, b.p. 67-70°/11 mm. Hg.).

Preparation of 3-Phenyl Thiophene

Again employing the method of Brown and Voronkov (94), α,β-dimethylstyrene, 88 g. (0.66 mole) described above was reacted with sulfur (3 g. at.) at 200° for 20 hrs. After product isolation, the crude 3-phenylthiophene was sublimed and then recrystallized three times from methanol to obtain 21 g. (0.13 mole, 19% yield) of 3-phenylthiophene melting at 91.0-91.5° (literature value 91.5-92.0° (94,57)). The infrared spectrum was obtained, Figure IX.

Preparation of 2-Phenyl Thiophene



Preparation of Rhodanine Adduct

Using the method of Campaigne and Cline (95) cinnamaldehyde, 39 g. (0.3 mole) and rhodanine, 40 g. (0.3 mole) were heated in a sodium acetate-glacial acetic acid mixture. After the reaction was complete, 0.5 hr., the reaction product was poured onto ice, filtered, and the solid product recovered by filtration was recrystallized twice for ethanol (95%) to obtain 50 g. (0.20 mole, 66%) of the rhodanine adduct (m.p. 223° (95)).

Preparation of Mercaptoacrylic Acid

Employing the method of Campaigne and Cline (95), 50 g. (0.20 mole) of the rhodanine adduct was reacted with sodium hydroxide (90 ml., 10% solution) in 3 l. of water at 85° for 0.5 hr. After acidification of the mixture the precipitate was collected on a filter to obtain 26 g. (0.12 mole, 62%) of the crude mercaptoacrylic acid.

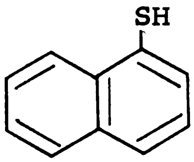
Preparation of 2-Phenyl-5-carboxy Thiophene

Again employing the method of Campaigne and Cline (95), 21 g. (0.10 mole) of the mercaptoacrylic acid described above was reacted with 25 g. (0.2 mole) of iodine in absolute ethanol for 16 hrs. at 25°. The reaction mixture was then poured into 2 l. of water, and the excess of iodine was destroyed by sodium bisulfite and the precipitate was collected on a filter. After air drying the precipitate for 16 hrs., it was dissolved in a sodium hydroxide solution (3 l. of 2%) and treated with 40 g. of potassium permanganate. The excess potassium permanganate was destroyed with sodium bisulfite and the solution was made acid with dilute hydrochloric acid. The precipitate formed was collected on a filter and dried (105°) to obtain 12.0 g. (0.06 mole, 62%) of 2-phenyl-5-carboxythiophene melting at 192-185° (literature value, m.p. 185-187° (95)).

Preparation of 2-Phenylthiophene

Again employing the method of Campaigne and Cline (95), the 12 g. (0.06 mole) of 2-phenyl-5-carboxthiophene described above was reacted with 44.5 g. (0.14 mole) of mercuric acetate at 140° for 3 hrs. The mixture was then acidified with 50 ml. of concentrated hydrochloric acid and the 2-phenylthiophene was recovered by steam distillation. The steam distillate was extracted with diethylether. The ether was removed by distillation and the crude 2-phenylthiophene was partially purified by sublimation. The sublimate was recrystallized 3 times for ethanol (95%) to obtain 6.4 g. (0.04 mole, 62%) of 2-phenylthiophene melting at 32.0-32.5° (literature values, m.p. 35-35° (95), 43-45° (57), 40-41° (89)). Infrared spectrum was obtained, Figure X.

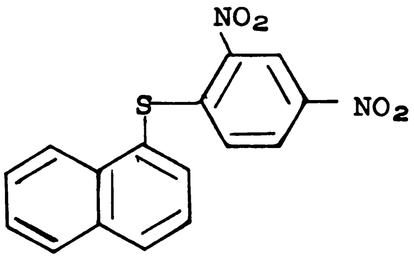
Preparation of α-Naphthalenethiol



Using the method of Dunigan (96) and Bost, Turner and Conn (69), 62.1 g. (0.3 mole) of 1-bromonaphthalene (K and K Laboratories) was reacted with 7.4 g. (0.31 g. at.) of Grignard grade magnesium turnings in 300 ml. of dry diethyl ether. After all of the 1-bromonaphthalene had been added the mixture was warmed in a hot water bath for a 0.5 hr. and 9.6 g. (0.3 g. at.) of sulfur was cautiously added to the reaction mixture. The reaction was exothermic and the diethylether tended to boil off. When all the sulfur had been added, the reaction mixture was warmed for an additional 0.5 hr. The mixture was then poured into 500 ml. of a saturated ammonium chloride solution.

The diethyl ether layer was separated, and the aqueous layer was extracted twice with 50 ml. portions of diethyl ether. The combined ether extracts were extracted with three, 30 ml. portions of 6N sodium hydroxide. The combined alkaline extracts were acidified with 110 ml. of 6N hydrochloric acid. The acidified solution was extracted with diethyl ether, and the ether extract was dried with anhydrous magnesium sulfate. The ether extract and 1-thionaphthalene were transferred to a distillation apparatus and the ether was removed under reduced pressure. The 1-thionaphthalene was distilled and the fraction boiling at 158-163°/20 mm. Hg. was collected. It weighed 28.6 g. (0.18 mole, 60% yield) and had a refractive index of n_D^{20} 1.6799 (literature value, b.p. 161°/20 mm. Hg. n_D^{20} 1.6802 (69,96)).

Preparation of 2,4-Dinitrophenyl-1-naphthyl Thioether



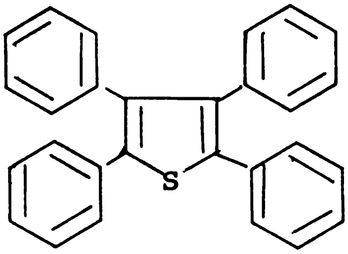
Using the method of Bost, Turner and Conn (69), 6 g. (0.037 mole) of 1-thionaphthalene in 50 ml. of methanol was reacted with 1.5 g. (0.038 mole) of sodium hydroxide in 10 ml. of water. The sodium salt of thionaphthalene solution was added to 12 g. (0.06 mole) of 2,4-dinitrochlorobenzene in 40 ml. of methanol. The reaction mixture was heated at its reflux temperature for 20 min. and then filtered rapidly. The filtrate was cooled in an ice bath and the solid thioether was collected on a Buchner funnel. The crude thioether was recrystallized three times from methanol to obtain 5.8 g. (0.018 mole, 48%) of 2,4-dinitrophenyl-1-naphthylthioether melting at 174.5-175.5° (literature value 176° (69)).

Anal. Calc'd for $C_{17}H_{10}O_4N_2S$: S, 9.81

Found: S, 9.68, 9.72, 9.55% (64).

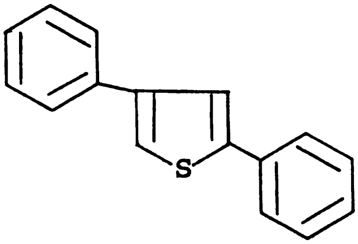
Infrared spectrum was obtained, Figure XI.

Preparation of Tetraphenylthiophene (Thionessal)



Using the method of Baumann and Fromm (91) 36 g. (0.20 mole) of trans stilbene (K and K, Laboratories) was heated at 250° in a reflux apparatus with 10 g. (0.31 g. at.) of sulfur until all evolution of hydrogen sulfide ceased. The crude thionessal was recrystallized five times from ethanol (95%) to obtain 20 g. (0.051 mole, 50%) of pure product melting at 182.5-184.0° (literature value 178° (91)).

Preparation of 2,4-Diphenylthiophene



Using the method of Campaigne (97), 40 g. (0.33 mole) of acetophenone in 300 ml. of absolute ethanol was cooled to 0° by immersion in an ice bath. Dry hydrogen chloride gas was passed into the solution until a slow rate of gas influx could be regulated and until 140 g. (3.84 moles) of hydrogen chloride (amount calculated to saturate the ethanol) had been added (approximately 6 hrs.).

Simultaneously, with the hydrogen chloride gas, hydrogen sulfide was passed into the solution. During the addition of the gaseous reactants the reaction mixture was kept at 0° by immersion in an ice bath. When all of the hydrogen chloride gas had been added, the ice bath was removed and as the reaction mixture was warmed to room temperature, hydrogen sulfide gas was passed continuously into the mixture.

After the reaction mixture had been warmed to room temperature, the hydrogen sulfide was passed into it for an additional 8 hrs.

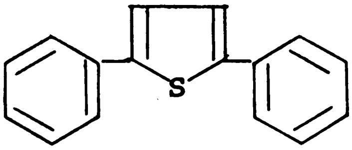
The reaction mixture, after the 14 hrs. of reaction time, was set aside in a refrigerator for 16 hrs. to allow crystallization of the product. This was collected by filtration and was recrystallized twice from acetone to obtain 21 g. of product melting at $107\text{-}108^{\circ}$.

A 21 g. quantity of the product was dissolved in 300 ml. of dry xylene and 50 g. of copper powder was added to the mixture. The mixture was brought to its reflux temperature and stirred for 3 hrs. It was then cooled, filtered and the excess xylene was removed by vacuum distillation.

The crude 2,4-diphenylthiophene was recrystallized four times from boiling methanol to obtain 11 g. (0.047 mole, 28%) of 2,4-diphenylthiophene melting at $120.5\text{-}121.0^{\circ}$ (literature value, $121.0\text{-}121.5^{\circ}$ (97)).

The infrared spectrum was obtained, Figure XII.

