

REACTIONS AND PROPERTIES OF THE
ISOMERIC DIHYDROTHIOPHENE 1,1-DIOXIDES

by
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**To the Memory
of
My Father**

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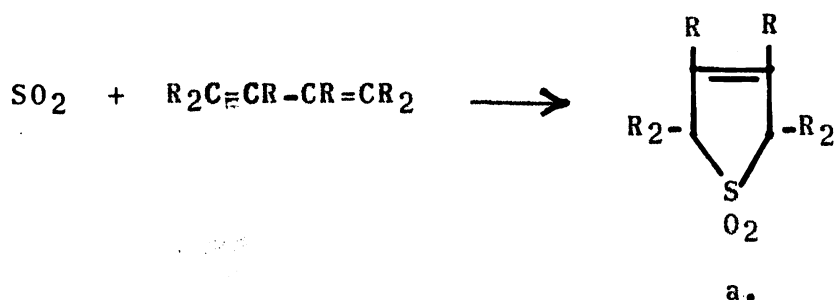
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INTRODUCTION

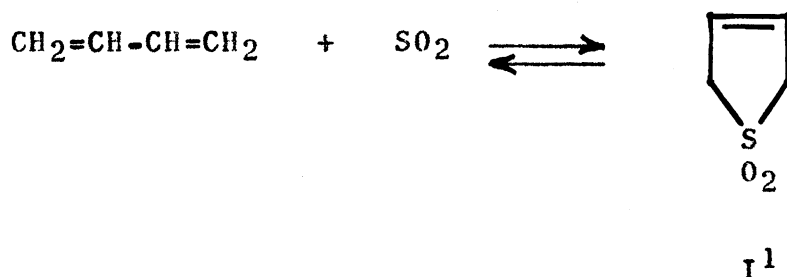
In recent years the alkadienes or diolefins have received the attention of not only the theoretical chemists but of applied chemists as well. One of the interesting reactions these dienes will undergo is the Diels-Alder reaction. If the dienophile used has a hetero atom present, it is possible to form a heterocyclic compound. The reaction of a 1,3-diene with sulfur dioxide (a dienophile) will form the cyclic sulfone (a).



At present, relatively little is known about the reactions of these cyclic sulfones. The choice of using the 2,5-dihydrothiophene 1,1-dioxide (I)¹ (viz. where R is H) in this study has a two-fold purpose. First of all, 1,3-butadiene and sulfur dioxide are readily available materials and secondly this sulfone is the parent member of a large number of cyclic β -sulfones.

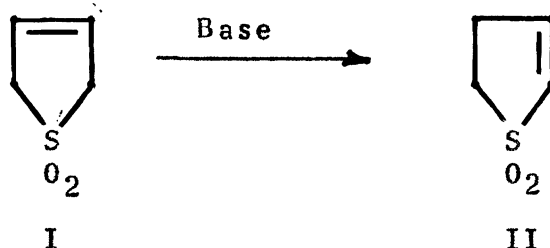
¹ All of the Roman numerals used throughout this work will be consistent with the assigned structures.

Thus, a thorough study of its properties and reactions



is of prime importance in the further study of the alkyl substituted cyclic sulfones.

Structurally, I contains a carbon-carbon double bond, a sulfone group and two α -methylene groups. When treated with a strong base the 2,5-dihydrothiophene 1,1-dioxide (I) will isomerize to the 2,3-dihydrothiophene 1,1-dioxide (II).



Structurally, II has only one α -methylene group but its carbon-carbon double bond is conjugated with the sulfone group. The 2,3-dihydrothiophene 1,1-dioxide (II)

1 In the skeleton formula I and for other formulas which appear throughout this dissertation the hydrogen atoms necessary to complete the valency of four for carbon are not shown except where special emphasis is desired.

is the parent member of the corresponding cyclic α -sulfones.

Thus, we have two polyfunctional molecules which are of interest since they permit several points for chemical attack. Ionic and free radical addition reactions to the double bond and any reactions which might bring about substitution at the α -methylene groups would be of interest. It should be noted here that in the preparation of the 2,3-dihydrothiophene 1,1-dioxide (I), the reaction is reversible. Thus, any substituted sulfones of I would provide an easy method of preparing substituted 1,3 dienes.

Of further interest would be the comparison of the reactions of I and II since the double bond shift (I \rightarrow II) should have an effect on any ionic reactions. Differences in chemical properties are to be expected since the α -sulfones have the double bond conjugated with the sulfone group while the β -sulfones do not.

The object of this investigation is a thorough study of the reactions of the 2,5-dihydrothiophene 1,1-dioxide and its isomer. Such an investigation would greatly extend our knowledge of these cyclic sulfones and the study of these chemical compounds would add to theoretical aspects of reactivity and molecular structure. The new compounds synthesized from the dihydrothiophene 1,1-dioxides

may have some practical value since many derivatives of I and II have been used as insecticides (1), in the purification of diene hydrocarbons (2, 3, 4), as selective solvents (5, 6, 7, 8, 9) and as stabilizers (10, 14).

There are several names which have recently been used to describe the same cyclic sulfones. The more frequently used names are given in Table I. The nomenclature used throughout this work is that recommended by E. J. Crane (12), Director and Editor of Chemical Abstracts and by M. A. Magill (13), Associate Editor of Chemical Abstracts.

TABLE I

NOMENCLATURE



2,5-Dihydrothiophene
1,1-Dioxide

3-Sulfolene

Butadiene Sulfone



Tetrahydrothiophene
1,1-Dioxide

Sulfolane

Dihydrobutadiene
Sulfone

Source

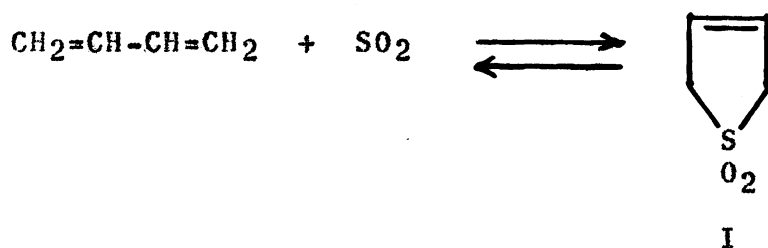
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Appeared
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Common
Name

HISTORICAL

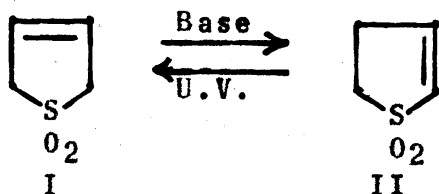
The first reported preparation of the 2,5-dihydrothiophene 1,1-dioxide (I) was that of Staudinger (11) in 1930. A mixture of 1,3-butadiene, liquid sulfur dioxide and 1% pyrogallol as an inhibitor (antioxidant) was allowed to stand for six days and I isolated. Since then many workers have improved upon the preparation of I,



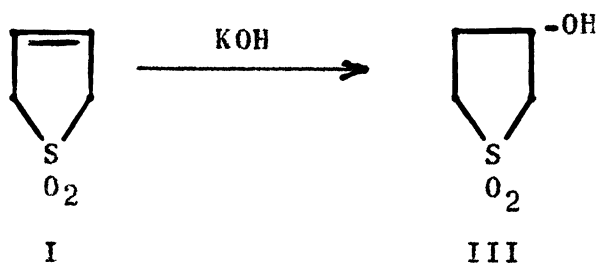
(15,16,17,18,19,20,21,22,23,24,25) the more notable being Backer and coworkers (17,20,24) and Van Zuydewijn (18, 19,21,23). Various antioxidants, such as, pyrogallol, hydroquinone and t-butylcatechol were used.

In recent years petroleum companies have studied the preparation of I and other sulfones primarily as a means of removing 1,3-dienes from hydrocarbon mixtures (26,27).

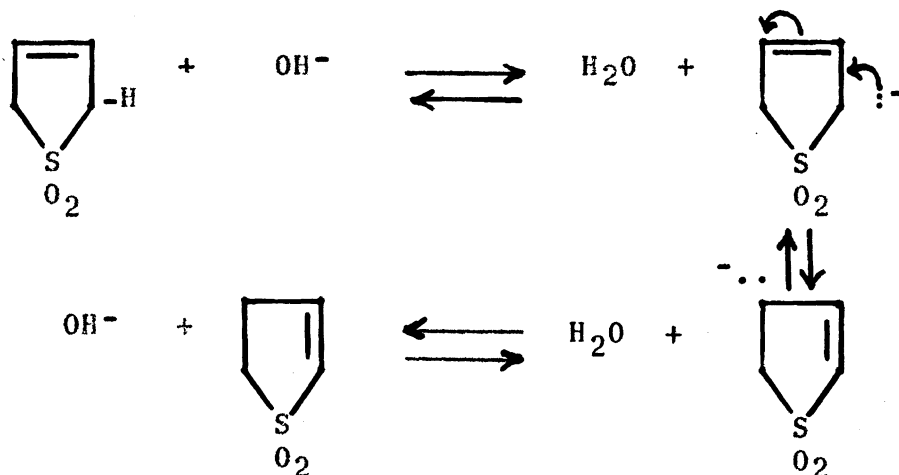
It was van Zuydewijn (21) who first effected the isomerization of I to the 2,3-dihydrothiophene 1,1-dioxide (II) using 0.5 N potassium hydroxide or ultraviolet radiation.



Many other workers have sought to improve the yield of this reaction (18, 19, 25, 28, 29), since the equilibrium lies far to the left. If a higher concentration of base is used, the 3-hydroxytetrahydrothiophene 1,1-dioxide (III) is mainly formed (19).

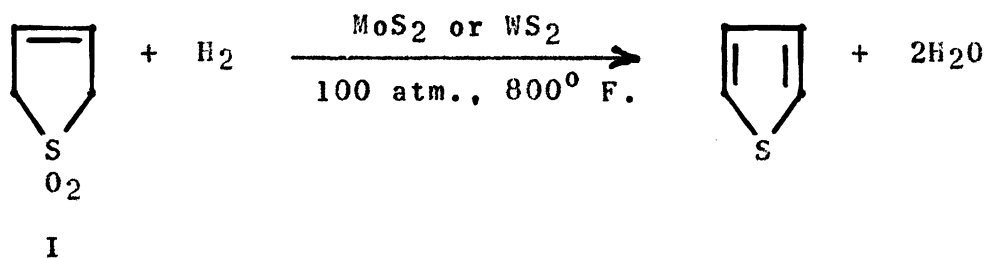


However, it should be pointed out that the alcohol (III) is not an intermediate in the isomerization of I to II, since under the same conditions it is not possible to go from the alcohol (III) to the 2,3-dihydrothiophene 1,1-dioxide (II) (37). Thus the mechanism for the isomerization is ionotropic, rather than addition followed by the elimination of water (18).

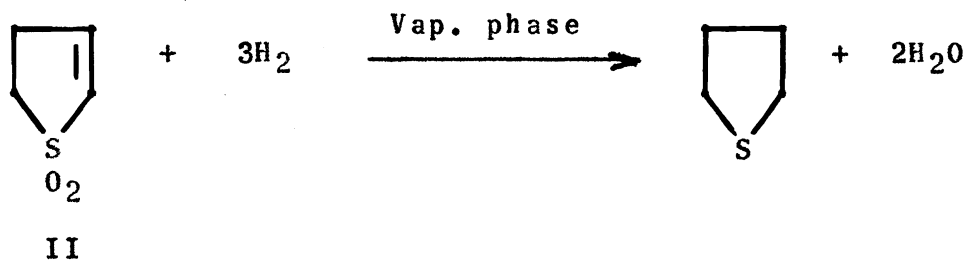


In contrast to the early discussions concerning the structure of the 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII) (30,31,32) the action of sulfur dioxide and 1,3-butadiene was presumed to give the compound which corresponds to a 1,4-adduct. Although the structure of this adduct was accepted as that represented by the 2,5-dihydrothiophene 1,1-dioxide, no direct confirmation was made at that time.

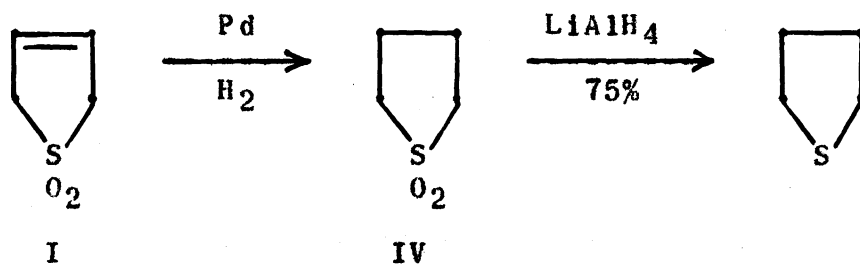
It was not until 1948 that Boyd (33) showed conclusively the structure of the 2,5-dihydrothiophene 1,1-dioxide (I) by its reduction to thiophene.



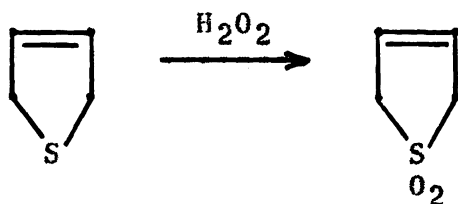
Later Moore and Trimble (34) reduced II to the tetrahydrothiophene.



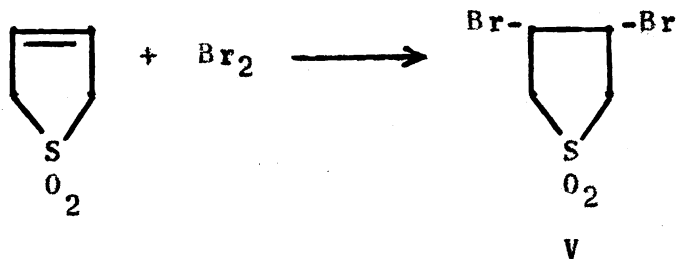
Bordwell and McKellin (35) found that the reduction of I with lithium aluminum hydride gave only a dark colored polymeric material; however, if the 2,5-dihydrothiophene 1,1-dioxide (I) was first hydrogenated to the tetrahydrothiophene 1,1-dioxide (IV), a 75% yield of the tetrahydrothiophene was realized.



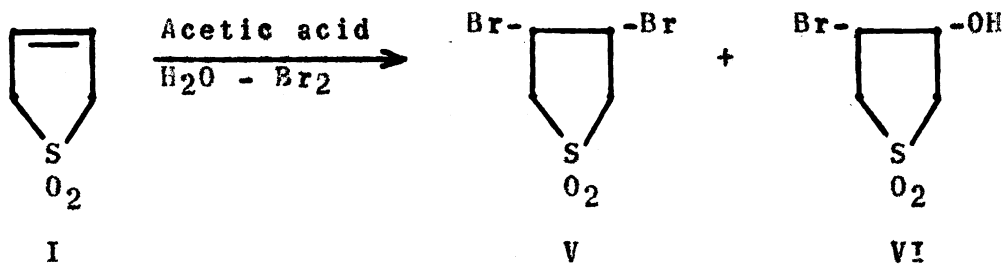
Birch and McAllen (36) presented further proof of the structure of I by the oxidation of the 2,5-dihydrothiophene with hydrogen peroxide to I.



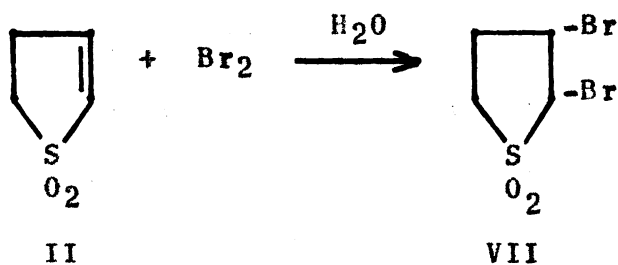
Although some reactions of I have been investigated, no definitive studies have been made. Bromine will add to the double bond of I to form the corresponding dibromo compound (V) (23). Backer and coworkers (38,39) have found that the bromination of I in a water-acetic acid



solution gave not only V, but also a bromohydrin (VI).











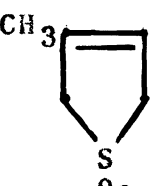

The bromination of II can only be accomplished in a water solution (23) and no bromohydrin is formed.



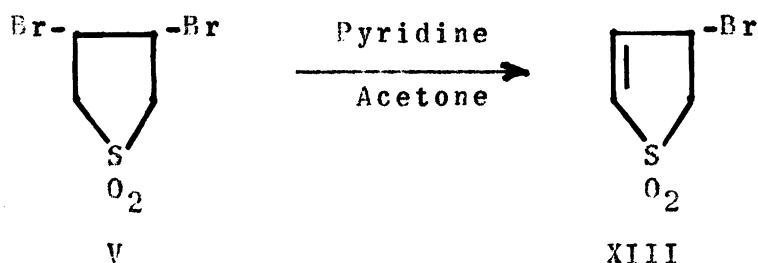
It should be noted here that many of the cyclic unsaturated sulfones have similar properties; thus, the dibromo derivatives furnish a quick and easy means of identification, since most of these compounds are solids. Table II gives some typical examples.