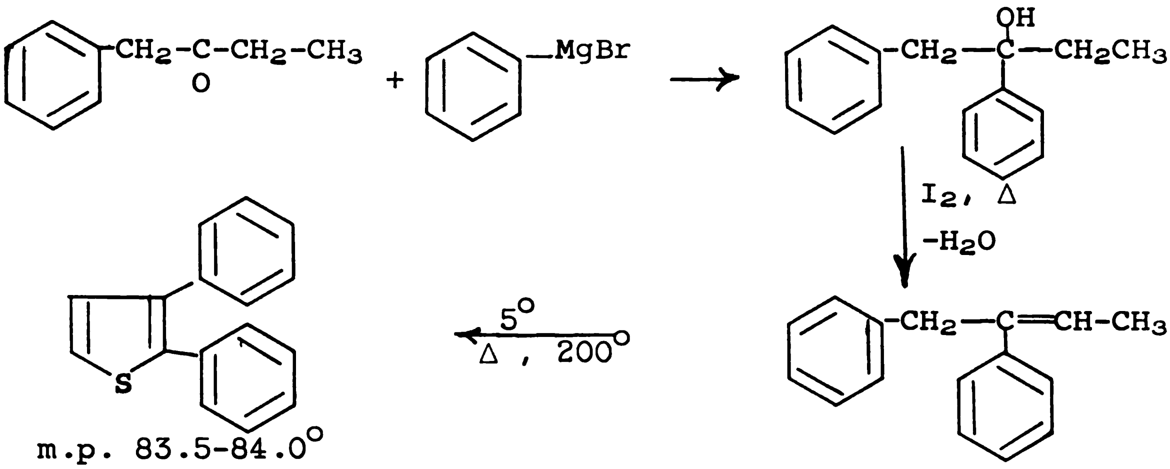
Preparation of 2,5-Diphenylthiophene (90)



Using the method of Kapf and Paal (90), 46.5 g. (0.2 mole) of diphenacyl (K and K Laboratories, dibenzoylethane) was reacted with 25 g. (0.11 mole) of phosphorous pentasulfide at 160-170° for 20 to 30 min. The reaction mixture was cooled and then vacuum distilled. The crude 2,5-diphenylthiophene was washed with 80 ml. of 3N sodium hydroxide solution and then with three, 50 ml. portions of water. The 2,5-diphenylthiophene was then recrystallized four times from boiling methanol to obtain 26 g. (0.11 moles, 55%) of a pure product melting at 155-156° (literature value 156° (90)).

The infrared spectrum was obtained, Figure XIII.

Preparation of 2,3-Diphenylthiophene



Preparation of Benzyl Ethyl Phenyl Carbinol

Using the method of Brown and Voronkov (94), 100 g. (0.675 mole) of 1-phenyl-2-butanone (Aldrich Chemical Co.) was reacted with 0.69 moles of phenyl magnesium bromide. After product isolation procedures, there was obtained 135 g. (0.595 mole) of crude ethylphenylbenzylcarbinol (88% yield).

Preparation of α-Benzyl-β-methyl Styrene (1,2-diphenyl-2-butene)

Again employing the method of Brown and Voronkov (94) the ethylphenylbenzylcarbinol (0.60 mole) described above was reacted with iodine (0.5 g.) at 200°. The reaction mixture was distilled to obtain 1,2-diphenyl-2-butene (0.46 mole, 76.5% yield, b.p. 142-150°/11 mm. Hg.)

Preparation of 2,3-Diphenylthiophene

Again employing the method of Brown and Voronkov (94) the 1,2-diphenyl-2-butene (95.5 g. 0.46 mole) described above was reacted with sulfur (3 g. at.) at 200° for 20 hrs. After product isolation procedures the crude 2,3-diphenylthiophene was sublimed and recrystallized five times from boiling methanol to obtain 2,3-diphenylthiophene (42 g., 0.18 mole, 39%) melting at 83.5-84.0° (literature value m.p. 83.0-84.0° (57)).

Anal. Calc'd. for $C_{16}H_{12}S$: C, 81.35; H, 5.08; S, 13.55; Found: C, 80.96, 81.21; H, 4.91, 4.96; S, 13.61, 13.58, 13.51 (64).

The infrared spectrum was obtained, Figure XV.

INFRARED SPECTRA

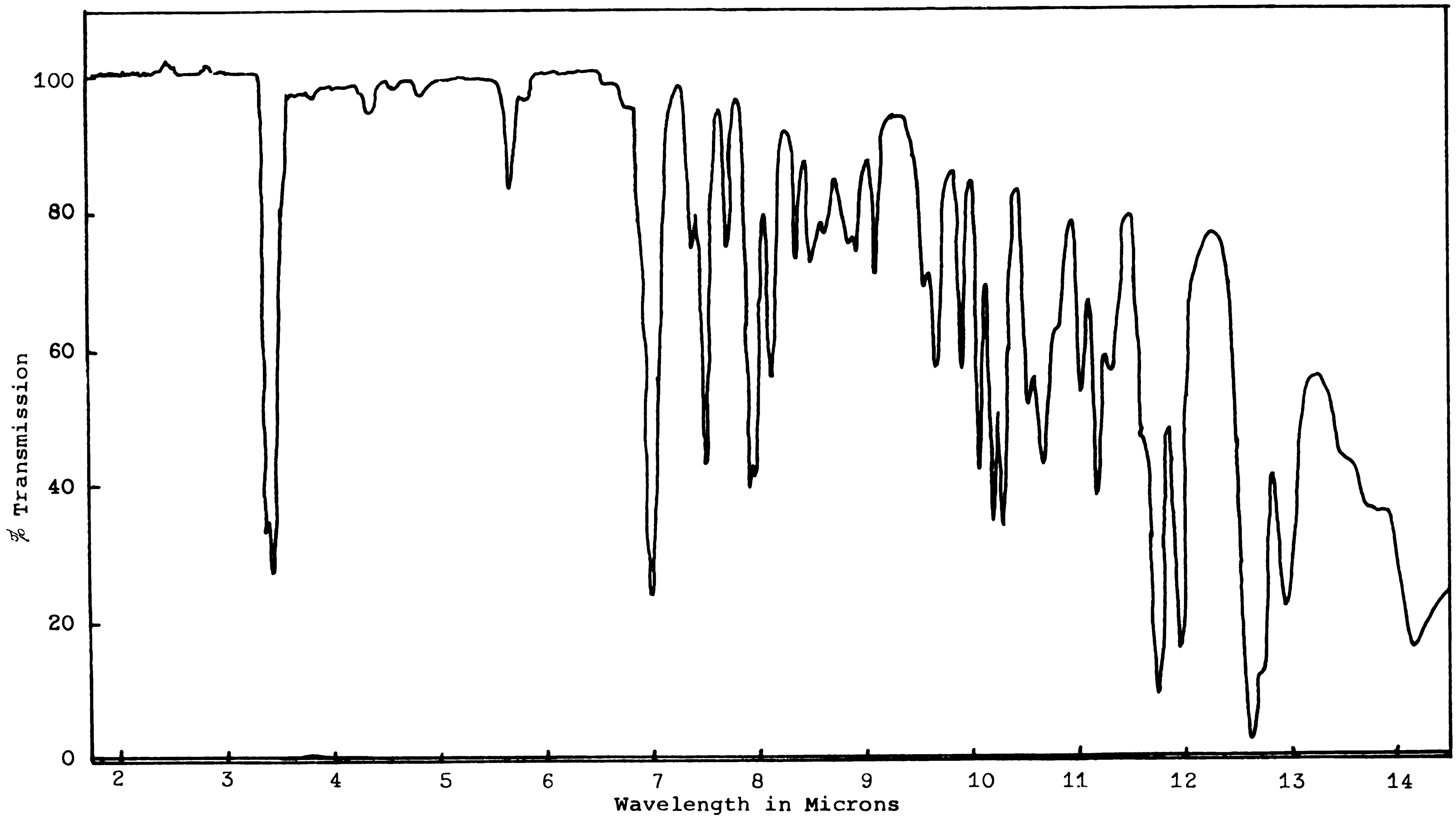


Figure I. 4-Chlorocyclohexene oxide. (5 mg. in KBr pellet)

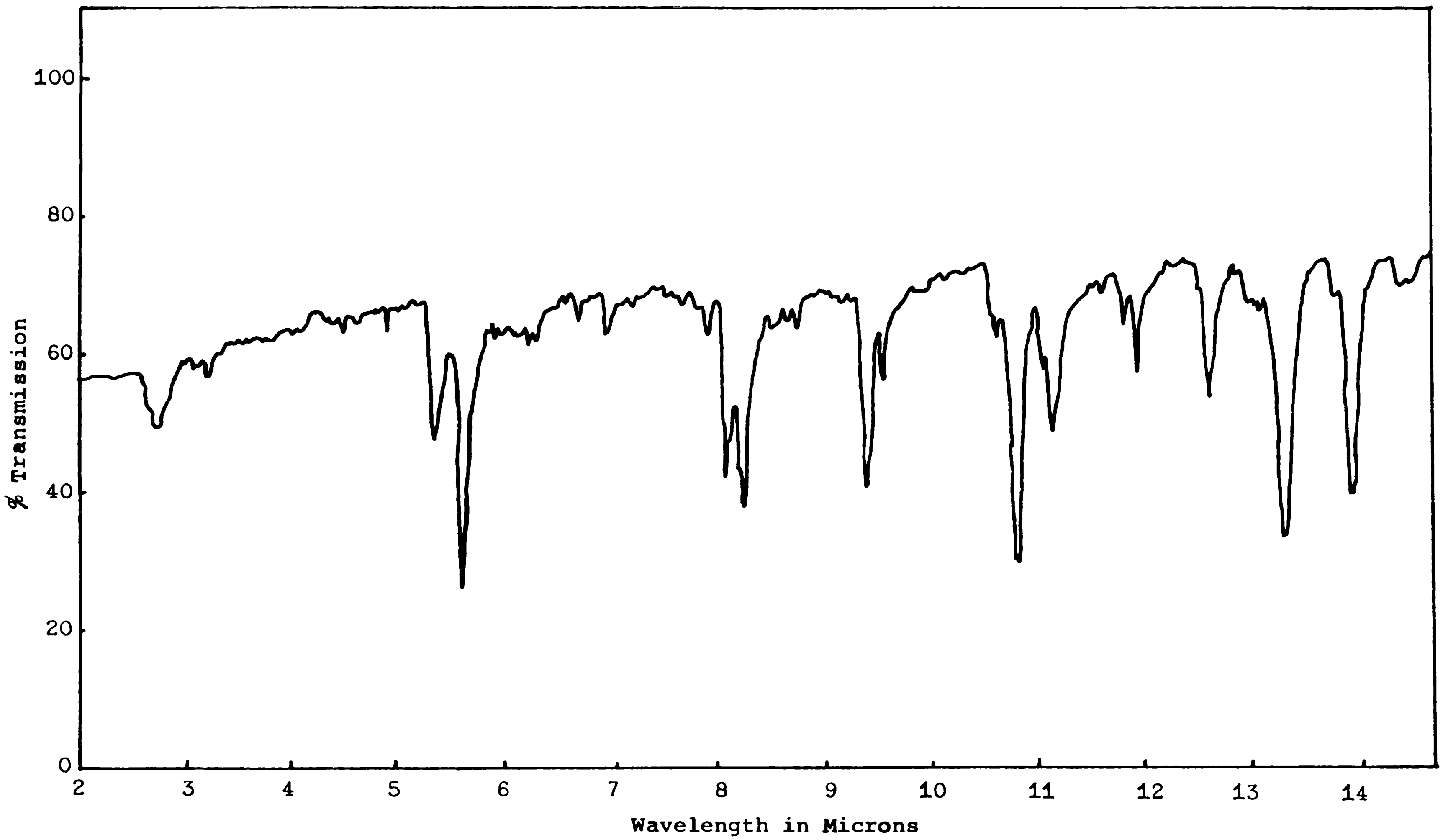


Figure II. 5,6,7,8-Dibenzo-1,2,3,4-tetrahydro-1,4-endothionaphthalene(2,3)anhydride. (5 mg. in KBr pellet)