TABLE II

Properties of Some Dihydrothiophene 1,1-Dioxides
and Their Dibromo Derivatives

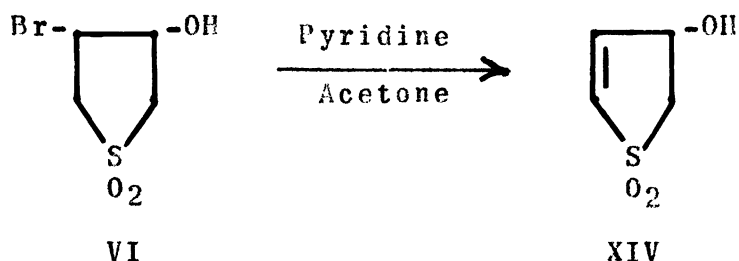
<u>Compound</u>	<u>M. P.</u>	<u>Dibromo</u>	<u>M. P.</u>	<u>Ref.</u>
	64.5-65.0 ⁰	Br-  -Br	141-142 ⁰	20,23
	49-50 ⁰		116-117 ⁰	21,23
	63.0-63.5 ⁰	Br-  -Br	125-127 ⁰	17,23
	79 ⁰		oil	19,41
	40.4-41.0 ⁰	CH ₃ -  -Br	121-122 ⁰	24

The 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) has been dehydrobrominated by Backer and Blaas (38) using pyridine to form the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII).



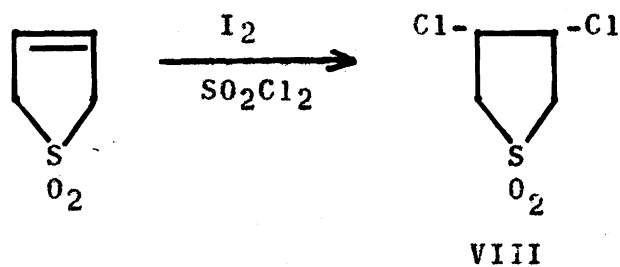
Bailey and Cummins (29) later claimed to have improved upon the procedure.

Backer and van Lohuizen have extended their dehydrobromination work to the bromohydrins (39), thus giving the 2-hydroxy-2,3-dihydrothiophene 1,1-dioxide (XIV).

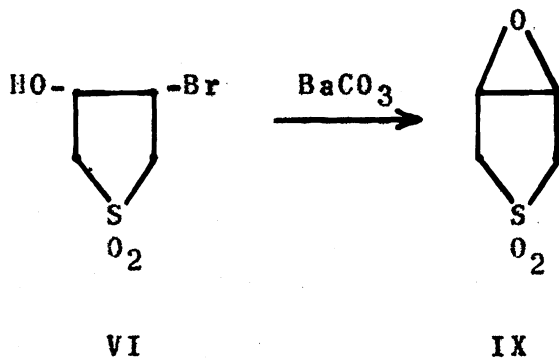


The addition of chlorine to I using chlorine gas has never been reported, however, Jordan and Kipnis (40) chlorinated I using sulfuryl chloride and a crystal of iodine to give

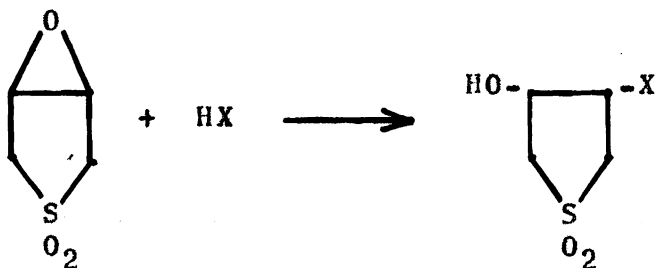
the dichloride (VIII).



The isomeric halohydrins have been synthesized by van Lohuizen and Backer (39) from the epoxide (IX).

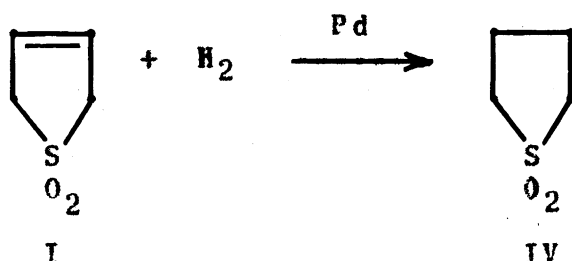


Addition of the various halogen acids gave the corresponding halohydrins.



[X = Br (VI); Cl (X); I (XI)]

The 2,5-dihydrothiophene 1,1-dioxide (I) has been hydrogenated to the tetrahydrothiophene 1,1-dioxide (IV) by various workers using palladium catalysts (20,23,35). More drastic conditions have been reported in patents (42,43,44). The saturated cyclic sulfones are



very useful in this research, since they are thermally stable and can be purified and identified without fear of dissociation. Table III gives the properties of some typical saturated sulfones and the dissociation temperatures of the corresponding 2,5-dihydrothiophene 1,1-dioxides.

The oxidation of I has been studied by van Zuydewijn (23) and he has shown that using different conditions, the cis and trans diols (XII) can be formed. Thus by treating I with peracetic acid the trans-diol

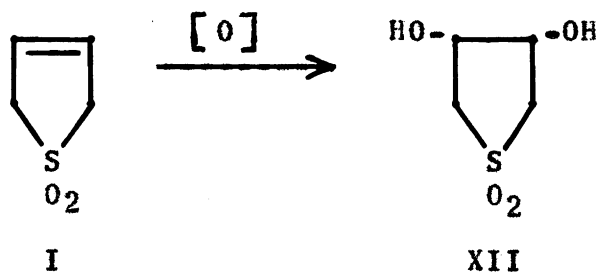

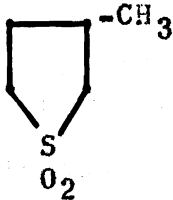
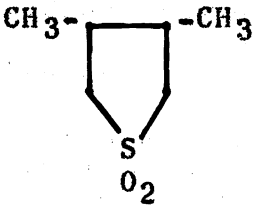
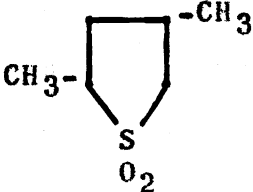


TABLE III

Properties of Some Saturated Cyclic Sulfones

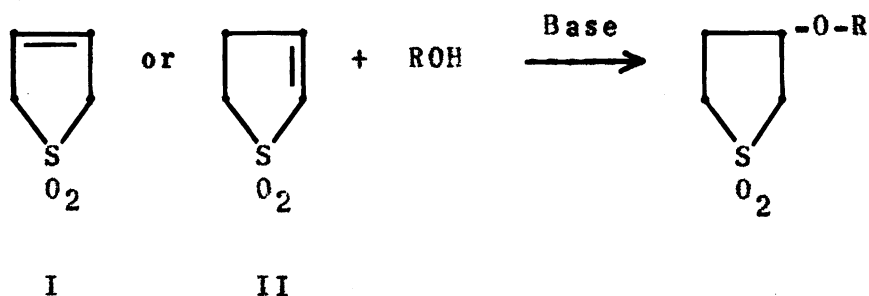
<u>Compound</u>	<u>M.P. (B. P.)</u>	<u>Dissociation Temperatures</u>		<u>Ref.</u>
		1	2	
	29-30°	stable	117-118°	20,23
	0-1°	stable	100-110°	20,23
	50-51°	260-265°	142-151°	20
	(123.5°/5mm.)	stable	106-118°	24,48

1 Dissociation temperature of the saturated sulfone

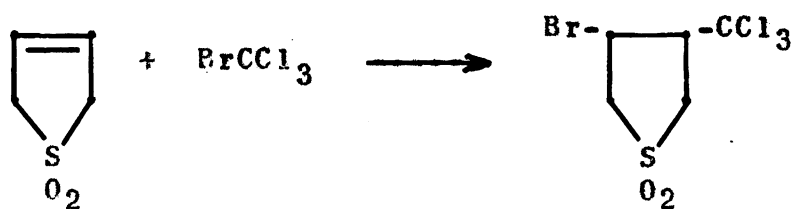
2 Dissociation temperature of the corresponding 2,5-dihydro compound.

is formed while the use of potassium permanganate gives the cis-diol.

The treatment of the 2,5-dihydro (I) or 2,3-dihydro (II) compound with base and an alcohol will give the same corresponding ether (45,46).



Kharasch and coworkers have accomplished an interesting free radical reaction with I using acetyl peroxide and bromotrichloromethane (47).



The physical properties of the 2,5-dihydrothiophene 1,1-dioxide (I) have been well studied and are listed on Table IV.

TABLE IV

Physical Properties of 2,5-Dihydrothiophene 1,1-Dioxides

<u>Property</u>	<u>Description</u>	<u>Reference</u>
Melting Point	64.5-65.0	20
Dissociation temperature ¹	117-118 ⁰	16
Solubility	Very soluble: benzene, chloroform, methanol, ethanol, acetone, sulfuric acid, nitric acid, toluene, acetic acid, xylene, liquid ammonia	
	Readily soluble: petroleum ether, n-octane, and ethyl ether.	16, 26, 49
Density	$d_{17} = 1.50$	49
Cell Dimension	a = 9.55; b = 11.35 c = 6.23 (All in Å ⁰) B' = 48 ⁰ 16'; space group C ₂ ⁵ h	49
Thermodynamic functions ²	H _{act.} = 33.6 ± 0.5 k cal./g. mole ΔS _{act.} = 8.9 ± 1.2 e.u. ΔF _{act.} = 30,100 cal./g. mole A = 7 x 10 ¹⁴ sec. ⁻¹	16

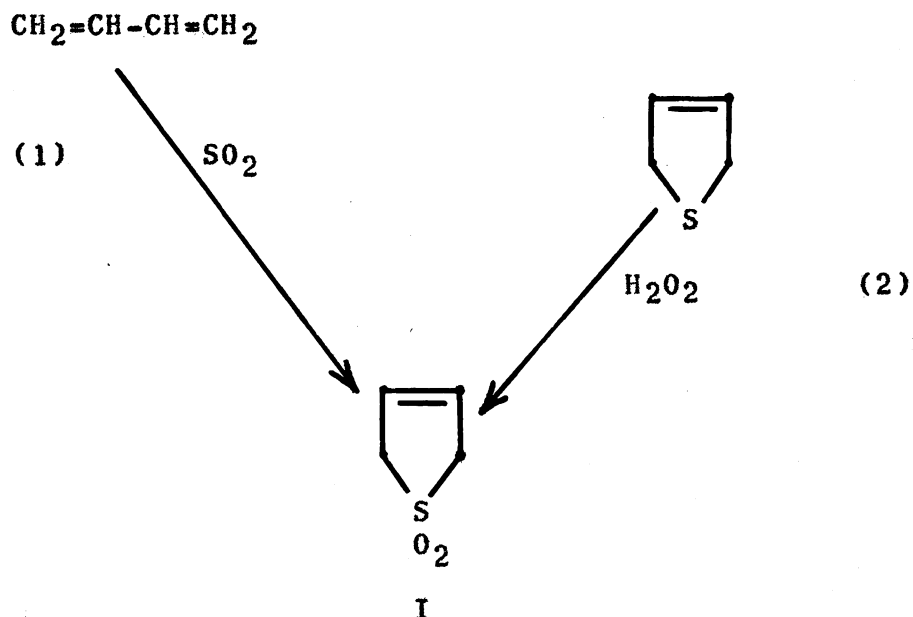
1 Value obtained at atmospheric pressure.

2 These functions are for the reaction of 1,3-butadiene and sulfur dioxide.

RESULTS AND DISCUSSION

A. Formation of the Isomeric Dihydrothiophene
1,1-Dioxides

The synthesis of 2,5-dihydrothiophene 1,1-dioxide can be accomplished by two general methods: (1) the 1,4-addition of a 1,3-diene to sulfur dioxide and (2) the oxidation of 2,5-dihydrothiophene.



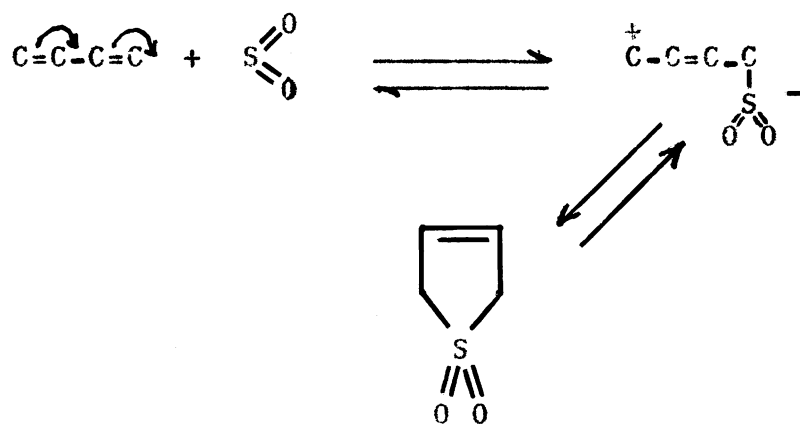
The first method is generally used in the preparation of the cyclic sulfones, since the reaction goes rather easily. The second method has gained importance in recent years as a means of proving the structure of certain substituted thiophenes, dihydrothiophenes and tetrahydrothiophenes (36,60,61,62) by their oxidation to the corresponding cyclic sulfone. At present, the latter method has no importance as a means of preparing cyclic

sulfones as such, since it requires the reduction of substituted thiophenes. This has been shown by Birch and McAllen (63) to be rather difficult since the reduction of thiophene with sodium in liquid ammonia gives 2,5-dihydrothiophene, 2,3-dihydrothiophene, 2-butene-1-thiol, butenes and hydrogen sulfide.

In the present study only the first method was used. A modification of the method described by Grummitt, Ardis, and Fick (16) was followed for the preparation of I. This method required the use of hydroquinone as an antioxidant (inhibitor) and an excess of sulfur dioxide. The use of excess sulfur dioxide was shown by Staudinger and Ritzen-thaler (22) to reduce the amount of polymer formed even without an antioxidant present. Grummitt, et al. (16) heated a mixture of two moles of sulfur dioxide, one mole of 1,3-butadiene and 2% hydroquinone to 100-105° for 12 hours.

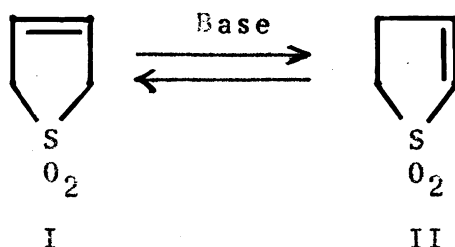
In this work a close study of pressure-temperature-time data indicated that the reaction was completed after four hours of heating. Data from a typical experiment are found in Appendix I. Reducing the reaction time to four hours the yields of I were increased 5-15%. A longer heating period could cause not only polymerization of I, but also the polymerization of the 1,3-butadiene present.

The mechanism for the 1,4-addition of sulfur dioxide to a conjugated diene is a polar process (16) which involves a diene of relatively low ionization potential and a molecule of high electron affinity.



Thus there is an electron transfer from the diene to the dienophile followed by cyclization of the intermediate adduct. This is analogous to the Diels-Alder reaction of a diene with maleic anhydride (64).

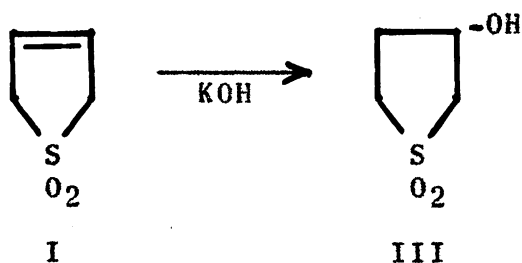
The preparation of the 2,3-dihydrothiophene 1,1-dioxide (II) is accomplished by the base catalyzed isomerization of I. This is an equilibrium reaction which



lies far to the left. A modification of the procedure of

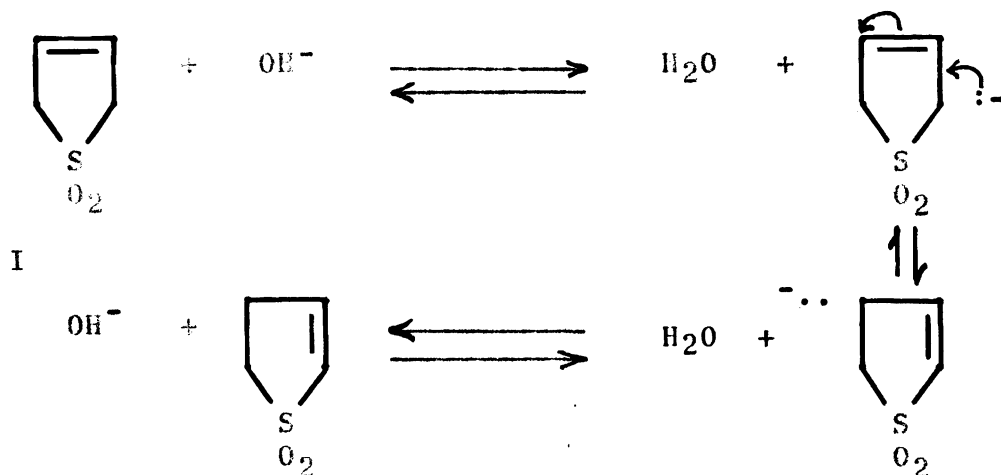
van Zuydewijn (21) and Bailey and Cummins (29) was used, since it was not possible to reproduce Bailey and Cummins work.

Since a concentrated solution of potassium hydroxide caused addition of water to give the 3-hydroxytetrahydrothiophene 1,1-dioxide (III), a dilute solution had to be used.



In this work I was treated with dilute potassium hydroxide and irradiated with ultraviolet light for 20 hours. Then a continuous extraction of the basic solution with chloroform was run. It was seen that if the reaction solution was acidified and then subjected to continuous extraction with chloroform, the yield of II was reduced from 49% to 24%, although Bailey and Cummins (29) claim a good yield from the extraction of the acidified solution.

The mechanism of the isomerization of I to II is ionotropic and not addition followed by the elimination of water (18).



The alcohol (III) could not be an intermediate in this isomerization, since it is not possible under the same experimental conditions to go from III to II (37).