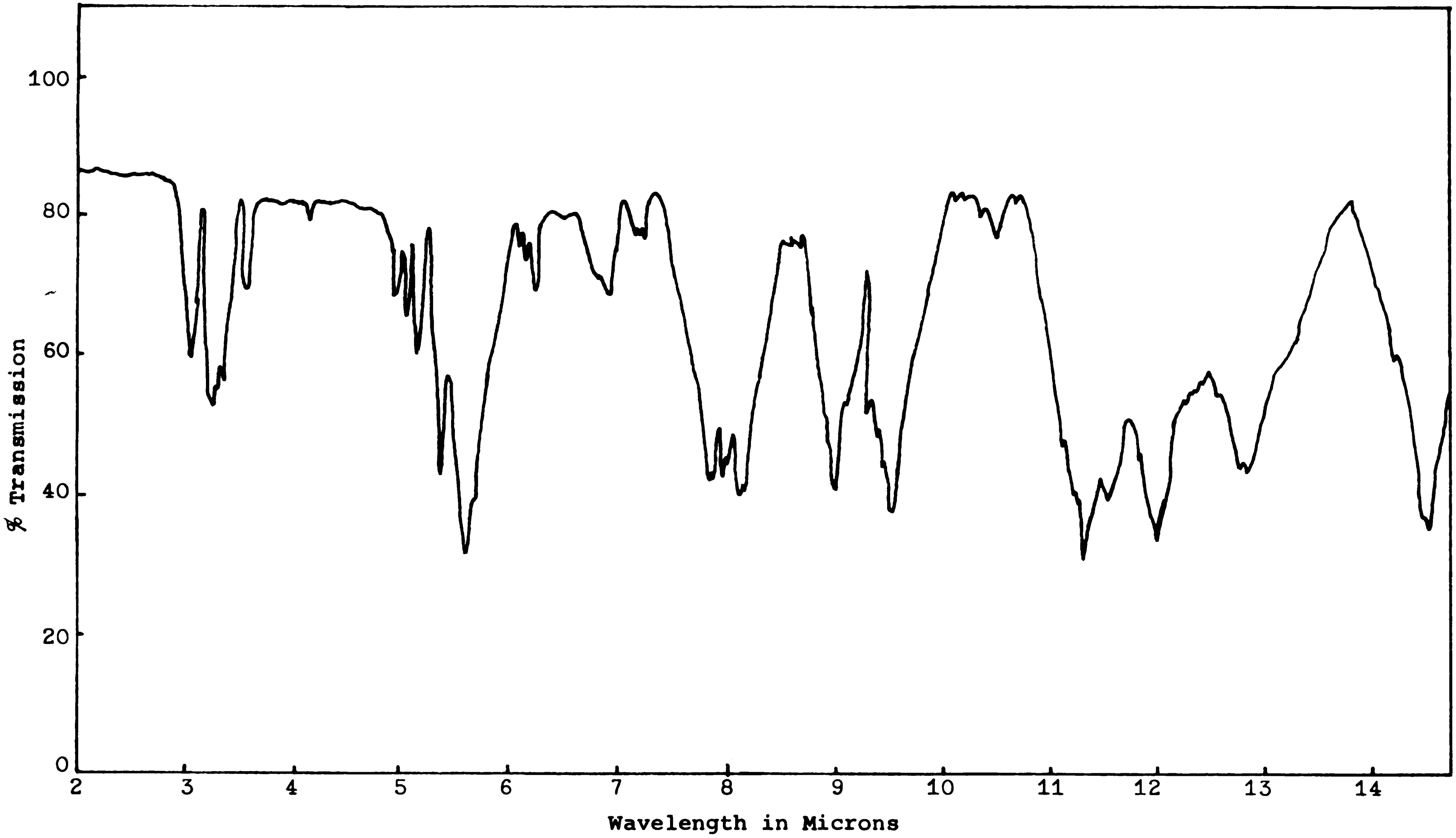


Figure III. 1,2,3,4,5,6,7,8-Octahydro-1,4-endothionaphthalene(2,3)anhydride.

(5 mg. in KBr pellet)

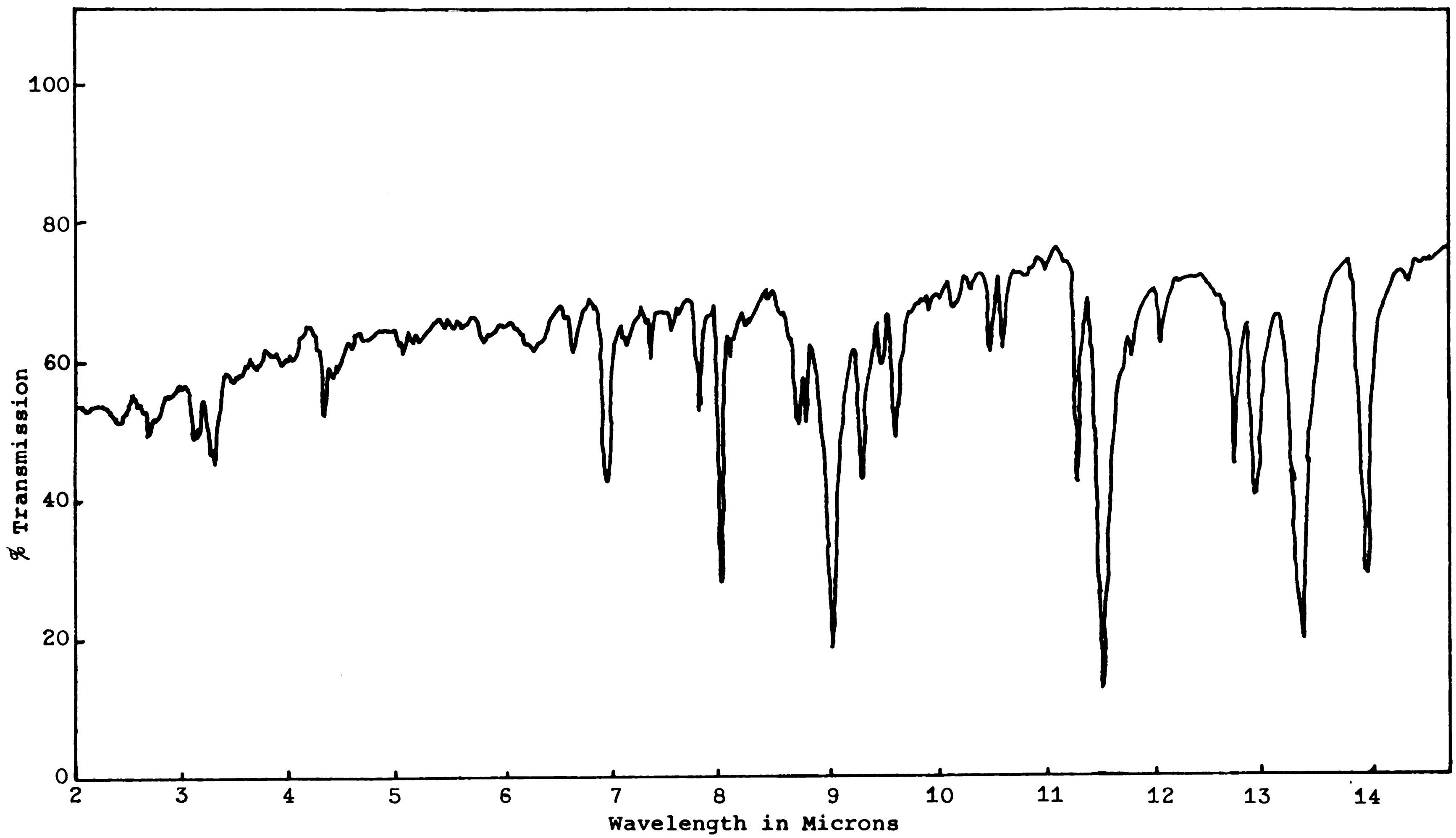


Figure IV. 5,6,7,8-Dibenzo-2,2,3,3-tetracyano-1,4-dihydro-1,4-endothionaphthalene.

(5 mg. in KBr pellet)

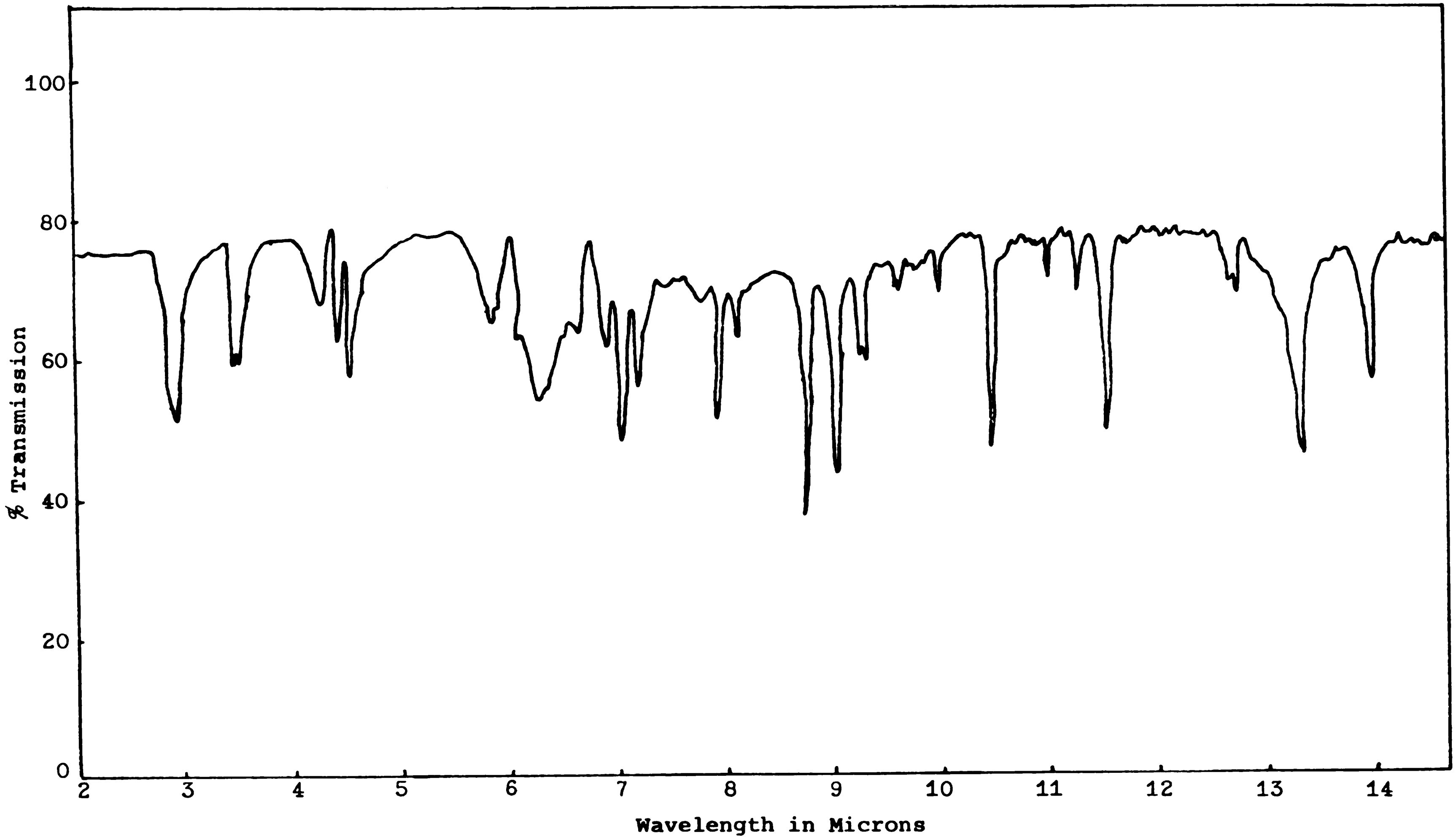


Figure V. 1,4,5,6,7,8-Hexahydro-2,2,3,3-tetracyano-1,4-endothionaphthalene.

(5 mg. in KBr pellet)

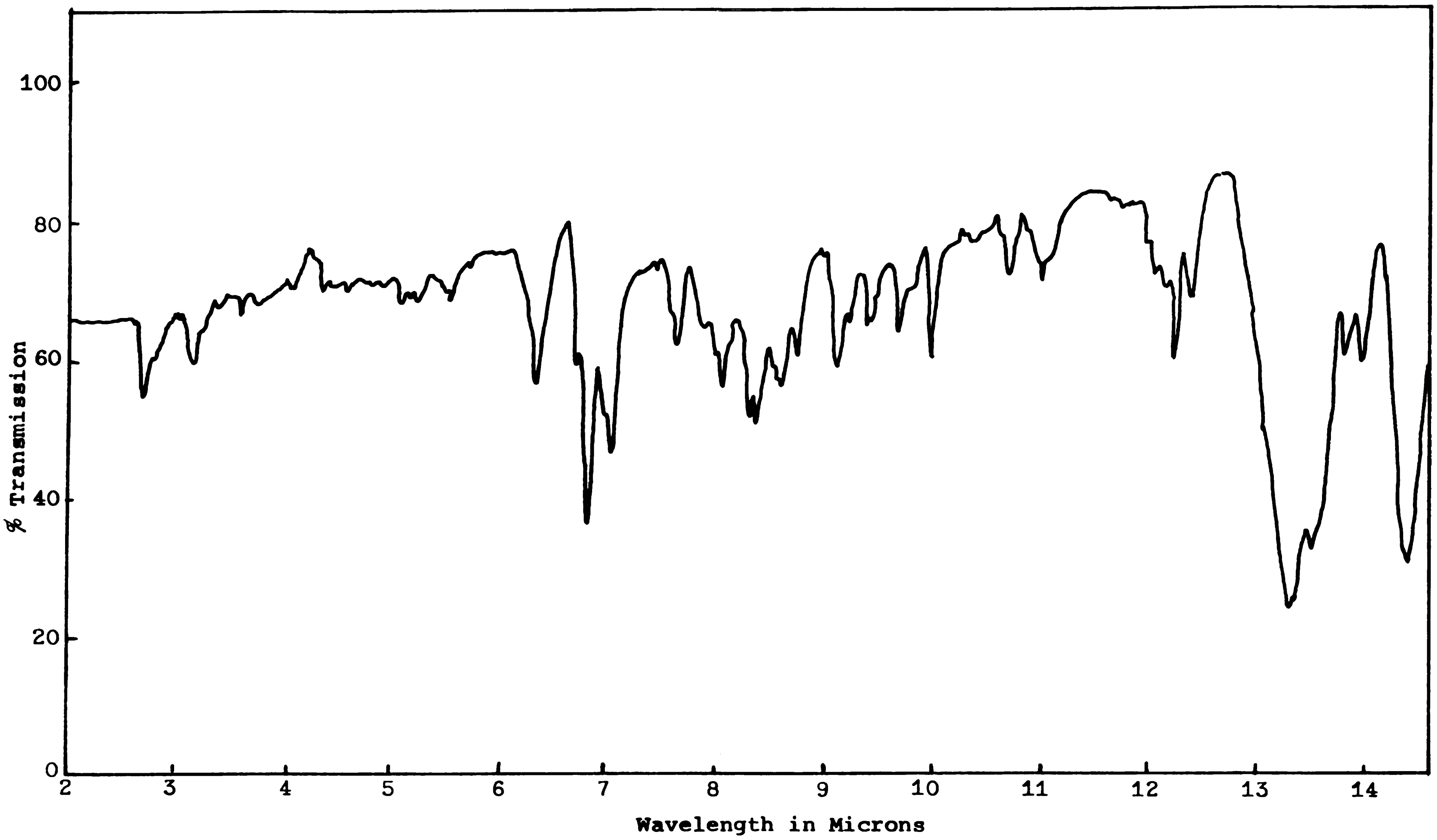


Figure VI. 1,4-Dihydro-1,4-endothionaphthalene. (5 mg. in KBr pellet)

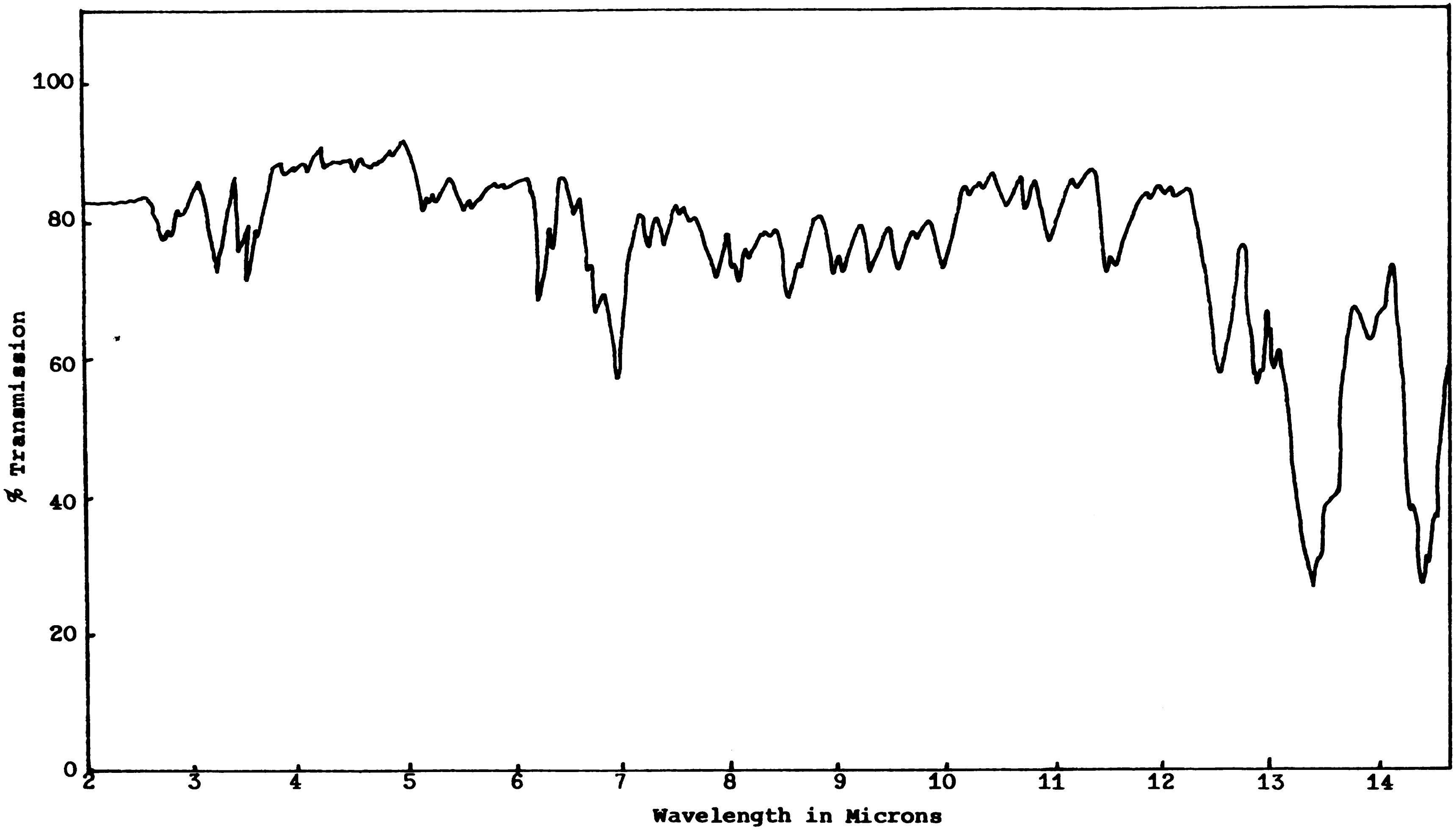


Figure VII. 6,7,8,9-Dibenzo-5,10-dihydro-5,10-endothioanthracene. (5 mg. in KBr pellet)