The 2,3-dihydrothiophene 1,1-dioxide (II) is thermally stable to temperatures as high as 200°. As was mentioned before it is formed in an equilibrium reaction and by heating the resulting mixture to 180°, all of the 2,5-dihydrothiophene 1,1-dioxide (I) will dissociate leaving crude II. Previous workers (18,29,37) have purified II by recrystallization from a benzene-petroleum ether mixture. However, it was found in this laboratory that the small amount of alcohol (III) which is formed during the reaction, can't be easily removed by this method. A vacuum distillation will give pure II. The infrared spectra of I and II are shown in Appendix III.

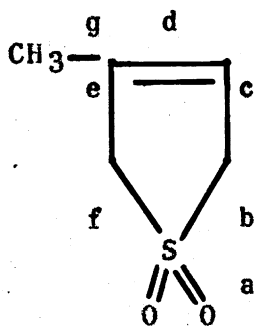
B. Addition Reactions to the Isomeric Dihydrothiophene 1,1-Dioxides: Ionic and Free Radical.

Before discussing the experimental results it would be advantageous to consider the structure of the sulfone molecule. One difficulty that we are immediately confronted with is the lack of physical data in the case of the 2,5-dihydrothiophene 1,1-dioxide (I). For example neither electron diffraction nor ultraviolet absorption studies are reported for I, but considerable work has been done on the 3-methyl-2,3-dihydrothiophene 1,1-dioxide (XXVII). The infrared curves of I and XXVII are very similar and since infrared and electron diffraction deal with vibrations of the molecule, one can assume that the overall structure of the two molecules are similar. By using the electron diffraction data of Jeffrey (74) for XXVII one can arrive at a clearer picture of the cyclic sulfones. Table VI shows the bond distances of XXVII both experimental and calculated.

The experimental values of the bond distances of XXVII are quite different from the usually assigned bond distances (77). This is to be expected if resonance occurs. There are many resonance forms which contribute to the overall structure of the molecule.

TABLE V

Bond Distances of 3-Methyl-2,5-Dihydrothiophene
1,1-Dioxide



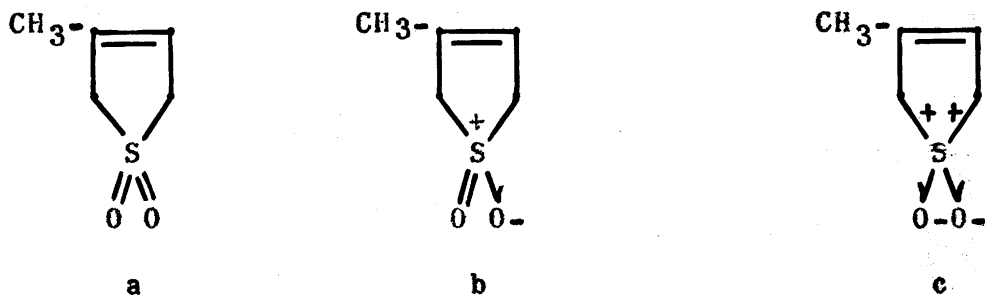
XXVII

<u>Bond</u>	<u>Exp. Value¹</u>	<u>Calc. Value²</u>
a	1.44	1.49
b	1.76	1.81
c	1.47	1.54
d	1.38	1.34
e	1.47	1.54
f	1.74	1.81
g	1.52	1.54

1 See ref. 74.

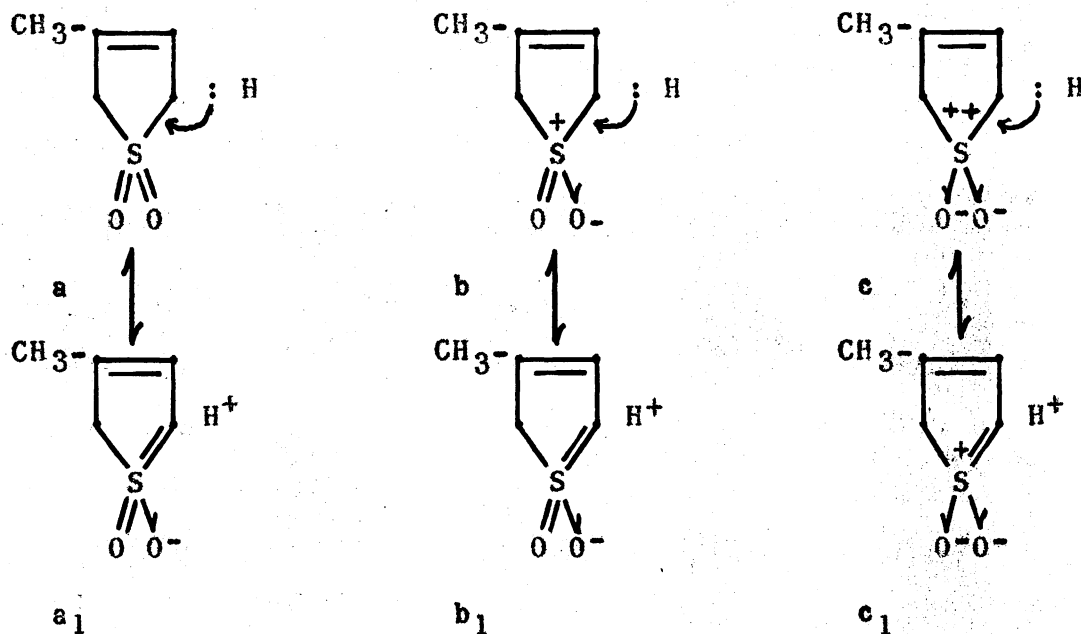
2 Calculated values obtained from Pauling, ref. 77.

Phillips, Hunter and Sutton (75) have suggested from bond length data that the sulfur-oxygen bonds are not coordinate links. There are four resonance forms of XXVII, which can be drawn depicting the sulfone group.



Structure c shows the non-expansion of the sulfur valence octet, while a and b (two forms) are based upon d-orbitals with ten or more electrons about sulfur. These resonance forms would help to account for the sulfur-oxygen bond difference of 1.44 to 1.49 Å. Additional discussion will further explain this difference.

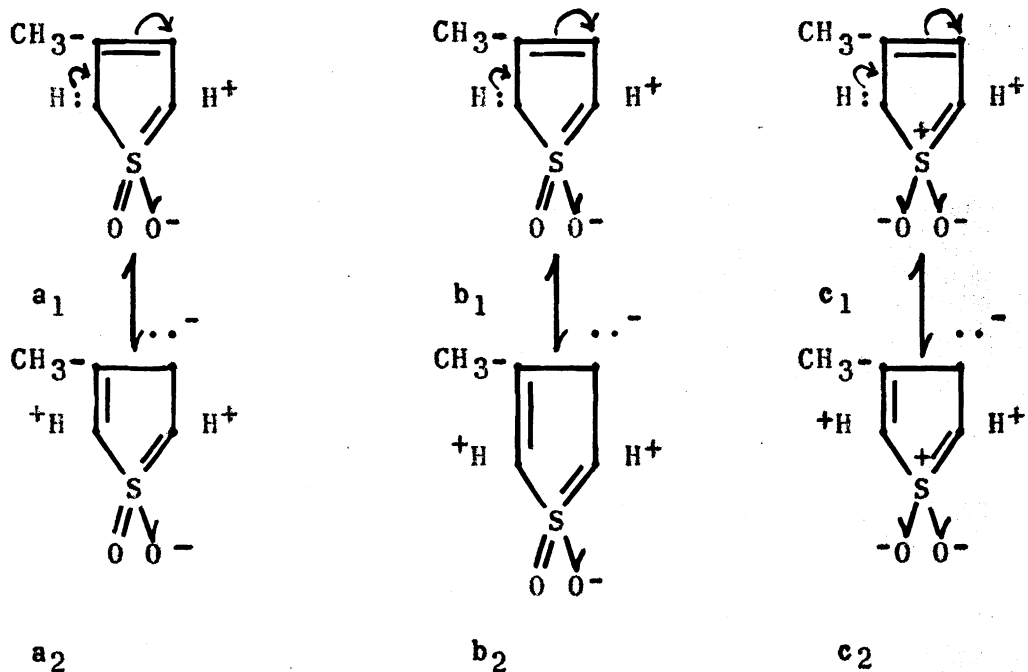
The resonance of the molecule can be further explained on the basis of hyperconjugation and thus explain the bond-distance differences of XXVII (74), which we assume to occur to some extent in I. The following could occur by resonance interaction of a d-orbital of sulfur with an adjacent orbital and expansion of the octet of sulfur. Using a, b and c, the following could occur:



These would account for the C-S bond shortening of 1.81 to 1.74 Å and also help to account for the sulfur-oxygen bond difference. Of course there are many forms which could be written for the above resonance. The acidity of the alpha hydrogens supports this hyperconjugation¹.

Further hyperconjugation can be illustrated as follows:

¹ For further treatment concerning the acidic hydrogens, e.g. reaction with Grignard reagents, etc., see section D of Results and Discussion.



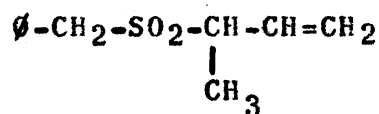
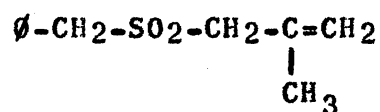
In the like manner there are many more resonance forms that could be written. Thus, the above structures could help account for the shortening of the C - C bond from 1.54 to 1.47 Å and the small lengthening of the C = C bond from 1.34 to 1.38 Å. Koch (76) has studied the ultraviolet absorption spectrum of XXVII and found that XXVII is highly transparent to ultraviolet light, absorbing considerably less than would be expected from the conventional formula XXVIIa. He compared the ultraviolet absorption spectrum of XXVII with methyl cyclohexene and found evidence to support the view that conjugation occurs in the sulfone molecule.

An interesting point to note is the very small change in the CH₃-C bond distance from 1.54 to 1.52 Å.

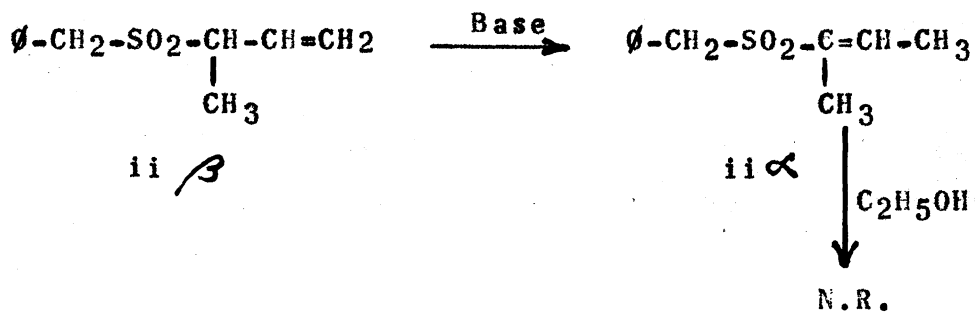
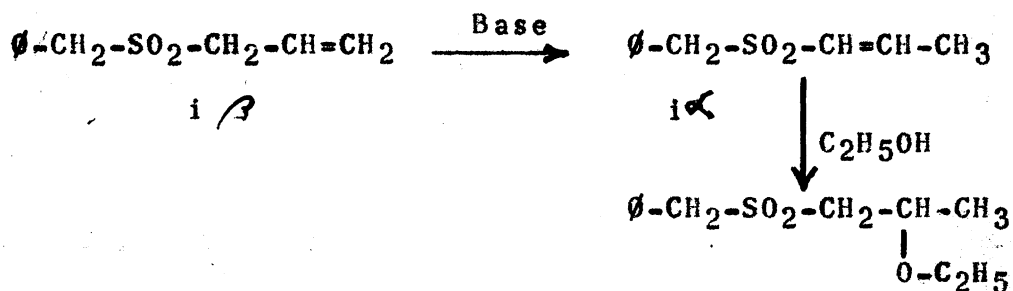
Evidently it does not play an important part in the resonance of XXVII and one can assume that I and XXVII will have similar resonance structures.

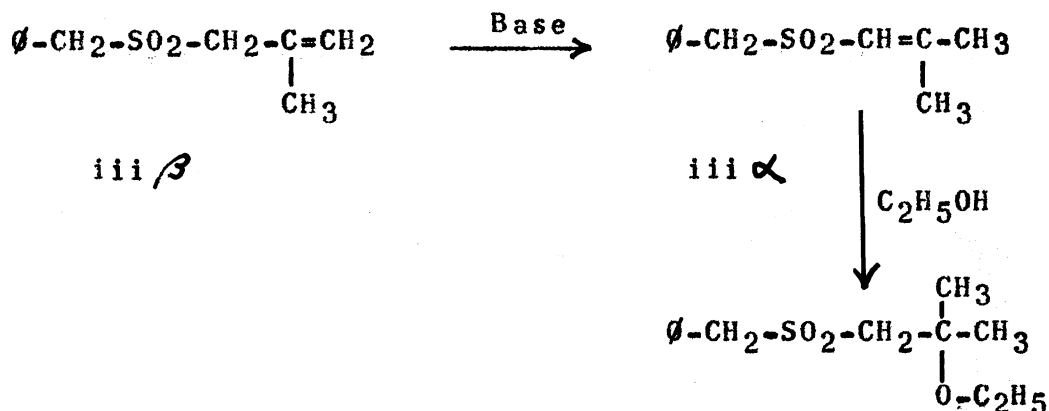
In order to gain some information concerning the double bond in the cyclic sulfones a study of the addition reactions familiar to simpler double-bonded compounds was made on the 2,5-dihydrothiophene 1,1-dioxide (I) and the 2,3-dihydrothiophene 1,1-dioxide (II). The results of these experiments are found in Table VII.

Nucleophilic additions to I and II are well known. Such products have commercial uses as insecticides (1, 45, 46, 57, 78, 79, 80, 81, 82, 83, 84) and as plasticizers (14, 57, 79, 85). The usual practice is to heat I or II with an alcohol, mercaptan, or amine in the presence of a base to give the corresponding saturated ethers, sulfides or amines. Morris (45) has obtained the same product, namely the 3-substituted sulfone, by reaction of I or II with an alcohol in the presence of a base. Backer and coworkers (59, 86, 87) have studied some nucleophilic addition reactions of the sulfones and now it is doubtful (87) that addition to the double bond in the 3-position occurs as such. Backer (87) studied the nucleophilic addition of ethanol in basic medium to the following compounds:

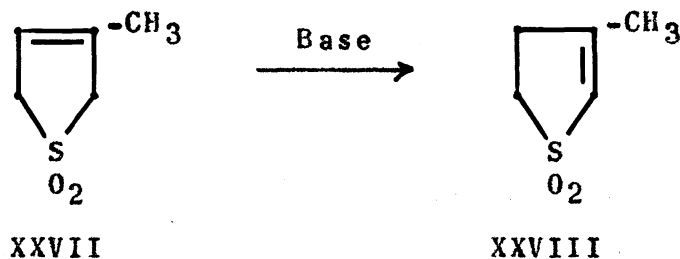
i β ii β iii β

In the case of i β , after 8 hours of reaction time, a 45% yield of the isomerized product (i α) was isolated and only after 72 hours was a 49% yield of the addition product obtained. In like manner ii β and iii β also isomerize first and then only iii α added alcohol. Thus the following occurs for i β , ii β , and iii β .

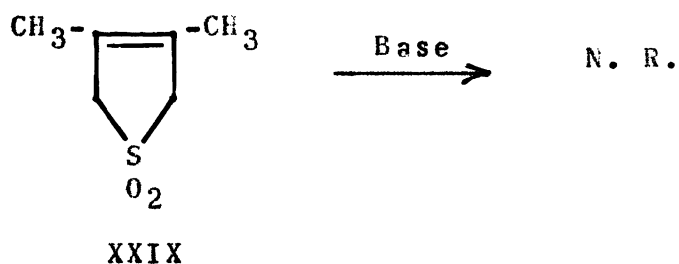




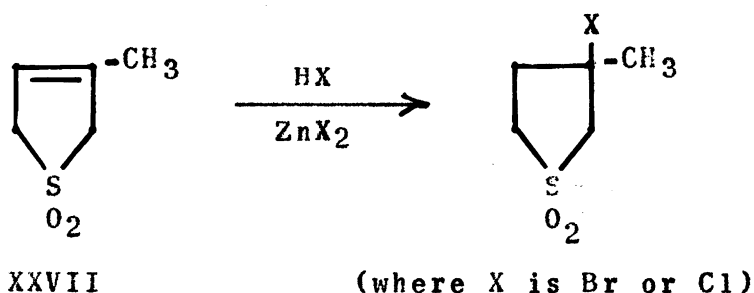
The nucleophilic attack on the 2,5-dihydrothiophene 1,1-dioxide (I) most probably goes through the isomerization to II followed by addition of the nucleophilic reagent. Yen (41) attempted to prepare 3-hydroxy-3-methyltetrahydrothiophene 1,1-dioxide by treating 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII) with a potassium hydroxide solution. However, only the isomerized product XXVIII was isolated. A true test of this theory would be



to see if it is possible to obtain an addition product from a nucleophilic reaction with 3,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide XXIX, since it is reported (87) that XXIX will not undergo isomerization.