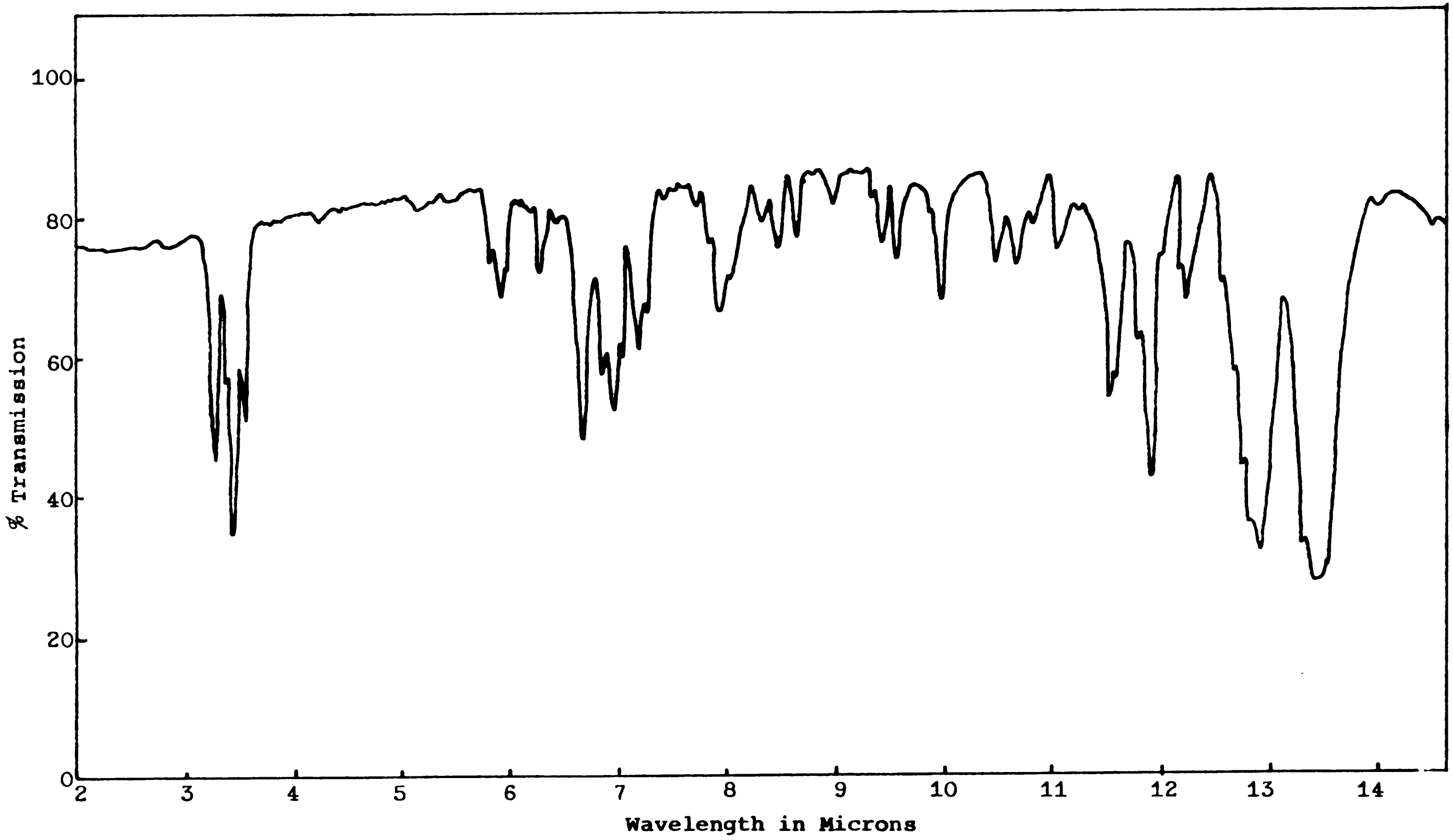


Figure VIII. 5,6,7,8,9,10-Hexahydro-9,10-endothioanthracene. (5 mg. in KBr pellet)

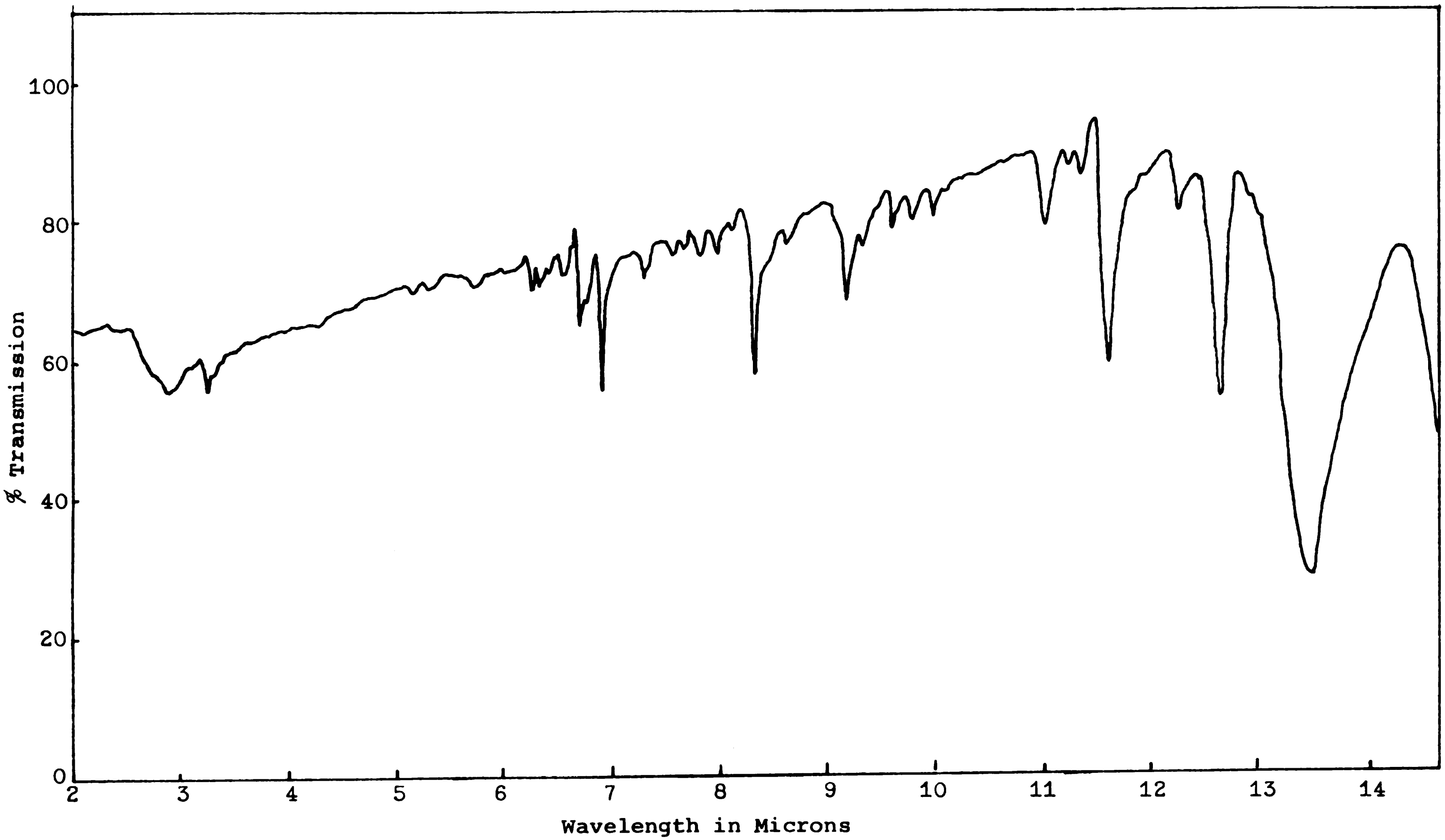


Figure IX. 3-Phenylthiophene. (5 mg. in KBr pellet)

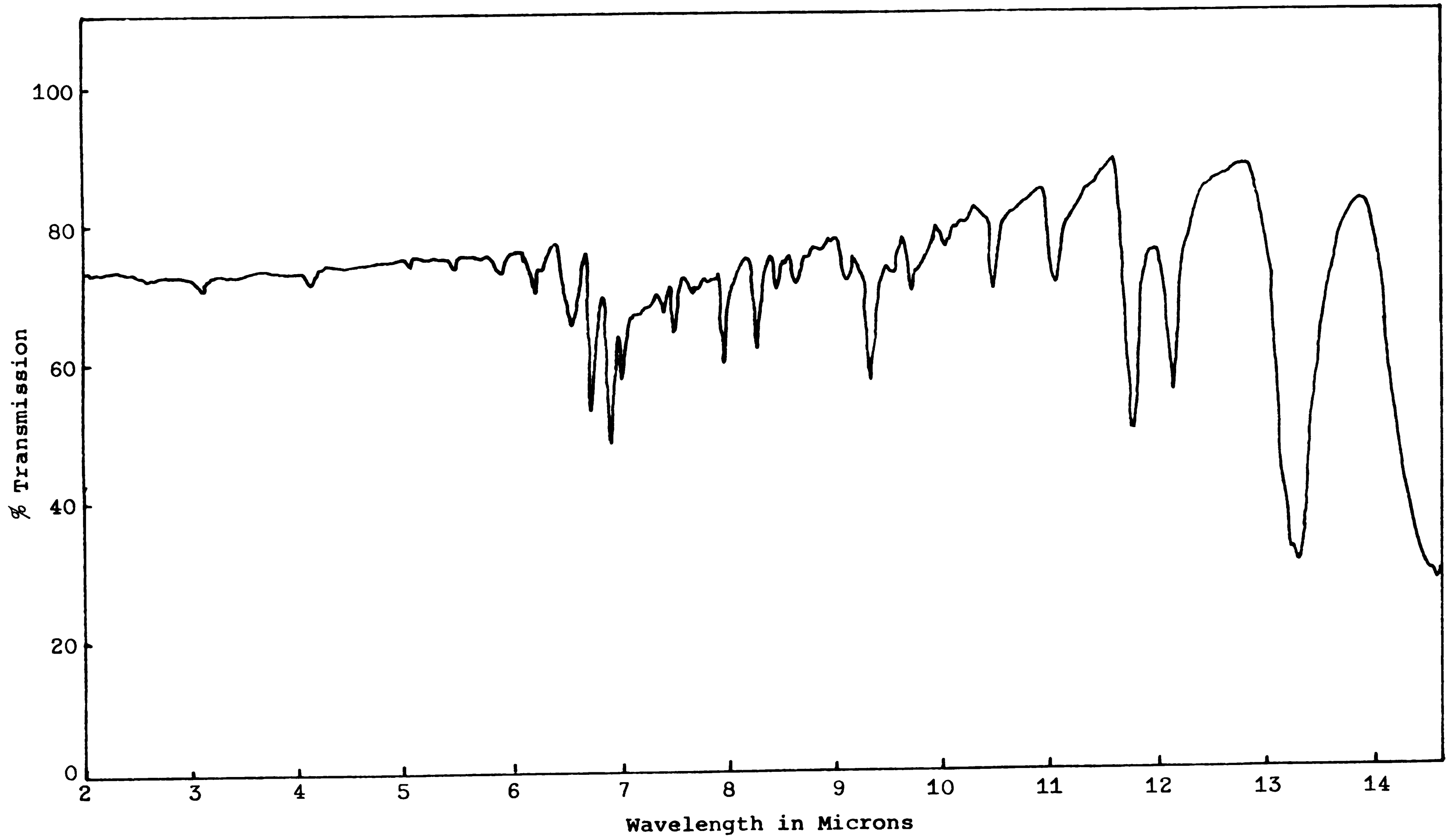


Figure X. 2-Phenylthiophene.

(5 mg. in KBr pellet)

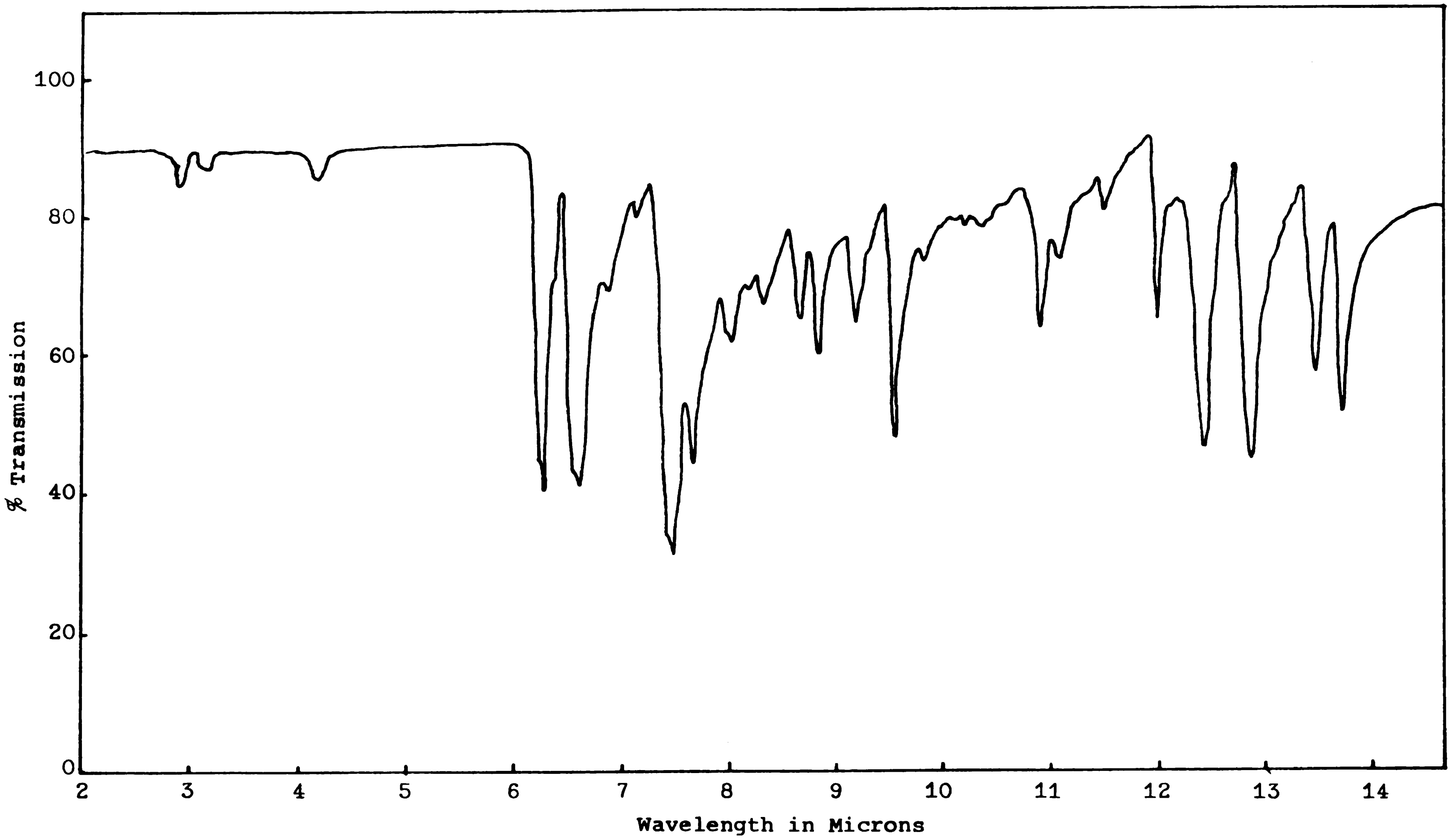


Figure XI. 2,4-Dinitrophenyl-1-naphthylthioether. (5 mg. in KBr pellet)

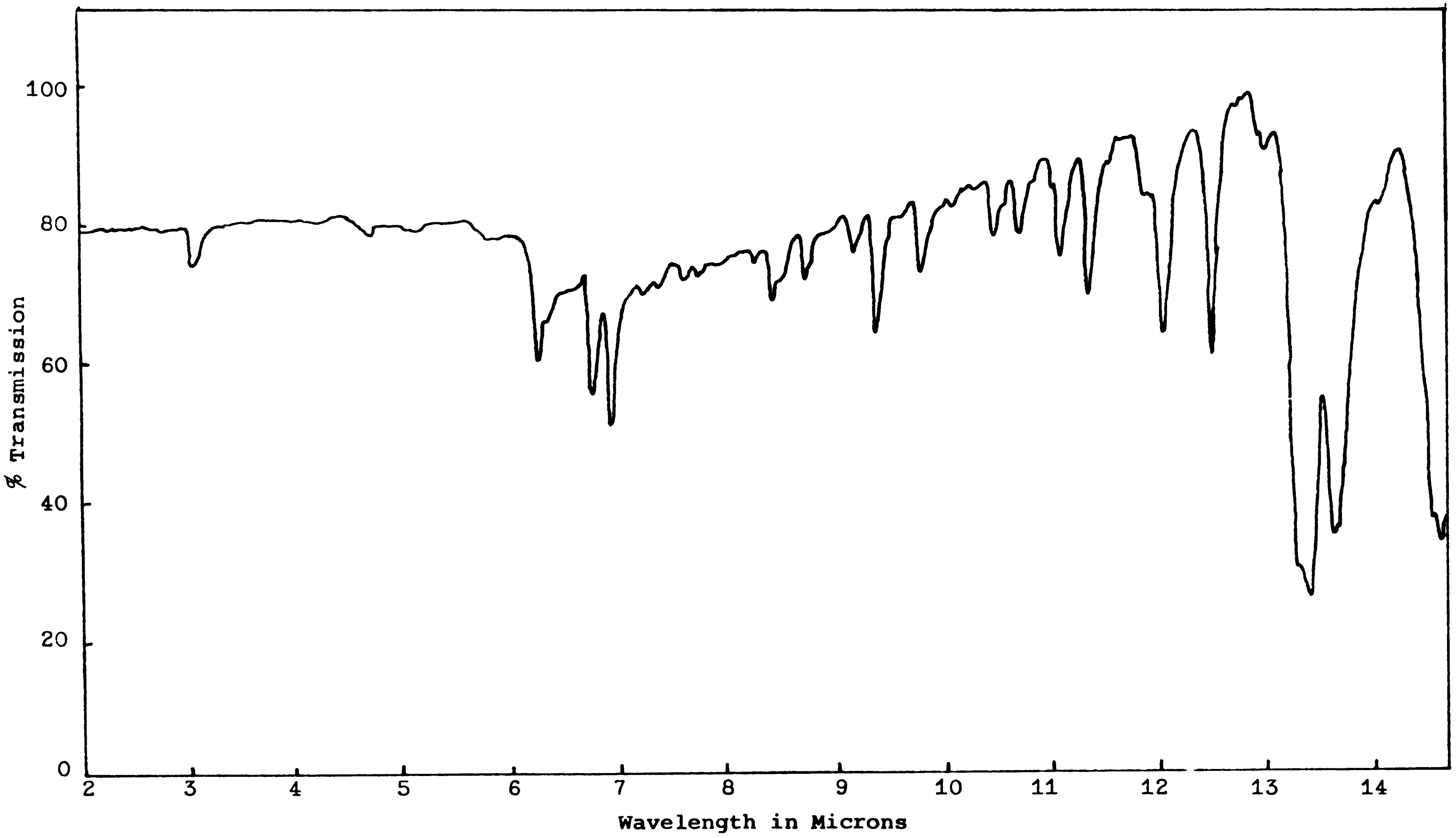


Figure XII. 2,4-Diphenylthiophene. (5 mg. in KBr pellet)