As indicated in Table VI, all of the attempted electrophilic additions reactions of hydrogen halides to I and II failed and the starting sulfone, I and II, were recovered. This fact might be correlated with the fact that the sulfone group is a strong meta-directing and deactivating group (64). As shown at the start of this section, there is some conjugation of the sulfone group and the double bond. Didot (88) has recently obtained the addition of hydrogen bromide and hydrogen chloride to XXVII using the zinc halides as catalysts. This can be explained in the case of XXVII by the presence of the

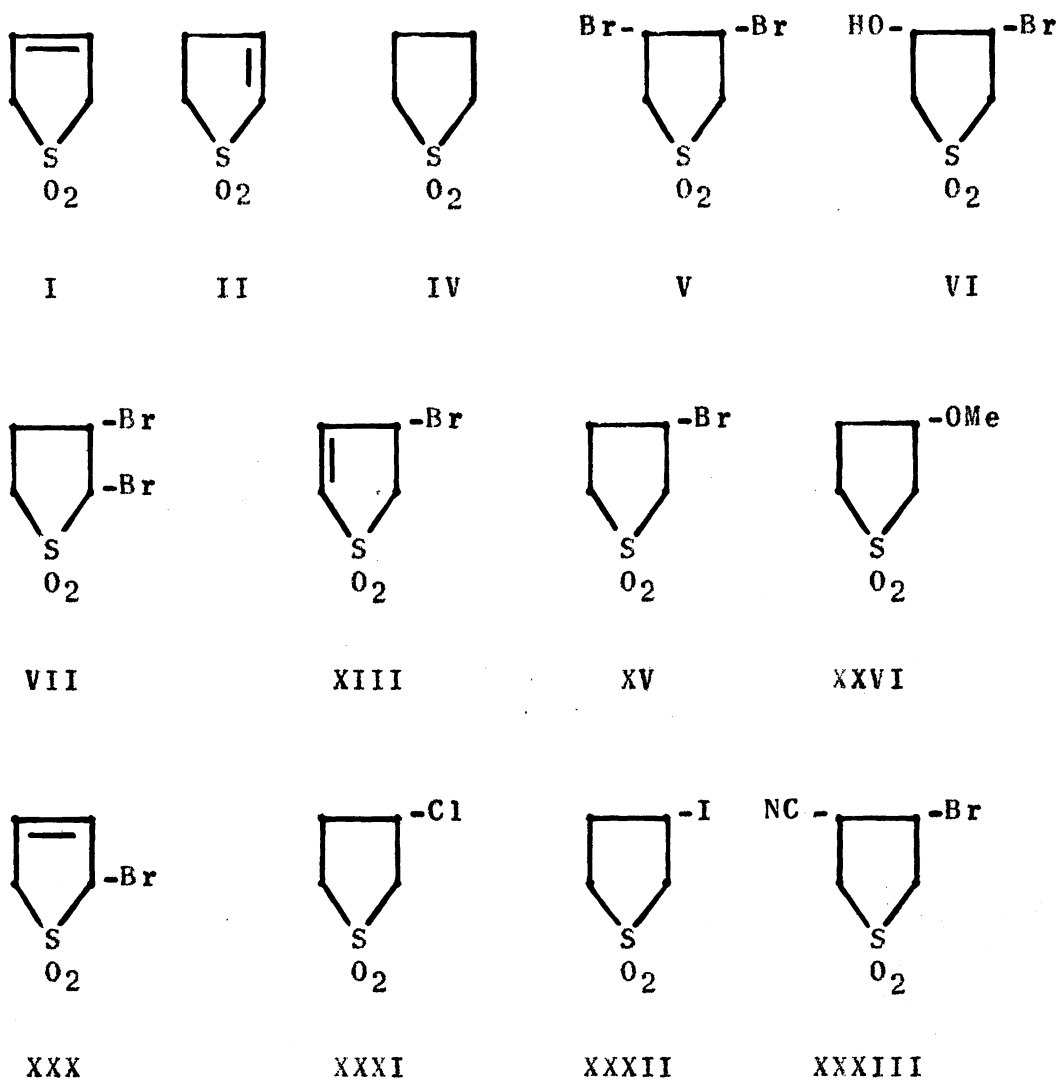


methyl group which would aid the electrophilic addition to the double bond by an inductive effect. An attempted addition of potassium bromide and potassium chloride to I

TABLE VI

Addition Reaction Studies of the Isomeric Dihydrothiophene 1,1-Dioxides

Key:



<u>Reactants</u>	<u>Reaction Medium</u>	<u>Expected</u>	<u>Isolated^a</u>	<u>%Yield^b</u>
HBr + I	Benzene	XV	I	98
HBr + AlCl ₃ + I	Benzene	XV	I	91

TABLE VI (cont.)

<u>Reactants</u>	<u>Reaction Medium</u>	<u>Expected</u>	<u>Isolated^a</u>	<u>%Yield^b</u>
HBr+ZnBr ₂ +I	HBr	XV	I	55
HBr + I	Acetic Acid	XV	I	85
HBr + Benzoyl peroxide + I	Benzene	XV	I	86
KBr + I	NH ₄ OH	XV	I	58
HCl + ZnCl ₂ + I	HCl	XXXI	I	60
KCl + I	NH ₄ OH	XXXI	I	30
HI + I	HI	XXXII	I	91
HCl + ZnCl ₂ + II	HCl	XXXI	II	63
CNBr + I	Benzene	XXXIII	I	62
H ₂ + Pd + I	Water	IV	IV	78
MeOH + KOH + I	MeOH	XXVI	XXVI	65
Br ₂ + I	Chloroform	V	V	95
Br ₂ + H ₂ O + I	Acetic Acid	V + VI	V + VI	43 + 20
Br ₂ + II	Water	VII	VII	57
NBS ^c + I	Chloroform	XXX	VI	69

a The identification of the isolated solids was effected through mixture melting points. IV and XXVI were identified by a comparison of their physical properties to those in the literature.

b In those reactions where starting material was isolated, the % yield is the % recovered.

c NBS is the abbreviation of N-bromosuccinimide.

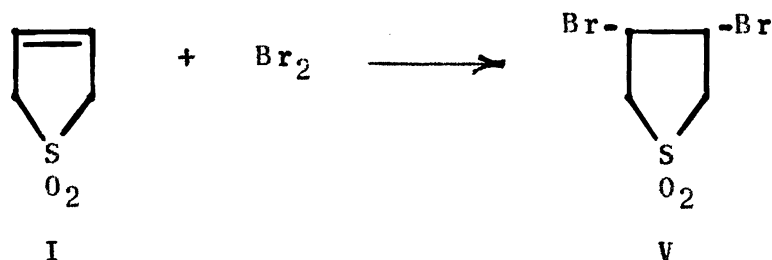
TABLE VI (cont.)

<u>Reactants</u>	<u>Reaction Medium</u>	<u>Expected</u>	<u>Isolated</u>	<u>%Yield</u>
Dibromatin ^a + I	Chloroform	XXX	VI	21
NBS + II	Chloroform	XIII	II & VII	17 + 55
Dibromantin + II	Chloroform	XIII	VII	56

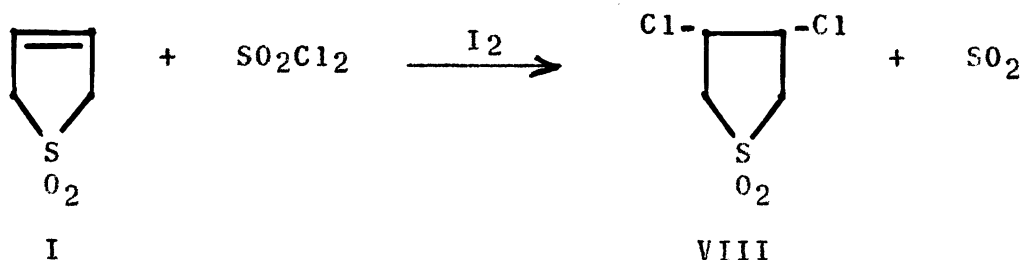
a Dibromantin is the trade name for 1,3-dibromo-5,5-dimethylhydantoin.

in ammonium hydroxide solution also failed. Although there is no report in the literature of a reaction of this type, it was thought that the bromide ion might add via nucleophilic attack followed by solvolysis. In both cases starting I and an oil which did not contain nitrogen or halogens were obtained.

Bromine adds readily to I to give V. The yields of V were increased at least 5% over the previously reported value (29) by performing the reaction at room temperature.

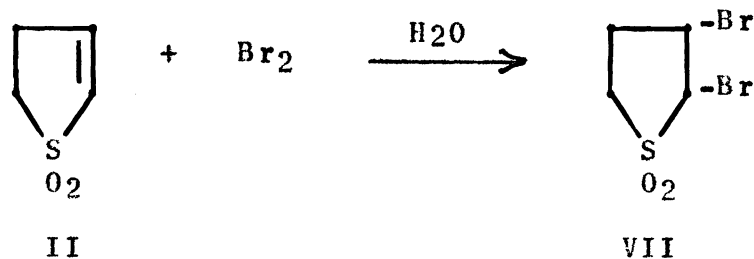


Jordan and Kipnis (40) have reported the preparation of the dichloro compound (VIII) by reacting I with sulfuryl chloride with a crystal of iodine present.

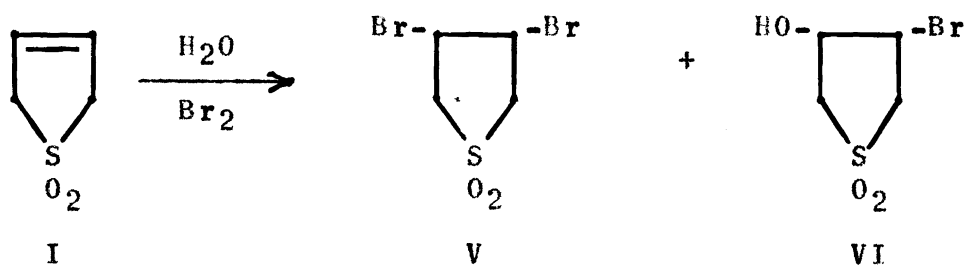


Bromine will not add to II in an organic solvent, but only in a water solution (37). The yield of the

dibromide VII is only 57% and the reaction is very slow. In the same manner when I is treated with bromine in an



acetic acid-water solution, both the dibromide V and the bromohydrin VI are obtained. The mechanism of the addition of bromine to I and II is not clear. It is possible for



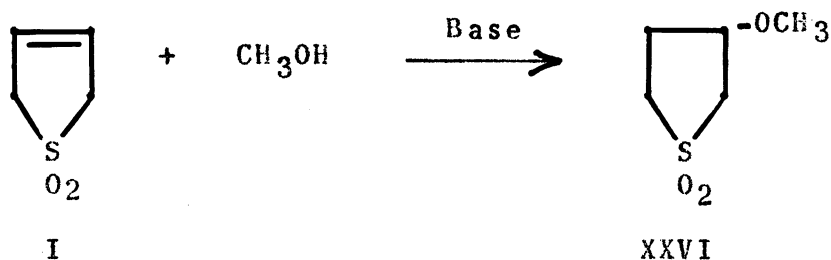
the reaction to go homolytically or heterolytically (89). From the results of I and bromine in chloroform and in water, it would seem that a two-stage addition mechanism of a non-acid electrophile occurs, since the bromohydrin VI is formed when water is present (90).

The addition of bromine to II in water could possibly be a nucleophilic addition of halogen, since the olefinic bond may be sufficiently polarized by the electron-demanding sulfone group adjacent to it. Ingold and

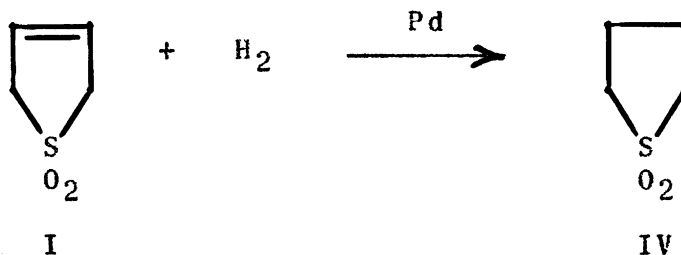
Ingold (91) have stated that there is evidence of nucleophilic addition of bromine to $\alpha\beta$ -unsaturated aldehydes and ketones.

Klopp and Wright (92) found that furan reacts with cyanogen bromide to yield a mixture of 2-bromo- and 2-cyanofuran. However, using the method of Elderfield and Hageman (93) I with cyanogen bromide only gave the starting sulfone.

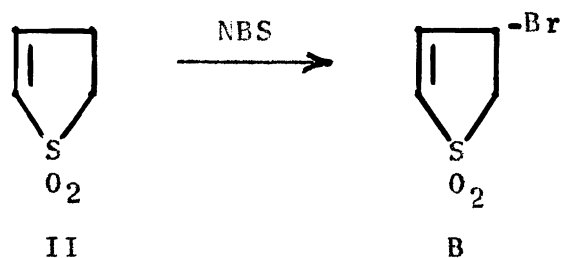
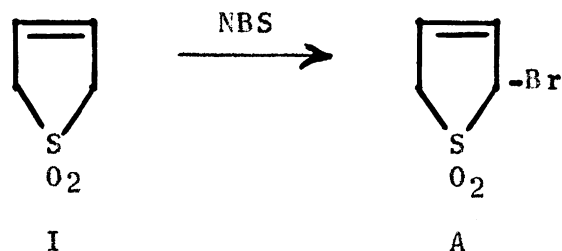
The nucleophilic addition of methanol to I in a basic solution using the procedure described in a British patent (57) gave a 65% yield of the 3-methoxy compound XXVI.



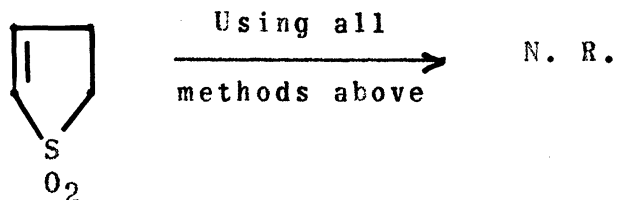
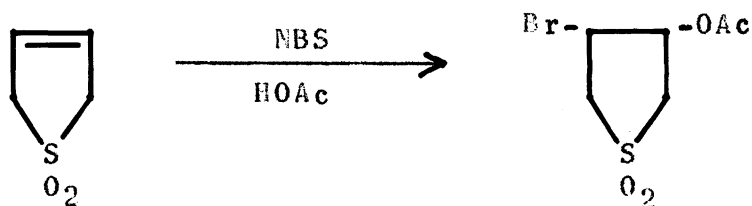
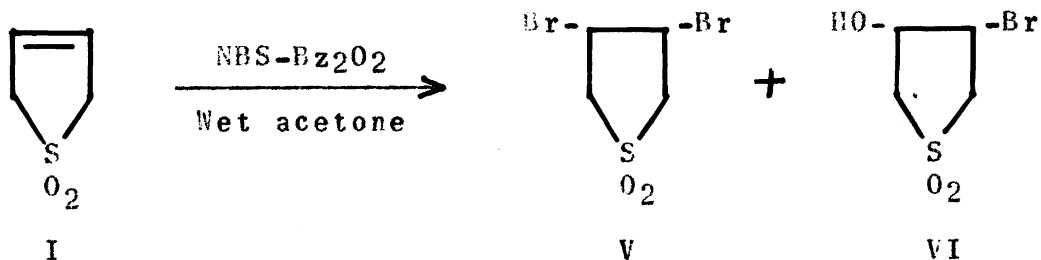
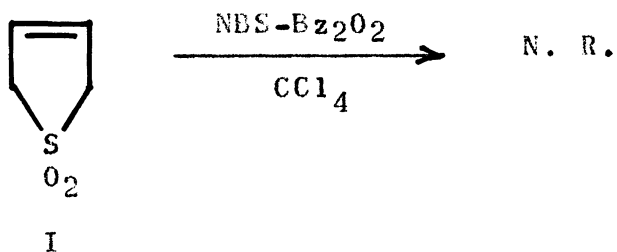
The hydrogenation of I to the tetrahydrothiophene 1,1-dioxide (IV) proceeded very smoothly using the method of Backer and Bolt (20). The use of palladium as a catalyst with hydrogen at atmospheric pressure provides a simple and accessible method of hydrogenating the sulfones.



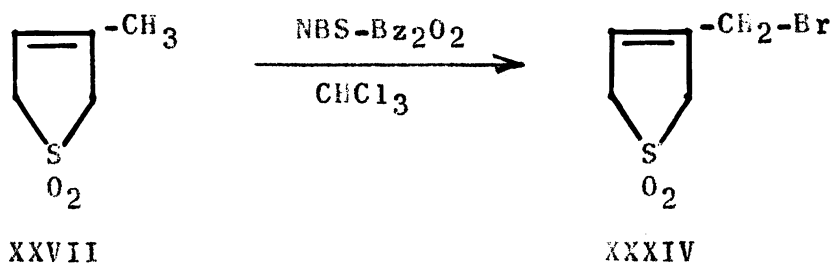
N-Bromosuccinimide (NBS) in the last few years has become an important brominating agent for such reactions as allylic substitution, side-chain bromination, addition reactions, etc. (94). In 1948 Backer and coworkers (95) attempted the bromination of I and II using NBS in order to prepare the following compounds.