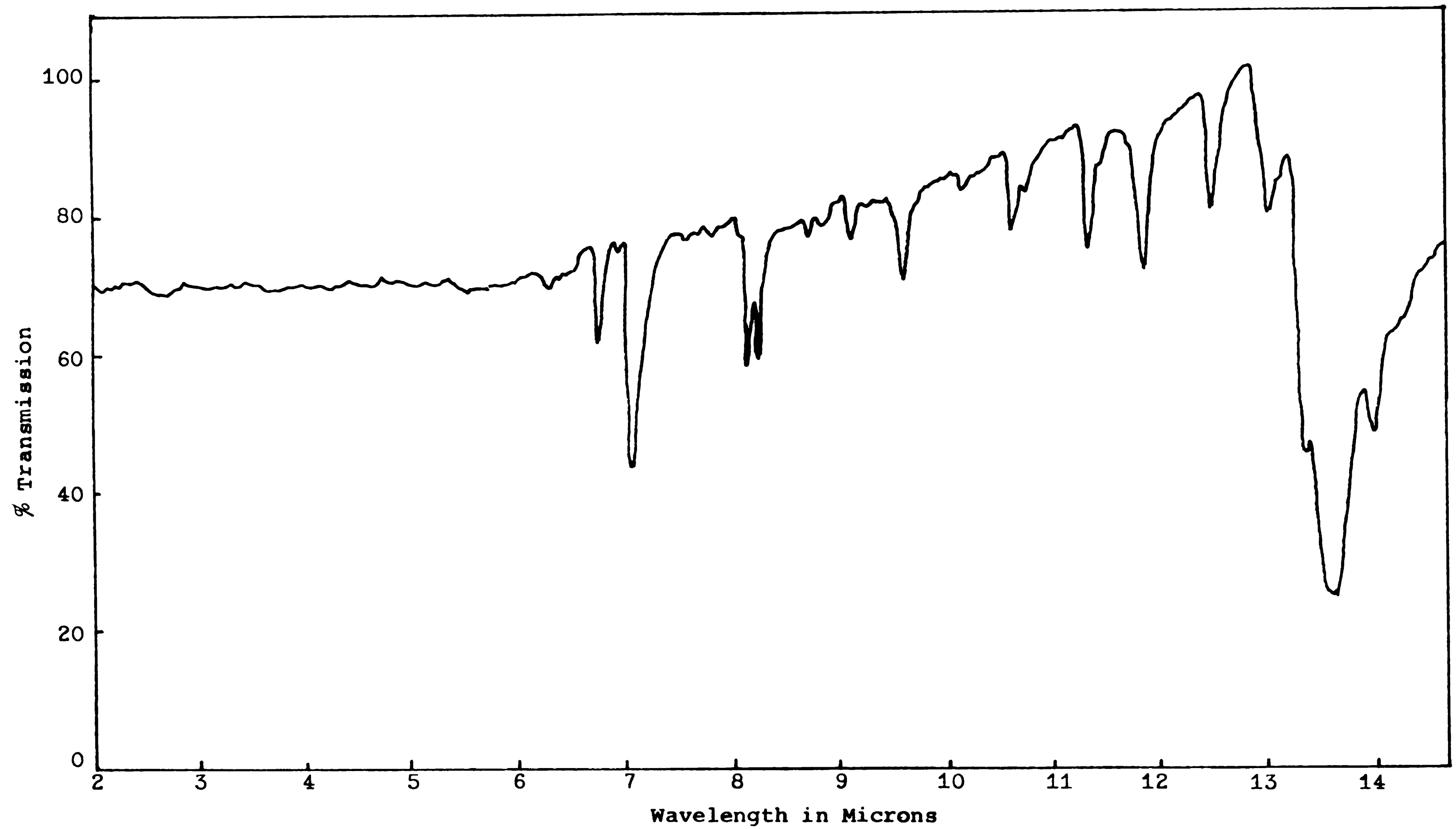


Figure XIII. 2,5-Diphenylthiophene. (5 mg. in KBr pellet)

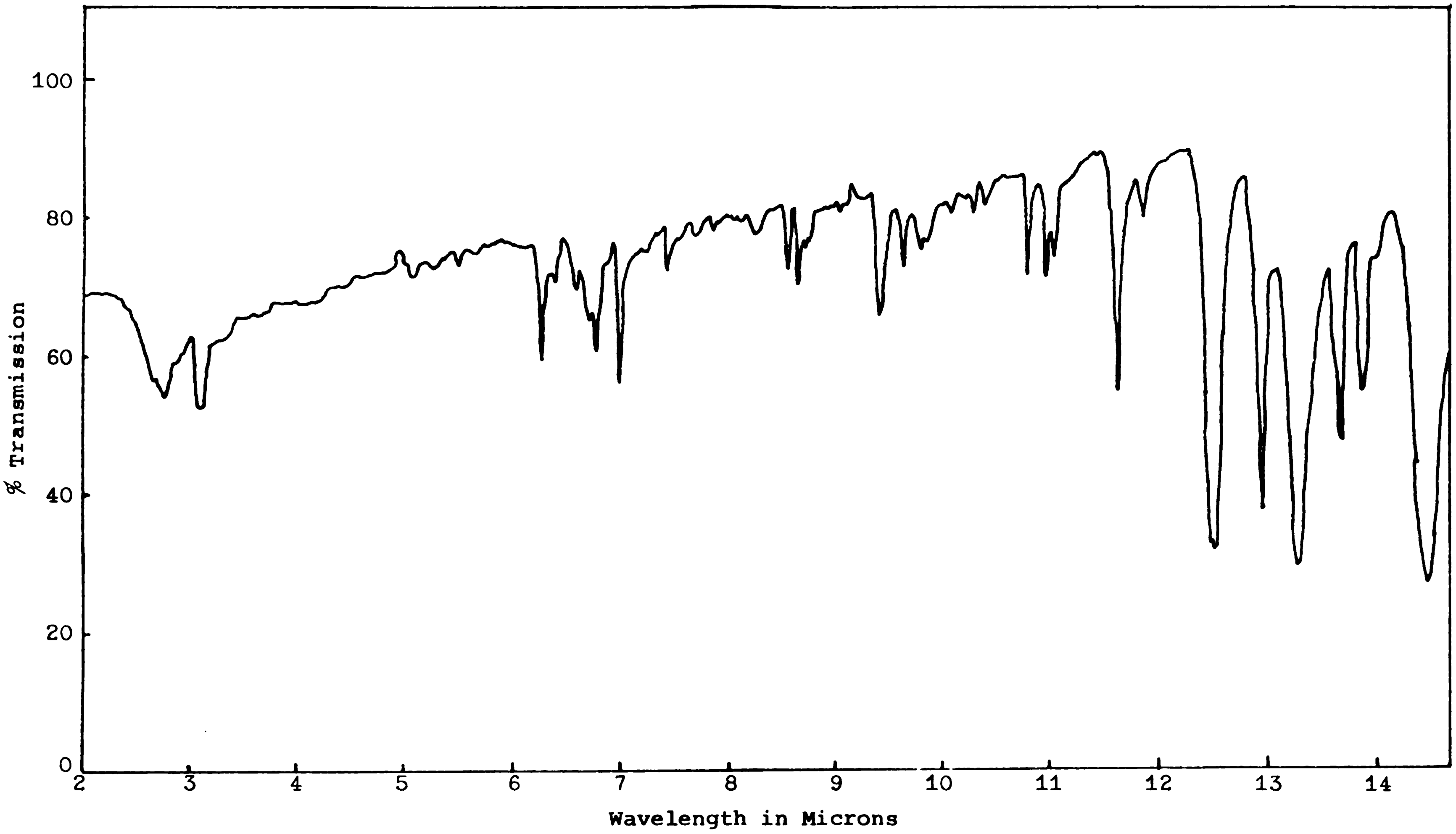


Figure XIV. 3,4-Diphenylthiophene. (5 mg. in KBr pellet)