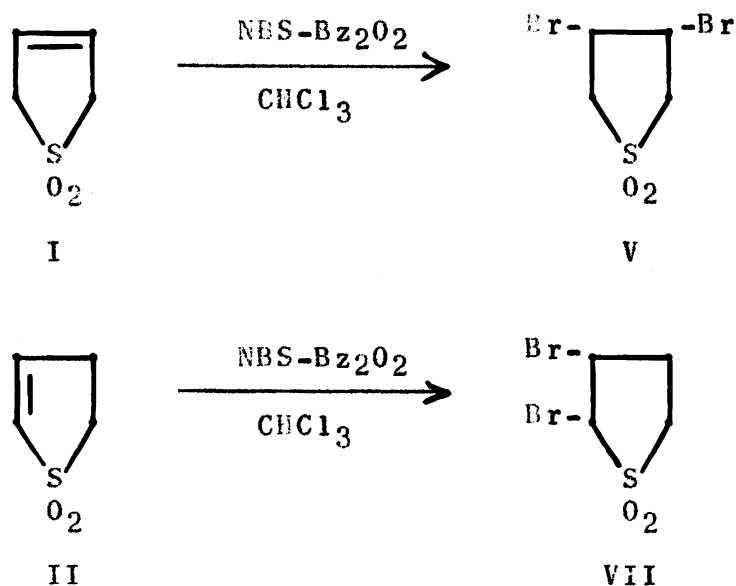
The desired products, A and B, were not realized and the following occurred:



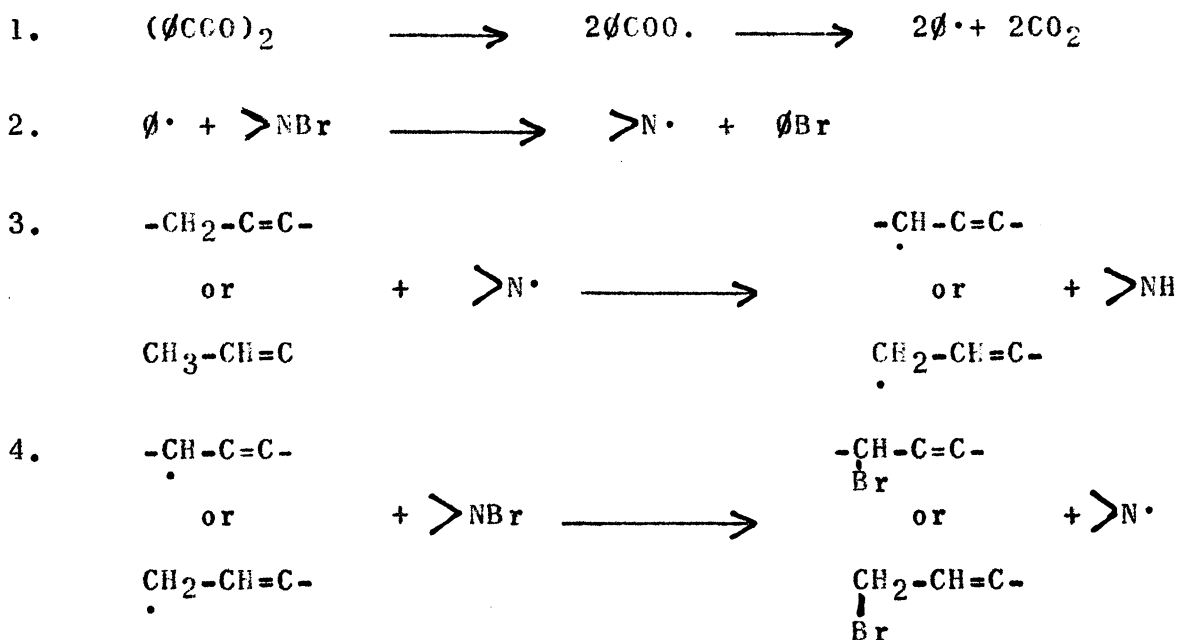
They thought that the sulfone group inhibits the expected allylic bromination. Recently Krug and Yen (96) have reported the side-chain bromination of 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII) to give the 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide (XXXIV). Using the procedure of Krug and Yen (96),



I and II were treated with NBS with benzoyl peroxide as catalyst. In the case of I the dibromo compound V was isolated in 69% yield and although Backer and coworkers (95) did not get any reaction with II, a 55% yield of VII was isolated by this method.



The free-radical mechanism proposed by Bloomfield (97) seems to be generally accepted for describing allylic substitution and side-chain bromination. Thus, it is seen from the following series of reactions that the important step is



the attack of the succinimide radical at an electron rich center to abstract a hydrogen atom followed by further attack of NBS at this center to produce more succinimide radicals. In the case of the 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII), there is an electron rich center for the electron deficient succinimide radical to attack. However, neither I nor II has an electron rich center in the allylic position and thus there was addition of bromine to the double bond. It should be noted that considerable oil, which could not be purified, was obtained in the above reactions of I and II with NBS.

A known homolytic addition to I has been reported by Kharasch and coworkers (98). They have added bromotrichloromethane to I using acetyl peroxide and obtained

the 3-bromo-4-trichloromethyltetrahydrothiophene 1,1-dioxide (XXXV).

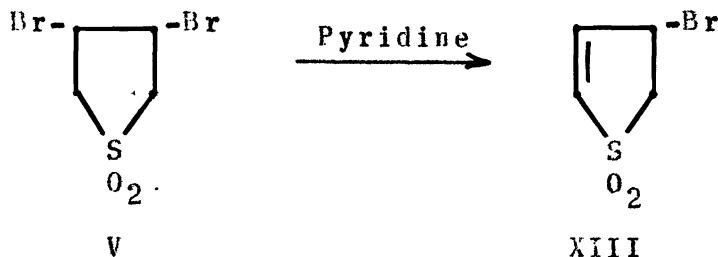
In recent years Orazi and coworkers (99,100,101, 102) have studied the reaction of 1,3-dihalo-5,5-dimethylhydantoin with various compounds. The 1,3-dibromo-5,5-dimethylhydantoin (Dibromantin) can be used in side-chain bromination (100) and the 1,3-dichloro-5,5-dimethylhydantoin and 1,3-dibromo-5,5-dimethylhydantoin have been used successfully in nuclear halogenation (101,102). An interesting reaction is that of thiophene with the above hydantoins to give good yields of the 2-halothiophenes. Orazi and coworkers (99) have compared the reaction of phenanthrene with NBS and various alkyl-substituted 1,3-dibromohydantoins and found the latter superior in the preparation of 9-bromophenanthrene.

The reaction of 1,3-dibromo-5,5-dimethylhydantoin using chloroform¹ and benzoyl peroxide with I and II produced only the dibromo sulfones. The amount of addition to I was only 21%, while in the case of II, a 56% yield of the addition product was realized.

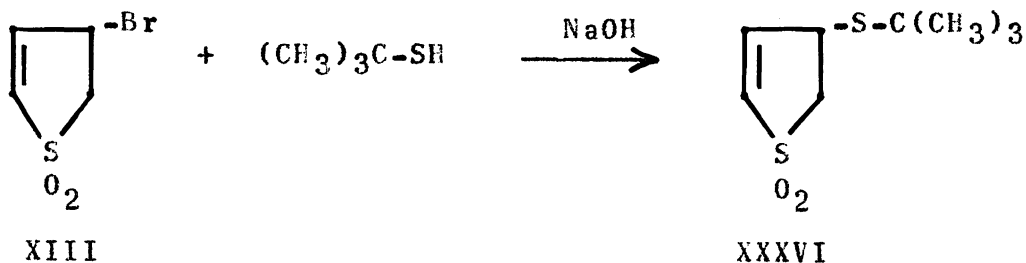
1 As a solvent chloroform is superior to the carbon tetrachloride generally used, since the 1,3-dibromo-5,5-dimethylhydantoin is more soluble in the former.

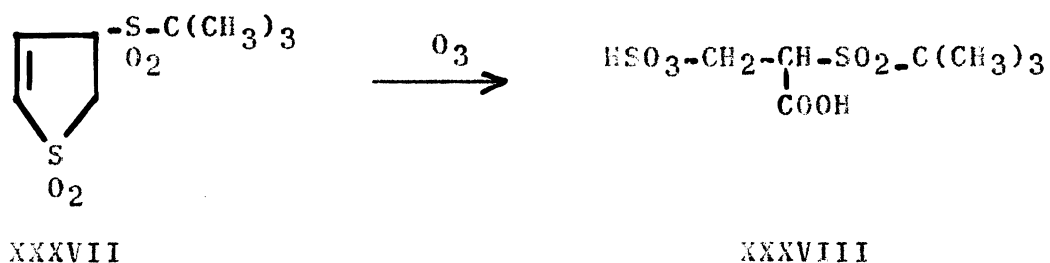
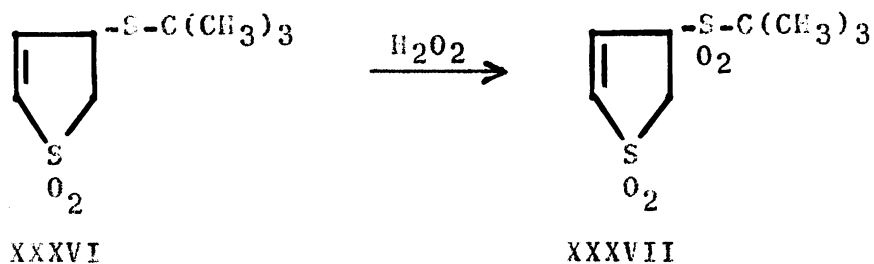
C. Elimination Reactions of the Isomeric Dibromotetrahydrothiophene 1,1-Dioxides and Some Displacement Reactions

Backer and Blaas (38) were the first to report the dehydrobromination of the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) to form the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII). This was accomplished by treating V with pyridine in acetone to give XIII, pyridine hydrobromide and a large amount of polymer.

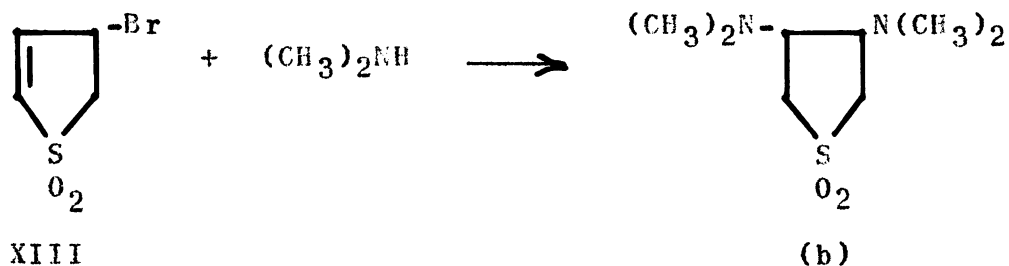


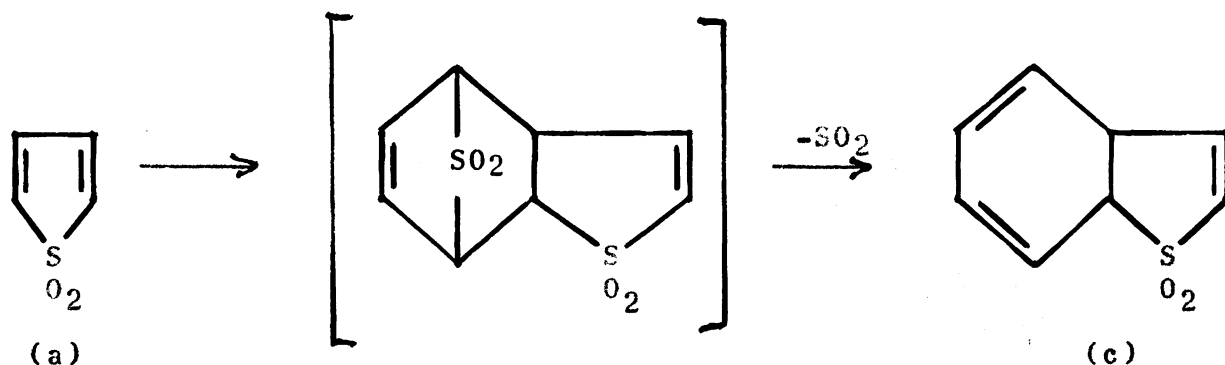
The structure assigned to XIII was proven by reacting XIII with the sodium salt of *t*-butyl mercaptan to give XXXVI. This compound was then oxidized with hydrogen peroxide to the corresponding sulfone XXXVII which was ozonized to give the dibasic acid XXXVIII.





Recently, Bailey and Cummins (29,103) have studied the dehydrobromination of V in an attempt to prepare the thiophene 1,1-dioxide (a) and see if it was aromatic or aliphatic in character. In an attempt to go from V to (a) using pyridine, a large amount of polymer was obtained. Upon treatment of XIII with dimethyl amine, both addition and substitution occurred. Finally a Hofmann exhaustive methylation was used to obtain (a). It was found that (a) was not stable and immediately dimerized to (c).



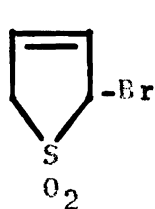


It seems that the elimination of hydrogen bromide using pyridine and acetone goes via an E 2 mechanism, since bimolecular reactions supervene in acetone¹. Backer and Blaas (38) and Bailey and Cummins (29) both used a mole ratio of 1:1.9 of sulfone V to pyridine and obtained large amounts of polymer. Decreasing the amount of pyridine gave the added disadvantage of having starting material present along with polymer and XIII². The polymer was formed after the pyridine salt was removed by filtration and the solvent was being removed. In the present study it was found that no polymer was formed, if the solution was first acidified before removal of solvent. This method increased the yield 20-25%.

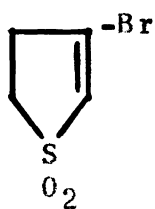
1 See ref. 89, pg. 454.

2 This fact would seem to indicate an E 2 mechanism, since in making runs of 1:1.2, 1:1.5 and 1:1.9 mole ratio of sulfone V to pyridine, there was obtained at the end of the reaction 5 g., 2 g., and 0 g. of starting sulfone V. All of the reactions were run the same number of hours. This would seem to show that the reaction depends upon the concentration of base.

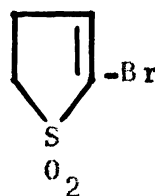
In this present work there is interest in the product formed by the elimination of hydrogen bromide from the 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII). This elimination would give three possible structures.



XVIIa



XVIIb



XVIIc

Structure XVIIa can be eliminated, since it does not give a positive silver nitrate test when warmed while the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) does. Also XIII gives an immediate reaction with sodium iodide¹ in dry acetone, while XVII does not even do so upon heating. Thus the possibility of an allylic bromide XVIIa could be ruled out. Wagner and Zook (107) state that vinyl halides show little or no reactivity toward sodium iodide.

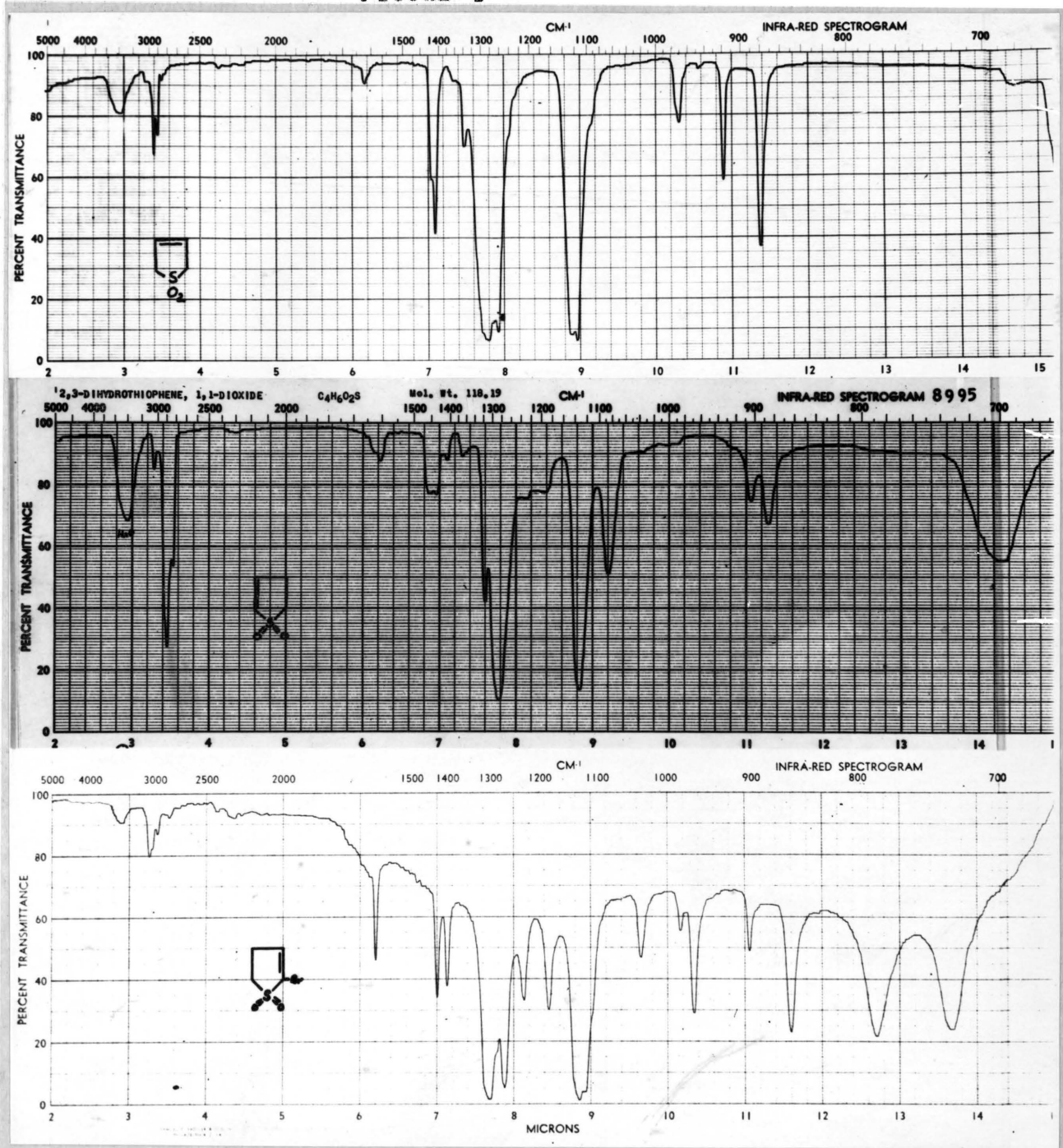
In order to assign to the monobromosulfone obtained from VII the correct structure, a study of its infrared spectrum was made. Because of the large number of absorption bands, the infrared spectrum of a molecule is a good "fingerprint" of that molecule (104). It has a

1 This reaction will be further discussed later in this section.

qualitative application in gross structural features and will only be used as an approximation of the structure here along with chemical and electronic interpretations. In Figure 1 the spectra¹ of the 2,5-dihydrothiophene 1,1-dioxide (I), 2,3-dihydrothiophene 1,1-dioxide (II) and the bromosulfone (XVII) are shown. A comparison of the principle absorption bands shows that XVII resembles II rather than I. This would give support for the elimination of XVIIa as a possible structure. It should be noted that Stark and Clark (105) recently have made assignment of the α and β -halocodides on the basis of infrared spectra. There is a marked difference between the α and β compounds, while the chloro, bromo and iodo compounds of the β -form have almost identical spectra. Hartough (106) has assigned the absorption frequency at 840 cm^{-1} to the vinyl, thiol, chloro, and bromo substituents in the 2-position of the thiophene ring. The bromosulfone XVII has a band at 860 cm^{-1} , which could correspond to the bromine in the 2-position of the sulfone (XVIIc) since the 3-halo-2,3-dihydrothiophene 1,1-dioxides (see Figure 2) do not show such a band. The 840 cm^{-1} band is absent in

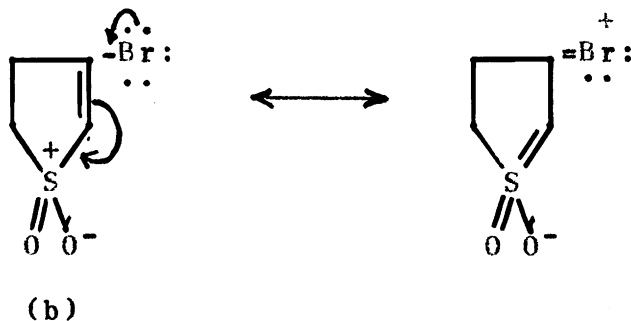
1 All infrared spectra were taken by Samuel P. Sadtler and Son, Inc., 1517 Vine Street, Philadelphia 2, Pa., unless otherwise stated. A Baird double-beam infrared spectrophotometer was used.