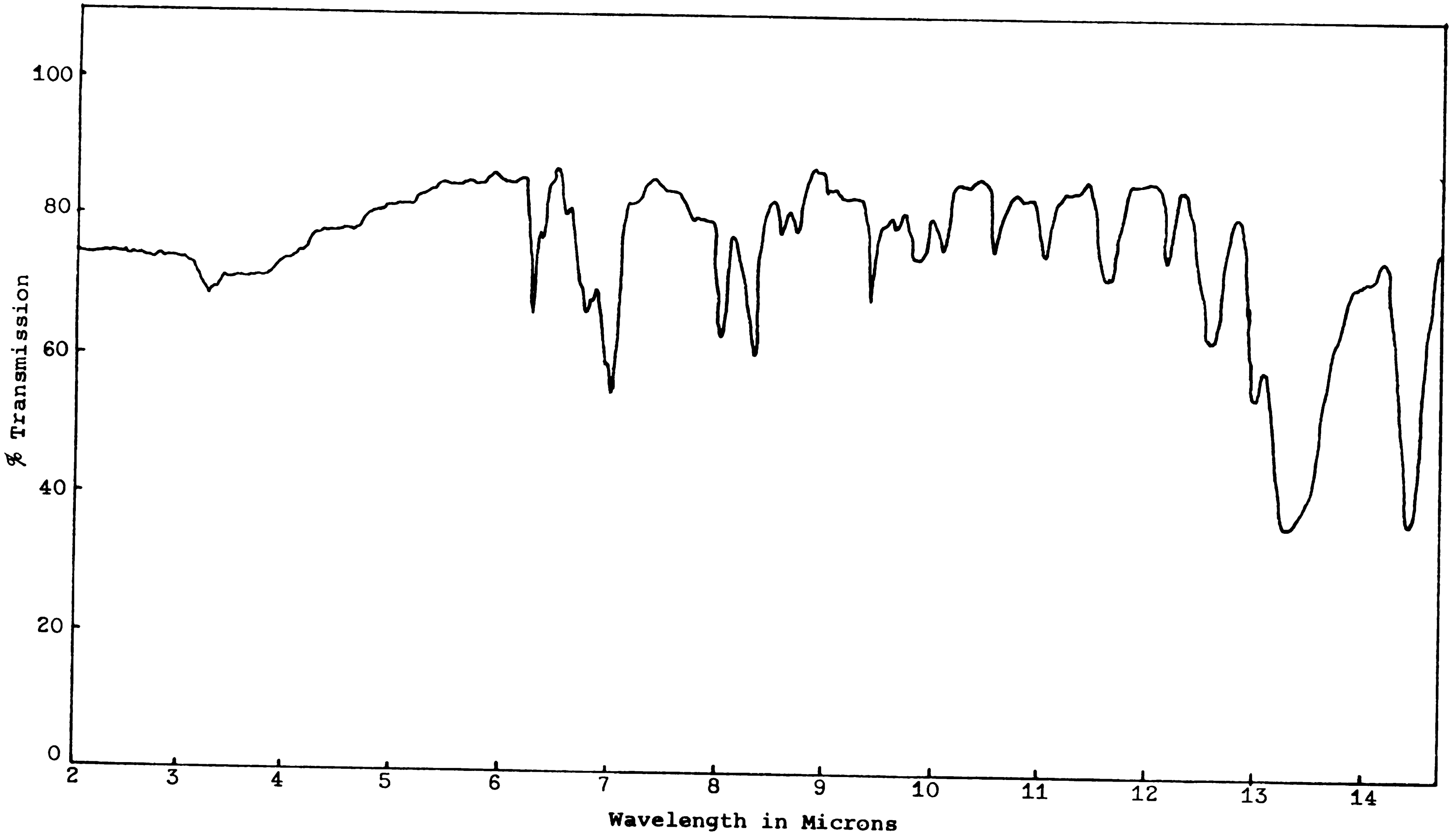


Figure XV. 2,3-Diphenylthiophene.

(5 mg. in KBr pellet)

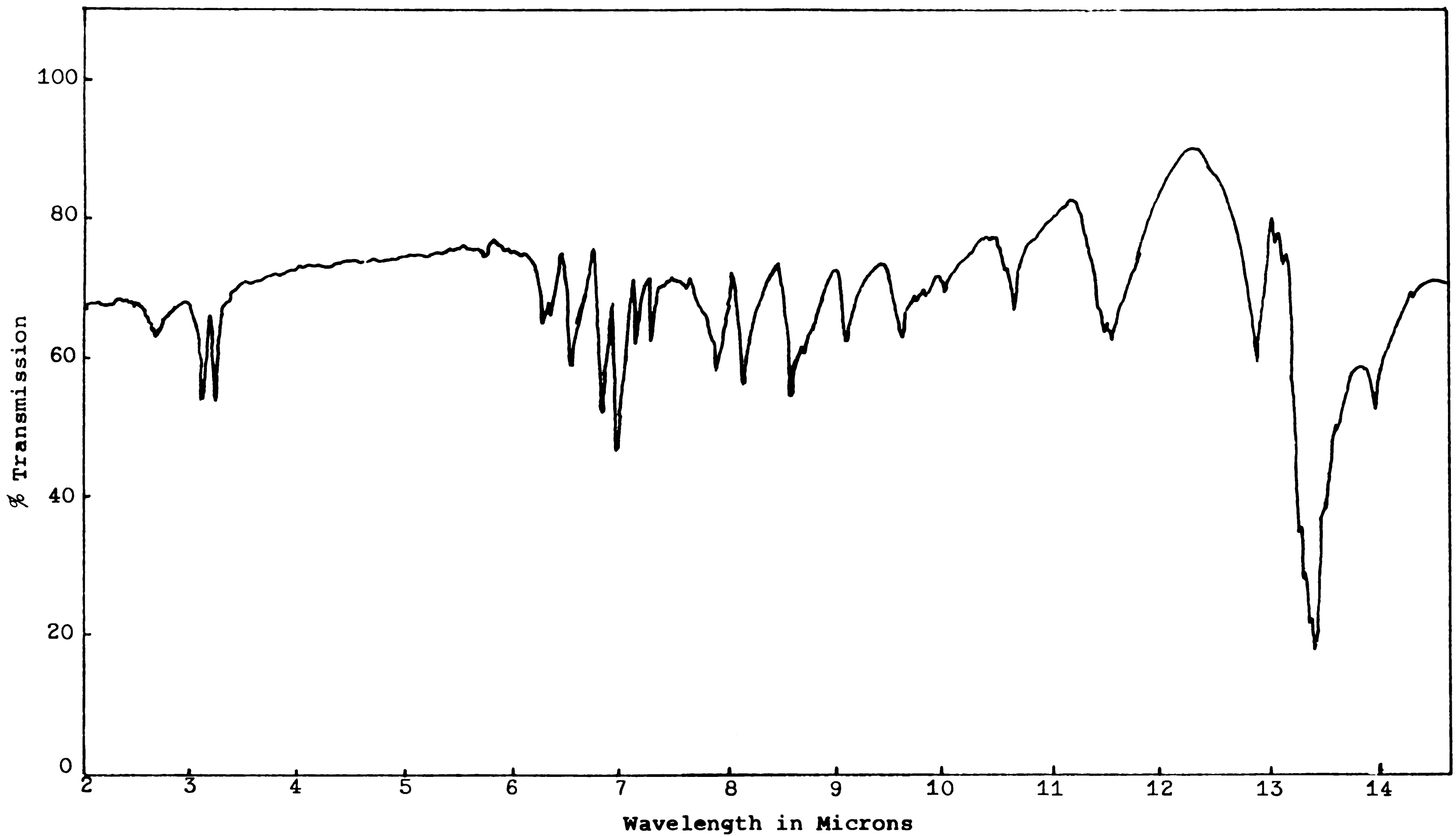


Figure XVI. 4,5,6,7-Dibenzoisothionaphthalene. (5 mg. in KBr pellet)

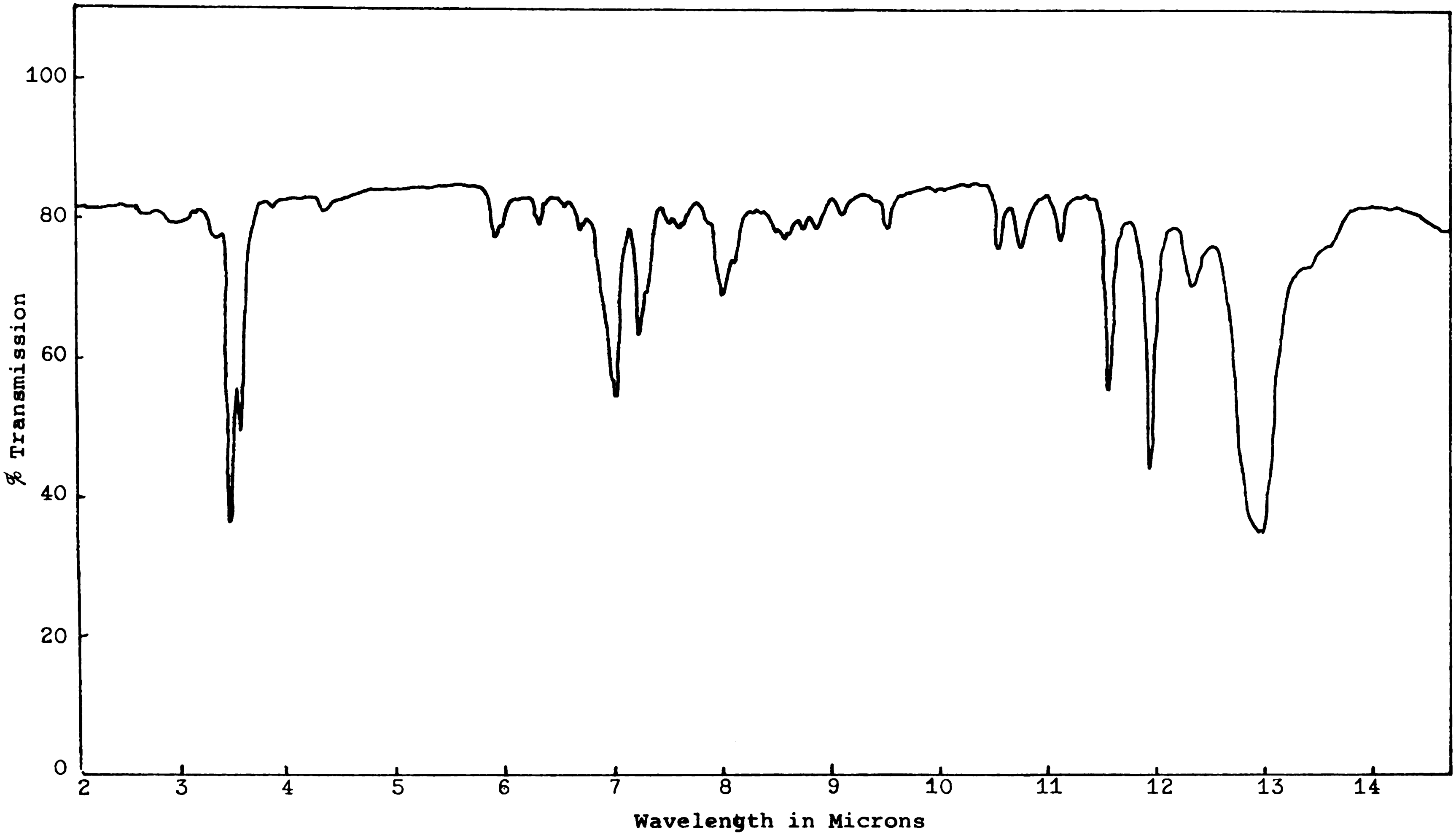


Figure XVII. 4,5,6,7-Tetrahydrobenzo[C]thiophene. (5 mg. in KBr pellet)