FIGURE 1



- 2,5-Dihydrothiophene 1,1-Dioxide (I)
 2,3-Dihydrothiophene 1,1-Dioxide (II)
 5-Bromo-2,3-Dihydrothiophene 1,1-Dioxide (XVIIc)

the 2,3-dihalothiophenes¹. Another interesting point is the position of the conjugated C=C stretching frequencies. Bellamy² (108) states that as conjugation increases, there is a shift to lower frequencies in non-aromatic systems in the region of 1650-1600 cm^{-1} . In Figure 1 the C=C band for the 2,5-dihydrothiophene 1,1-dioxide (I) is at 1625 cm^{-1} , while for the 2,3-dihydrothiophene 1,1-dioxide (II) the band appears at 1605 cm^{-1} . This shift of the C=C band is expected, since the double bond in II is directly conjugated with the sulfone group, while in I it is only conjugated per se in one of its resonance forms. Now looking at structures XVII b and c, the following could occur for structure b, using only one of the many resonance structures of the sulfone group. This



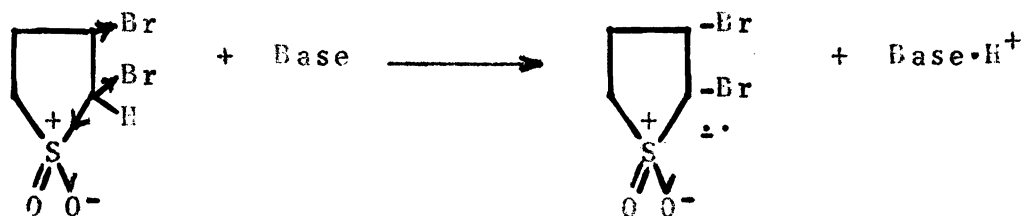
shift cannot occur with structure XVIIc. Therefore, if

1 See ref. 106, pgs. 116 and 118.

2 Unless otherwise noted, all of the assignments and interpretations are based on those of Bellamy, ref. 108.

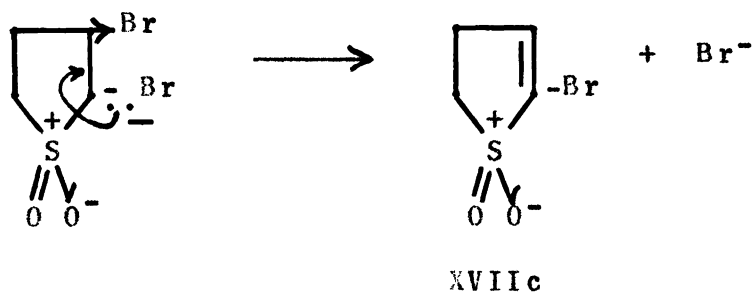
the bromosulfone is XVIIb, it should have a lower C=C stretching frequency than II. However, it is higher, 1615 cm^{-1} , as compared to the 1605 cm^{-1} for II. It would seem that the infrared spectrum favors the assignment of structure XVIIc.

Certain theoretical considerations also favor XVIIc. Doering and Hoffmann (109) and others¹ have established the fact that the α -hydrogens of a sulfone have certain acidic properties. The sulfone group and both bromine atoms can exert a $-I_s$ effect, so that the



hydrogen on the α -carbon should be more acidic than that of the β -carbon. Since the elimination seems to be E 2, the first attack is that of the base to abstract a proton. Subsequently a bromide ion is removed from the carbon α to the site of the removed proton followed by the formation of the α, β double bond to give XVIIc.

1 These works on the acidity of α -hydrogens will be discussed in detail in Section D.



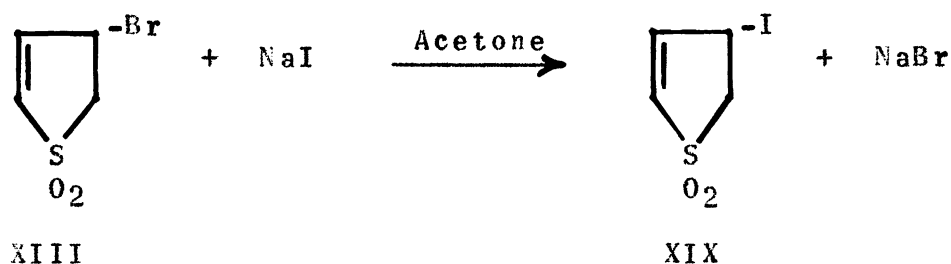
Thus, on the basis of the reactions studied, infrared spectra and electronic interpretation, the proposed assignment of structure XVIIc to the dehydrobromination product of 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII) seems to be valid.

It might be noted that XVIIc was hydrogenated in an attempt to prepare the 2-bromotetrahydrothiophene 1,1-dioxide, a known compound, however, hydrogenolysis of the carbon bromine bond occurred.

The exchange of chlorine or bromine atoms for iodine is an important method for preparing iodo compounds. The exchange reaction is usually effected by heating the halogen compound with a solution of sodium iodide in dry acetone and sodium halide is precipitated.

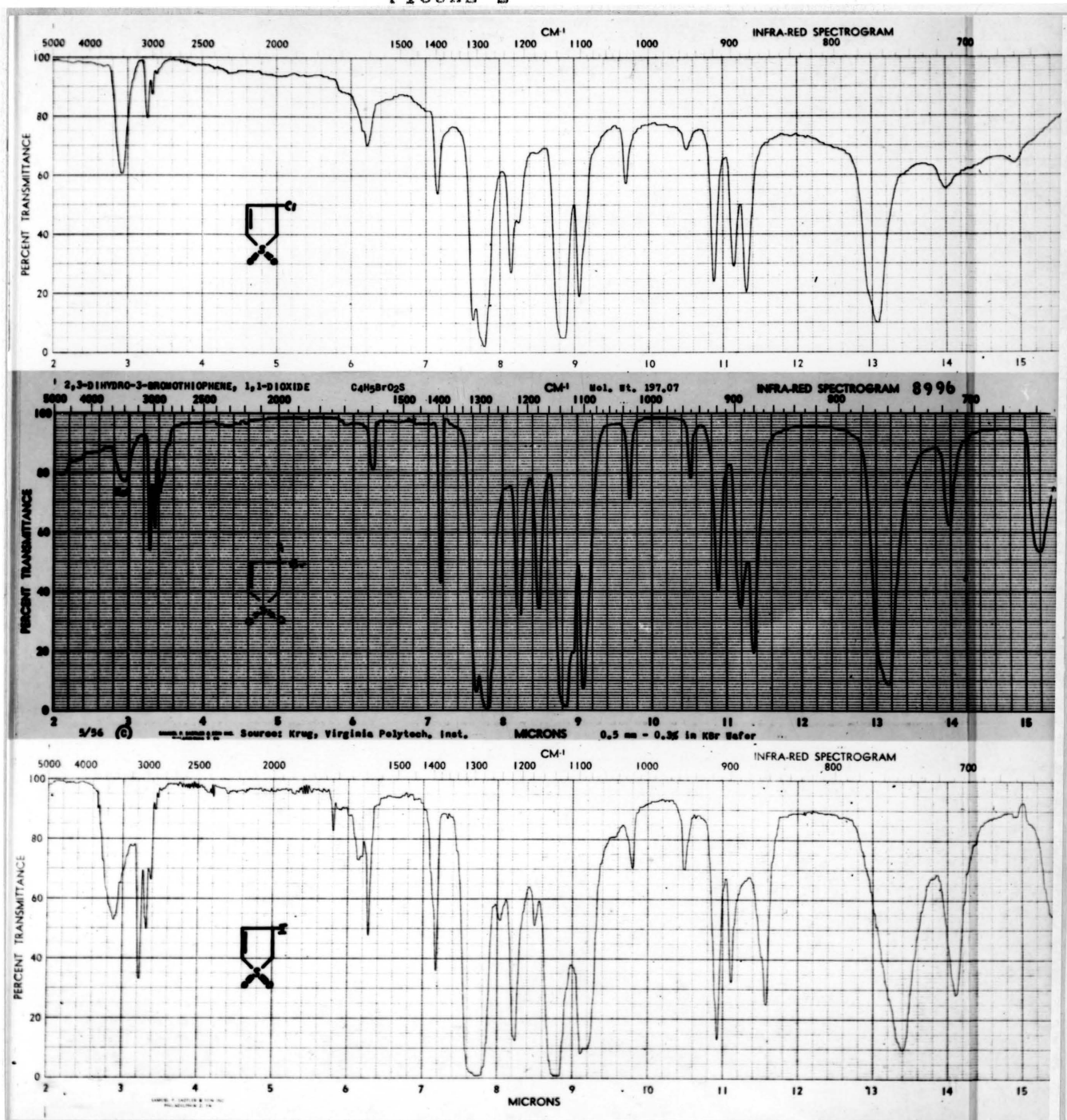
The preparation of 3-iodo-2,3-dihydrothiophene 1,1-dioxide (XIX) from the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) was effected using the method of Brody and Bogert (110) by reaction of XIII with sodium iodide in anhydrous acetone. The bromide XIII was so reactive that no heat was necessary and immediate precipitation

of sodium bromide was realized in a 94% yield. The pure iodide (XIX) was obtained in a 53% yield. The substance gives an immediate reaction with silver nitrate solution and upon standing in air will gradually decompose. Its infrared spectrum was run and is curve c in Figure 2.



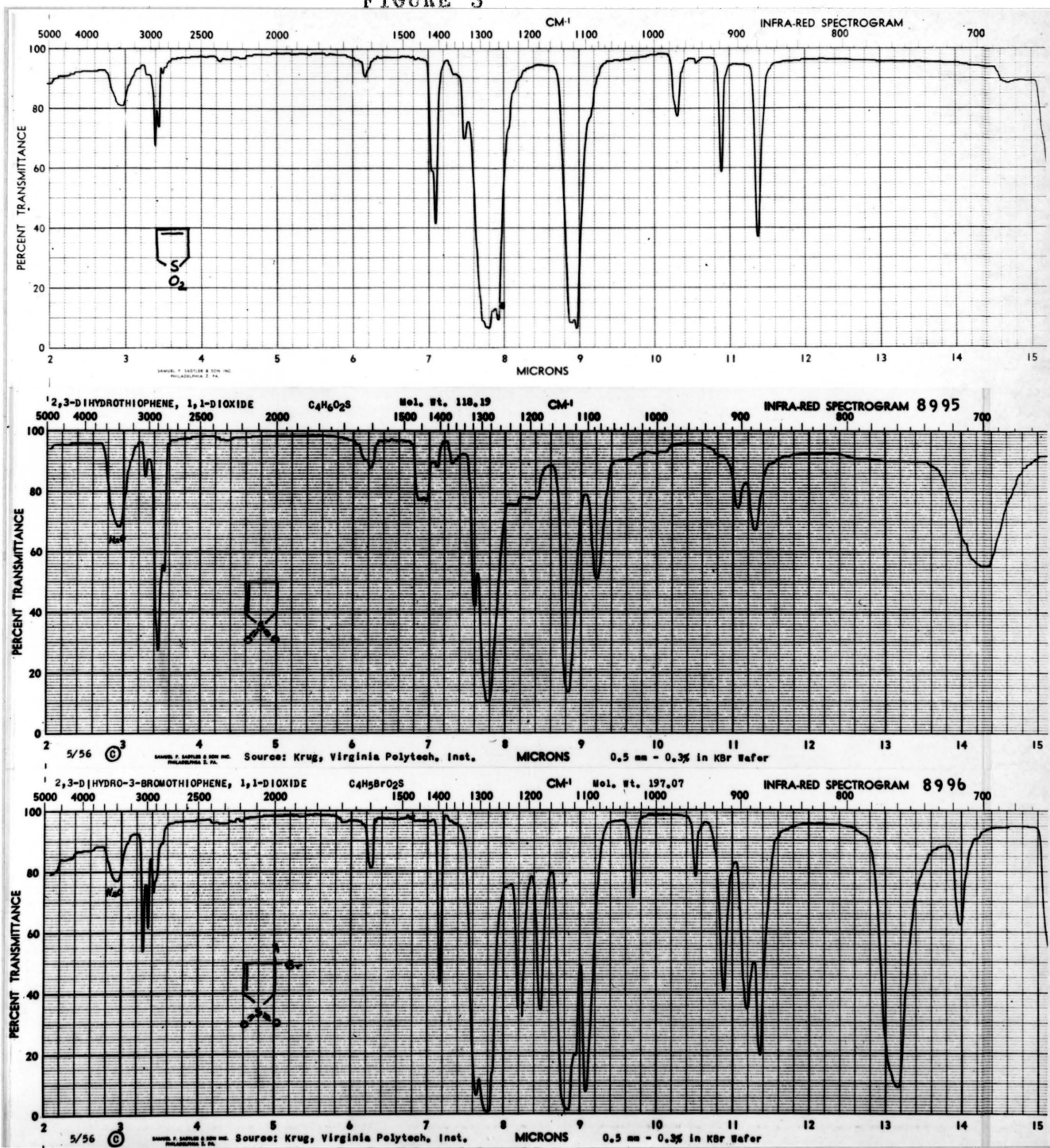
The 3-chloro-2,3-dihydrothiophene 1,1-dioxide (XX) was obtained by substitution of chlorine for iodine using the method of Oppenheim (111) for the conversion of allyl iodide to allyl chloride. A solution of the iodide (XIX) and mercuric chloride in absolute ethanol was heated to reflux. Removal of the alcohol gave the red mercuric iodide and a mixture of organic and inorganic solid. Since mercuric iodide and mercuric chloride are soluble in many organic solvents the purification of the chloride (XX) was difficult. A 42% yield of XX was realized. The infrared spectrum of XX is curve a in Figure 2. A comparison of the spectra of the 3-halo-2,3-dihydrothiophene 1,1-dioxides in Figure 2 show that they have the same structural features. In Figure 3 the

FIGURE 2



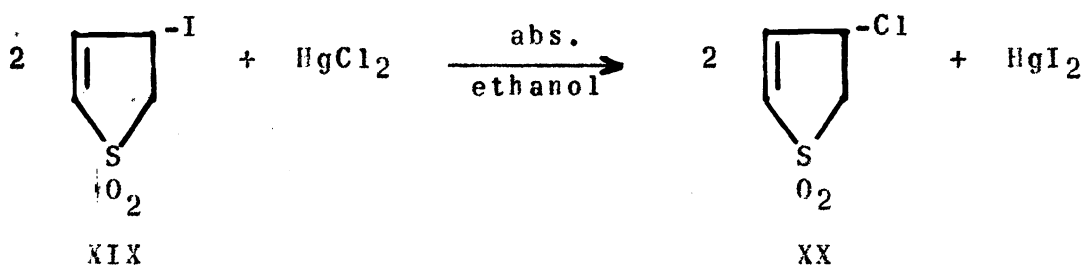
- 3-Chloro-2,3-Dihydrothiophene 1,1-Dioxide (XX)
 3-Bromo-2,3-Dihydrothiophene 1,1-Dioxide (XIII)
 3-Iodo-2,3-Dihydrothiophene 1,1-Dioxide (XIX)

FIGURE 3

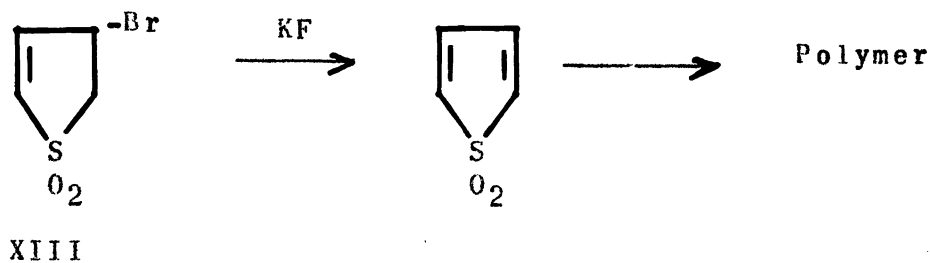


2,5-Dihydrothiophene 1,1-Dioxide (I)
 2,3-Dihydrothiophene 1,1-Dioxide (II)
 3-Bromo-2,3-Dihydrothiophene 1,1-Dioxide (XIII)

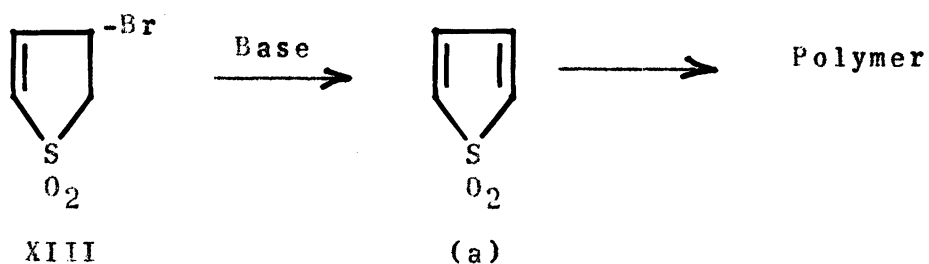
spectrum of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) is compared with the spectra of the 2,5-dihydrothiophene 1,1-dioxide (I) and the 2,3-dihydrothiophene 1,1-dioxide (II), and XIII resembles II. Thus, there is no doubt that the structures assigned to the iodo and chloro compounds (XIX and XX respectively) are correct.



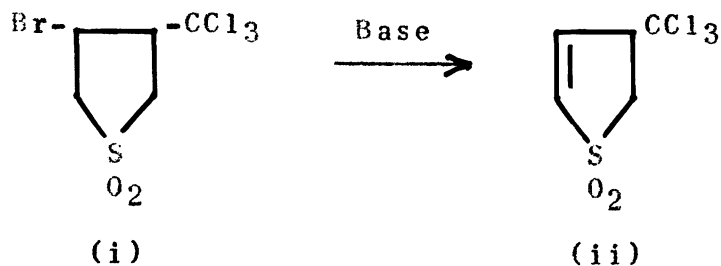
Using the method of Hoffmann (112) the attempt to prepare the 3-fluoro-2,3-dihydrothiophene 1,1-dioxide (XXI) failed. The 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) was warmed with potassium fluoride in ethylene glycol to give a 14% recovery of XIII and 3.3 g. of polymer, which contained sulfur, but no halogens. It is possible that dehydrobromination occurred and the resulting thiophene sulfone polymerized.



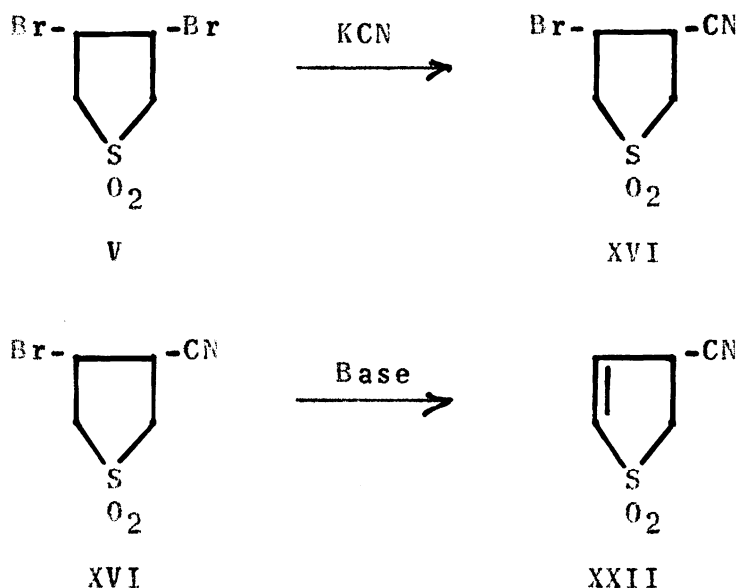
The final displacement reaction studied was that of the bromosulfones with metal cyanides. In an aprotic medium, the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) failed to react with copper (I) cyanide. Heating XIII with copper (I) cyanide without solvent gave only a tar. Aqueous solutions of potassium or sodium cyanide and XIII gave polymers, which contained sulfur but no bromine or nitrogen. The pH of these solutions was approximately 9, therefore dehydrohalogenation could occur leading to the formation of the unstable thiophene 1,1-dioxide (a).



Kharasch and coworkers (47) were able to dehydrobrominate the 3-bromo-4-trichloromethyltetrahydrothiophene 1,1-dioxide (i) and obtain the 3-trichloromethyl-2,3-dihydrothiophene 1,1-dioxide (ii).



The preparation of the 3-bromo-4-cyanotetrahydrothiophene 1,1-dioxide (XVI) from the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) was attempted, since XVI could be dehydrobrominated to give the 3-cyano-2,3-dihydrothiophene 1,1-dioxide (XXII). When V was heated with copper (I) cyanide without solvent, 61% of starting material was isolated along with some tar. The reaction of V with potassium cyanide in methanol gave a 56%

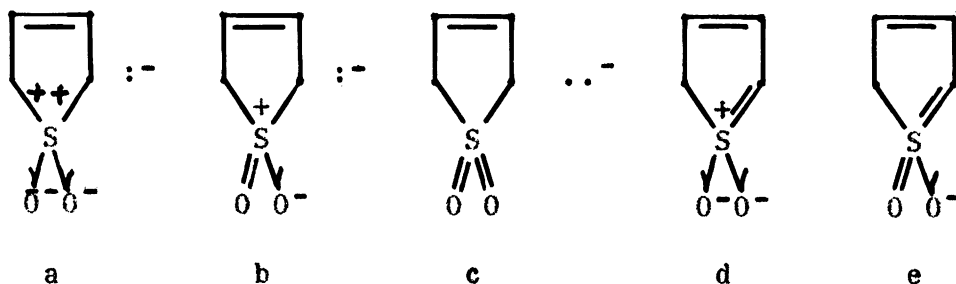


recovery of starting sulfone, polymer containing sulfur but no bromine or nitrogen, and about a gram of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII). Dehydrobromination of V is clearly established by the isolation of XIII as a reaction product and shows that alkali cyanide solutions are basic enough to cause dehydrobromination. It should

be pointed out that many of the displacement reactions involving a halide and a cyanide are run using pyridine as a catalyst. Pyridine was not used with the bromo-sulfones since it would cause dehydrobromination immediately.

D. Metalation Reactions with the Isomeric
Dihydrothiophene 1,1-Dioxides and
Various Halogen Derivatives

As early as the turn of the century, Hinsberg (122) noticed that the sulfone group imparted acidic properties to the adjacent methylene groups. Fehnel and Carmack (123) studied the ultraviolet absorption spectra of compounds containing the sulfone function and found that strong conjugative effects were apparent in the spectra of the anions formed by the methylene disulfones and β -ketosulfones in alkaline solutions. These observations are of interest, since they give support to the question of the ability of the sulfonyl sulfur atom to accommodate more than eight electrons in its valence shell. There are two theories regarding the sulfone linkage which would explain the stabilization of carbanions formed. Sutton (75) regards the sulfur oxygen linkage as essentially a covalent double bond involving expansion of the sulfur valency octet. He explains that the stabilization of a carbanion adjacent to a sulfone group is due to the

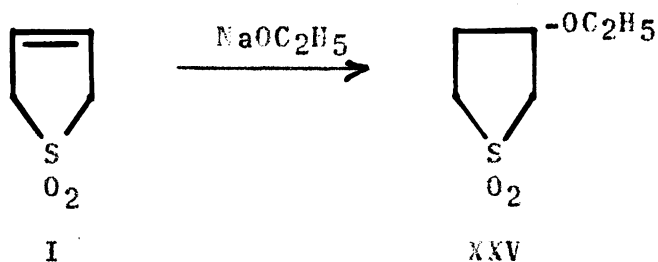


resonance hybrids and relies on the resonance energy as well as coulombic attractions. Thus in the case of I, the carbanion would be stabilized by the resonance hybrid of a, b (two forms) and c, and would rely on the resonance energy, as well as coulombic attractions from structures d and e (two forms). The other theory is that of Arndt and Eistert (124) who formulate a polar coordinate single bond in sulfones and no expansion of the sulfur octet. Stabilization of the anion to the sulfone group is attributed only to coulombic attraction of the carbanion by the two positive charges on sulfur. Thus, the former theory superimposes resonance interaction of a d-orbital of sulfur with an adjacent orbital and involves expansion of the octet of sulfur, while the latter involves solely electrostatic interaction of the two positive charges on sulfur with the adjacent function. Doering (109) recently explained the acidity of a bridgehead α -hydrogen in a bicyclic trisulfone using d-orbital resonance.

In any event the α -hydrogens are acidic in nature¹ and the carbanion can be stabilized as shown above. Thus I and II should undergo metalation reactions similar to carbonyl compounds.

1 The acidity of the α -hydrogens will be shown by the Grignard reactions.

Sodium ethoxide is used in the alkylation of acetoacetic esters. It could not be used with the dihydrothiophene 1,1-dioxides, since in an alcoholic solution addition to the double bond occurred to form the ether.



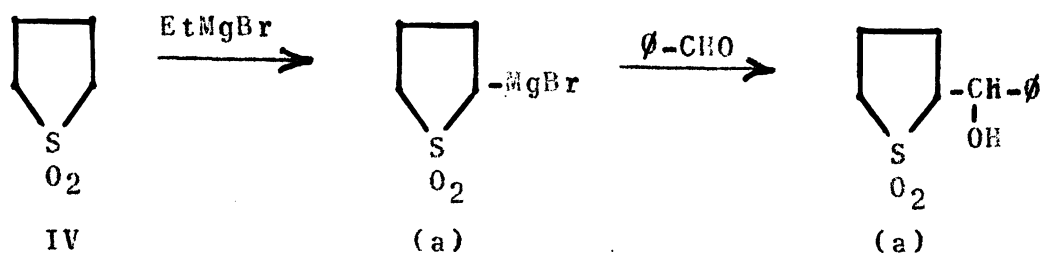
Sodium amide has been used to alkylate nitriles, which are less reactive than carbonyl compounds, and compounds which do not readily enolize. Zimmerschied and Arnold (125) have been able to alkylate thiophenes using sodium amide and alkyl halides. In our work all that was isolated from the reaction was a red tar. The sulfone I is stable in liquid ammonia, since solubility studies were made from which the recovery of I was quantitative.

Sodium dispersions and sodium hydride (126) are used in the alkylation of compounds having active methylene groups. Although in both reactions using a sodium dispersion and sodium hydride a gas was slowly evolved, work-up of the mixtures after an alkyl halide was added only gave starting sulfone.

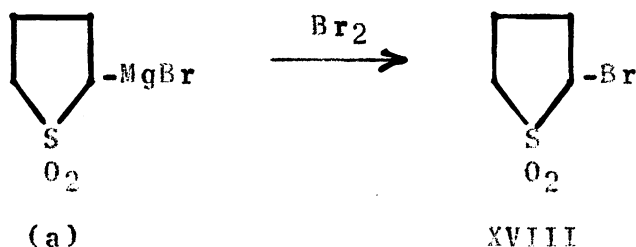
In 1937 van Zuydewijn (18) was the first to report the reaction of a Grignard reagent with a cyclic sulfone and this was only a passing note in the paper. It was stated that two moles of a Grignard reagent will react with one mole of I to give some gas and some addition, but no product was isolated. In recent years there have been many reports in the literature of reactions of acyclic and saturated cyclic sulfones with Grignard reagents and n-butyl lithium. A few examples will be cited.

Field (65,127) has studied the reaction of methyl phenyl sulfone with methylmagnesium iodide and observed that the sulfone will undergo replacement of up to three hydrogen atoms. The reaction of benzaldehyde with the sulfone after reaction with two moles of Grignard reagent will give the β -phenyl- β -hydroxyethyl phenyl sulfone.

Truce and Buser (128) have studied the metalation of dialkyl sulfones and the tetrahydrothiophene 1,1-dioxide (IV). From the latter with benzaldehyde, they obtained only a 4% yield of the 2-(phenylhydroxymethyl)-tetrahydrothiophene 1,1-dioxide. Faith (129) has also effected a reaction with the tetrahydrothiophene 1,1-dioxide



by treating the Grignard complex (a) with bromine and thus obtained the 2-bromotetrahydrothiophene 1,1-dioxide (XVIII).



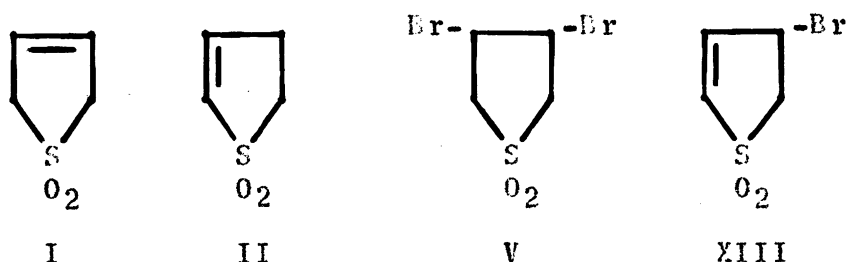
There are numerous examples of the use of *n*-butyl lithium in the metalation of aryl sulfones, followed by carbonation (130,131,132).

With the exception of the brief comment by van Zuydewijn (18) a detailed description of the reactions of *β*-unsaturated cyclic sulfones with Grignard reagents does not appear in the literature. From the data shown in Table VII and Appendix II, there is only one type of reaction that gave a product other than polymer and that is the use of a "direct" Grignard reaction in a 2:1 mole ratio of Grignard reagent to sulfone I.

A close study of gas data will help in the interpretation of the Grignard reaction.

TABLE VII

Metalation of the Cyclic Sulfones



<u>Sulfone</u> ¹	<u>RMgX</u>	<u>Alkylating Agent</u>	<u>Mole Ratio</u>	<u>Gas</u> ²		<u>Product Obtained</u>
				Obs.	Theo	
XIII A	MeMgI	MeI	1:1:1	0.64	2.24	Polymer
V A	MeMgI	MeI	1:2:2	0.86	1.12	Polymer + 22% V
I A	<u>n</u> -BuLi	Acetyl Chloride	1:3:1	2.82	6.71	58 g. of black tar
I A	EtMgBr	Acetaldehyde	1:1:1	4.2	4.48	Solid which polymerized
I A	MeMgCl	Blank run	1:2	4.92	5.62	20 g. of
		Hydrolysis:		1.13	5.62	light yellow plastic
I B	EtMgBr	Blank run	1:1	1.42 ³	4.48	Polymer & 46% I

1 After the Roman numeral, A stands for "inverse" Grignard reaction and B stands for "direct" Grignard reaction.

2 All gas calculated at S.T.P. and the theoretical gas calculated on the basis of 22.4 l. per mole of sulfone used.

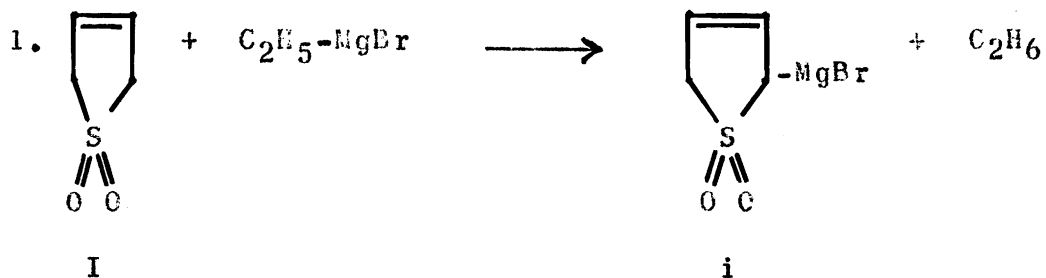
3 When approximately 40% of I was added, gas evolution ceased.

TABLE VII (cont.)

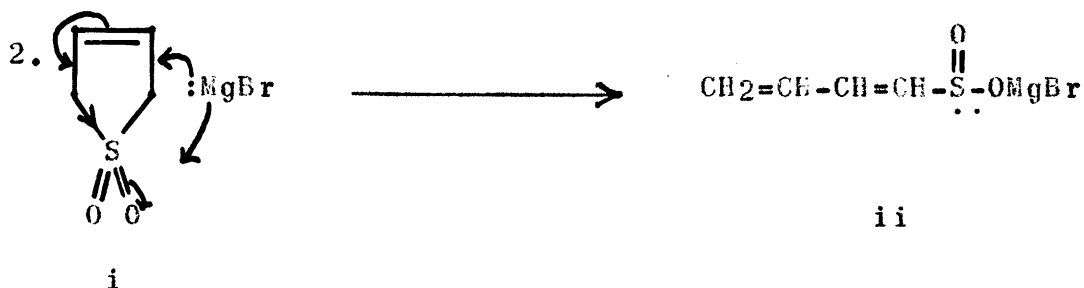
<u>Sulfone</u>	<u>RMgX</u>	<u>Alkylating Agent</u>	<u>Mole Ratio</u>	<u>Gas</u>		<u>Product Obtained</u>
				<u>Obs.</u>	<u>Theo.</u>	
I B	EtMgBr	Me ₂ SO ₄	1:2:2	- - - -		Oil, C ₁₂ H ₂₂ S ₂ O ₃
II A	MeMgI	MeI	1:1:1	1.05 *1.30	2.24	Polymer
II B	EtMgBr	Me ₂ SO ₄	1:2:2	1.17 *3.19	3.72 3.72	Polymer & 50% II

* Gas observed on hydrolysis.

From the "inverse" reaction data using a 1:1 mole ratio of sulfone I and Grignard reagent (this is the case where the Grignard reagent is added to the sulfone), an equivalent amount of gas is evolved. Thus the first step in the reaction is:

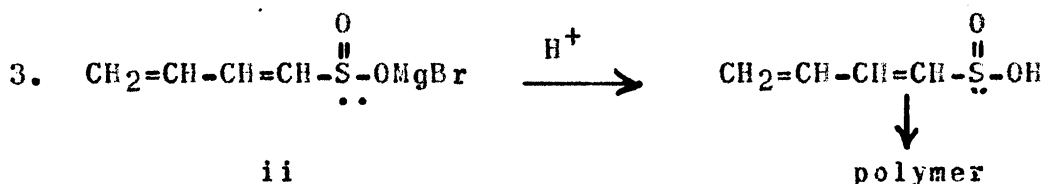


If i is hydrolyzed, I is not obtained, but a polymer. Thus it seems that i does not remain as such but could rearrange.

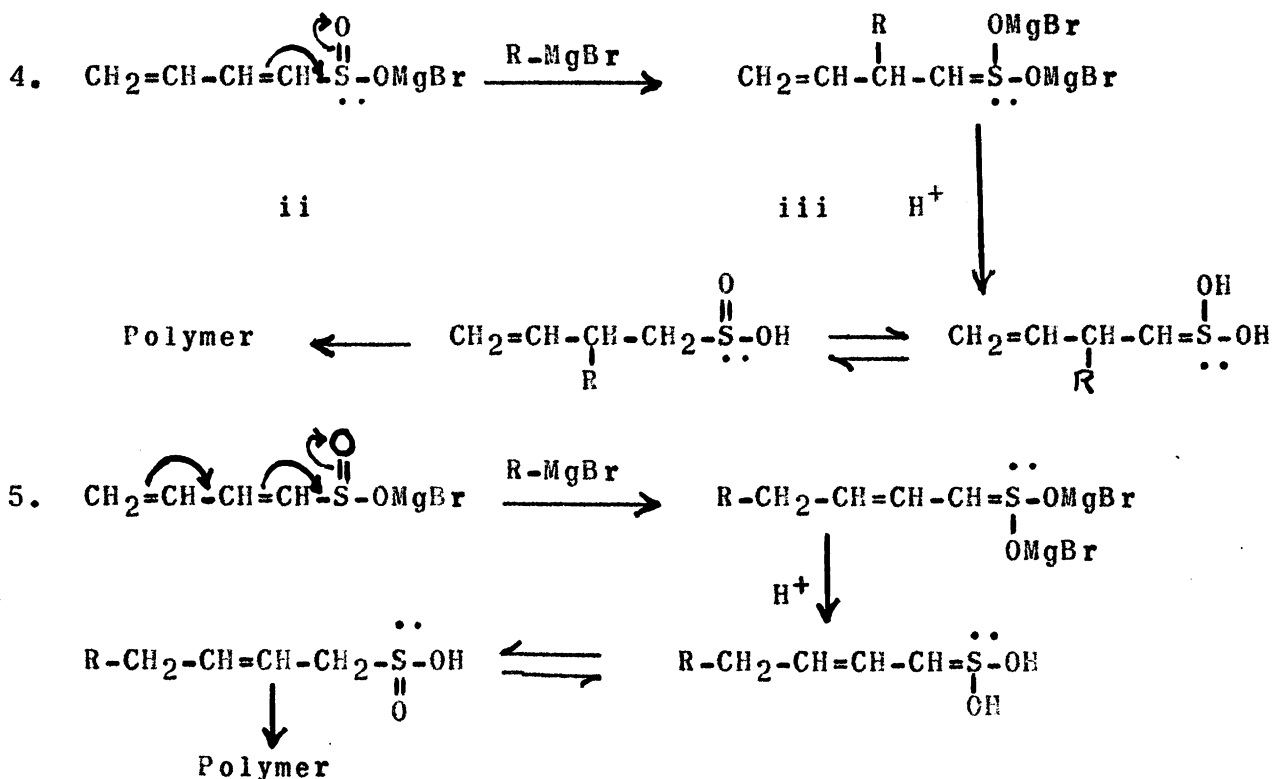


That step 2 is possible is brought out by Eigenberger (133) who treated the 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII) with potassium in ether and obtained an unstable sulfinic acid which underwent polymerization readily. Thus if ii is hydrolyzed a sulfinic acid is

obtained, which then polymerizes and thus accounting for the experimentally observed results.

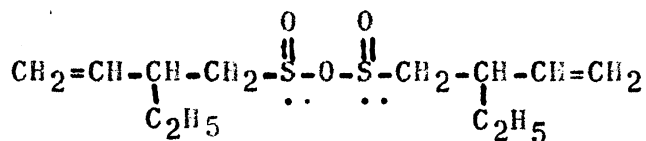
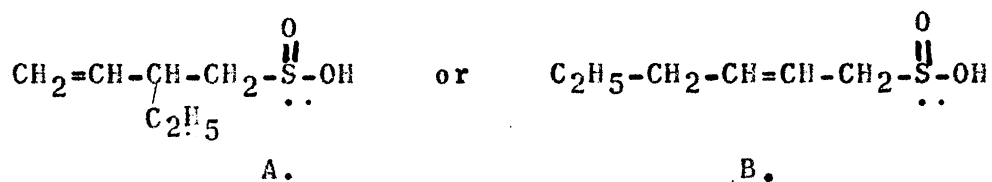


From the gas data of the "inverse" Grignard reaction using two moles of Grignard reagent for each mole of sulfone, one mole of reagent is accounted for by step 1, but upon hydrolysis the other mole of gas does not appear. Thus it seems that there is the possibility of addition to ii which could occur in two ways. Step 4 shows the 1,4-addition and step 5 the 1,6-addition.

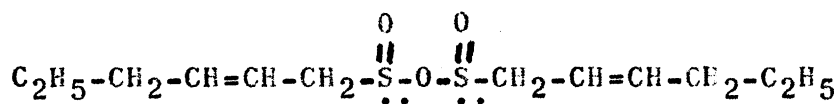


Support for the above proposals can be gained from the data of the "direct" Grignard reaction with I on a 1:1 mole ratio. When about 40% of the sulfone was added, gas evolution ceased. Work-up of the reaction mixture gave a 46% recovery of I and polymer. In "direct" addition, the Grignard reagent is in excess and as soon as step I occurs, step 4 or 5 could occur and thus account for the data and the recovery of I.

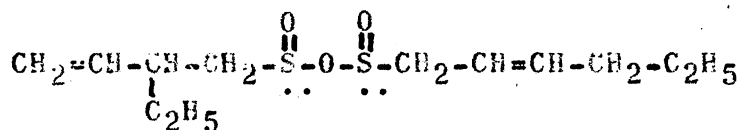
It is seen that polymerization could occur in all steps, since sulfinic acids are not stable. A possible explanation of the structure of the oil isolated from the "direct" Grignard reagent 2:1 mole ratio having the formula $C_{12}H_{22}S_2O_3$ could be made using these facts. Steps 1 and 2 occur followed by either 4 or 5 or both. Thus hydrolysis after steps 4 or 5 would give either A or B or both. These could then combine on distillation to give a sulfinic anhydride with a structure A-A, B-B or A-B.



A-A



B-B



A-B

That a sulfinic anhydride is plausible as a possible product can be shown from some of the tests made. The material readily decolorized a bromine solution thus showing unsaturation. Sulfinic anhydrides are reported to be unstable (70), and the compound isolated is also unstable. The determination of its molecular weight by the Rast method gave values of 262, 221, 230, while the calculated molecular weight (for $\text{C}_{12}\text{H}_{22}\text{S}_2\text{O}_3$) is 278. The infrared spectrum is shown in Figure 4 and the detailed analysis and assignment of absorption maxima together with wave lengths, frequencies and intensities of maxima is shown in Table VIII. These, although they do not prove the structure, indicate that the sulfinic anhydride is possible.

An analysis of the infrared spectrum was made in

consultation with Wartman¹ (134), who has commented as follows: "There are apparently no infrared spectra of sulfinic anhydrides available in the literature and we do not have any in our files. Consequently, we are not able to state that there is infrared evidence for the sulfinic anhydride linkage, per se. We do feel that the intense absorption between 1010 cm^{-1} and 1060 cm^{-1} is very probably due to the S=O bond, based on the available data on sulfoxides. The bands at 3090 cm^{-1} , the $1600\text{--}1700\text{ cm}^{-1}$ region and the $800\text{--}1000\text{ cm}^{-1}$ region point to the presence of unsaturation in the molecule. The multiplicity of bands indicates the possible presence of several types of substituted ethylene bonds. In summary, it may be stated that there is some infrared evidence for the type of compound you postulate from other data."

No specific structure will be assigned to the oil isolated from the Grignard reaction. The evidence points to a sulfinic anhydride, which could be either structure A-A, B-B, A-B or a mixture of these. The main point is that the data from the Grignard reactions support the proposed steps of the reaction.

1 The author is greatly indebted to W.B. Wartman, Jr., spectroscopist, American Tobacco Company, Research Laboratory, Richmond, Virginia, for his suggestions and comments on this structure.

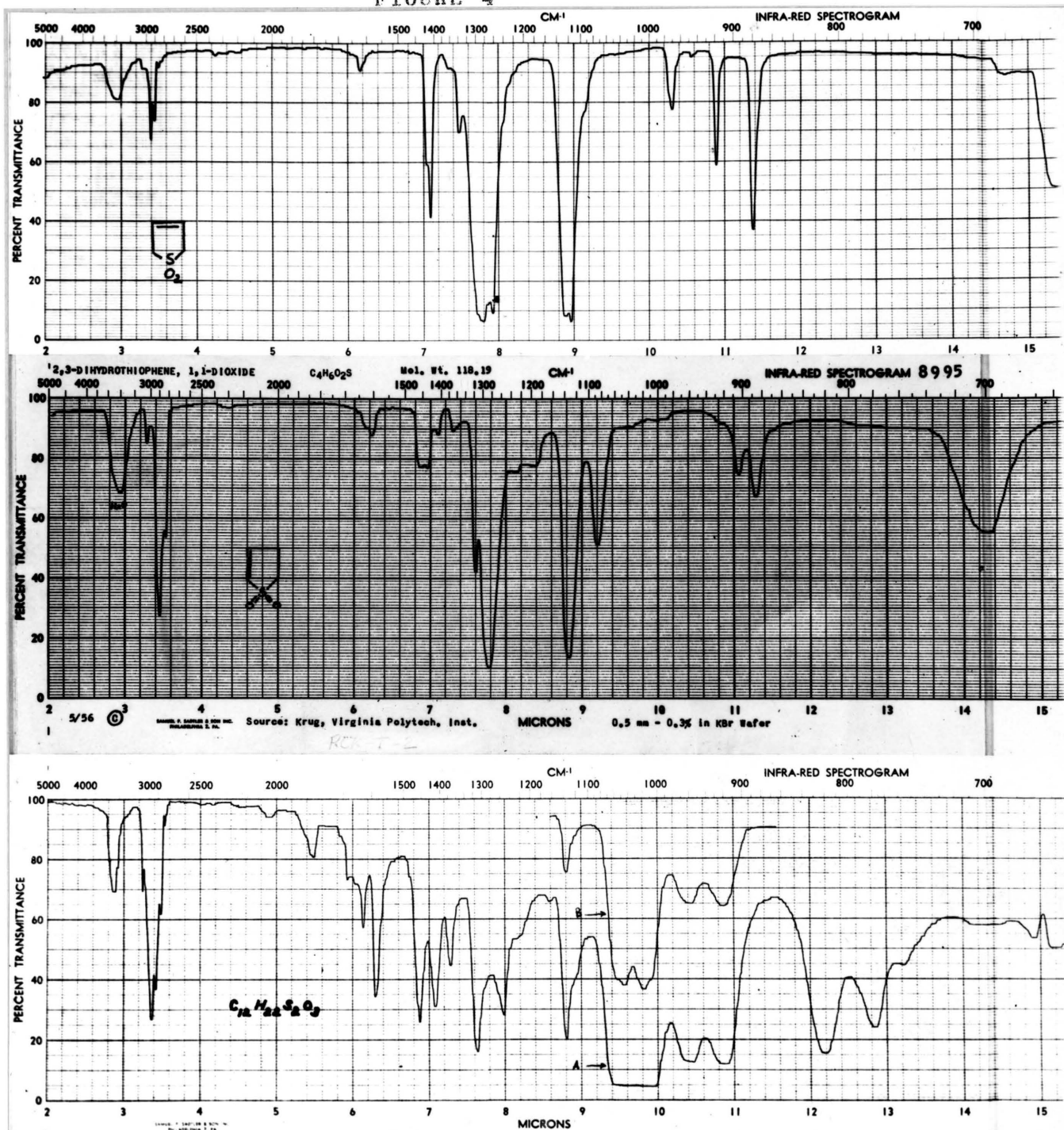
TABLE VIII

Wave Lengths, Frequencies, Intensities, and Assignment
of Absorption Maxima of the Oil ($C_{12}H_{22}S_2O_3$)

$\lambda(\mu)$	ω (cm^{-1})	I ^a	Interpretation of Vibrations
2.88	3472	m	OH stretch; intermolecular H-bonding; single bridge
3.25	3077	m	=C-H stretch
3.38	2959	s	-CH ₃ asymmetrical stretch
3.50	2817	m	-CH ₂ - stretch
5.50	1980	w	-C=C- asymmetrical stretch
6.15	1626	m	-C=C- stretch
6.30	1587	s	-C=C- stretch
6.88	1453	s	-CH ₂ - scissor
7.08	1412	s	-C=C-H in-plane C-H bend
7.30	1370	m	-CH ₃ symmetrical bend
7.65	1307	s	O=S=O asymmetrical stretch
8.00	1250	m	-S=O stretch
8.80	1136	s	O=S=O symmetrical stretch
9.58	1044	m	-S=O stretch ?
9.80	1020	m	-S=O stretch ?
10.40	962	b	R ₁ HC=CHR(trans) C-H bend
10.88	918	b	RHC=CH ₂ C-H bend
12.20	820	b	R ₁ R ₂ C=CHR ₃ C-H bend
12.85	778	b	

^a w, weak; m, medium; s, strong; b, broad - for notations in this table.

FIGURE 4



2,5-Dihydrothiophene 1,1-Dioxide (I)
 2,3-Dihydrothiophene 1,1-Dioxide (II)
 Oil (C₁₂H₂₂S₂O₃) from Grignard Reaction
 A 0.02 mm. between salts
 B 0.01 mm. between salts

E. Alkylation, Condensation and Acylation Studies of the Isomeric Dihydrothiophene 1,1-Dioxides.

As seen in Sections B and D, the sulfones have acidic-type hydrogens in the alpha position. In order to complete the studies of the isomeric dihydrothiophene 1,1-dioxides a number of alkylation, condensation and acylation reactions were investigated. The results are summarized in Table IX.

A Friedel-Crafts reaction was attempted using aluminum chloride as catalyst and tertiary butyl chloride as the alkylating agent. Only a dark tar was isolated and hydrogen sulfide was detected during the reaction. It might be noted that Comey (113) has also detected hydrogen sulfide and the formation of a dark tar in the reaction of thiophene with acid chlorides and aluminum chloride as catalyst.

Ciapetta (114) and Egloff and Hulla (115) have been able to alkylate olefins using isoparaffins in sulfuric acid. Following the method of Ciapetta (114), isobutane and I in sulfuric acid gave a 95% recovery of starting material.

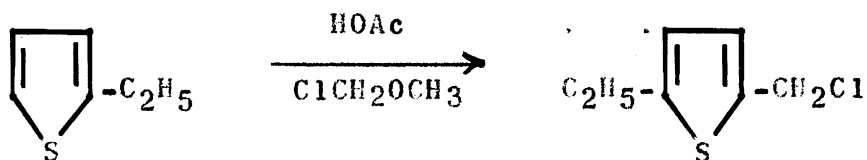
Cogniant and Cogniant (116) have effected the chloromethylation of 2-ethylthiophene using chloromethyl ether in glacial acetic acid. Using their method, the

TABLE IX

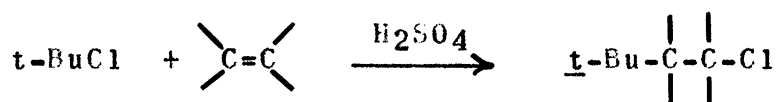
Alkylation, Condensation and Acylation Reactions

<u>Sulfone</u>	<u>Agent</u>	<u>Catalyst</u>	<u>Isolated</u>	<u>% Recovery</u>
I	t-BuCl	AlCl ₃	tar	--
I	Isecbutane	H ₂ SO ₄	I	95
I	ClCH ₂ OCH ₃	Glacial HOAc	I	91.5
I	t-BuCl	H ₂ SO ₄	I	93
II	t-BuCl	H ₂ SO ₄	II	81
I	2-butanone	<i>β</i> -alanine in benzene	I	81
I	2-butanone	Piperidine & Glacial HOAc	tar	--
I	2-butanone	<i>β</i> -alanine in diisopropyl ether	I	66
I	2-butanone	<i>β</i> -alanine in methyl acetate	I	90
II	2-butanone	<i>β</i> -alanine in benzene	II	92
II	2-butanone	Ammonium Acetate in benzene	II	85.6
I	Acetone	Zinc chloride & acetic anhydride	I	99
I	N-methyl-formanilide	Phosphorous oxy-chloride	I	48
I	Acetyl chloride	Pyridine	I	99

2,5-dihydrothiophene 1,1-dioxide (I) was recovered in 91.5%.



Schmerling (117) has reported the condensation of alkyl halides with olefins in sulfuric acid to give saturated halo compounds. Both I and II were thus

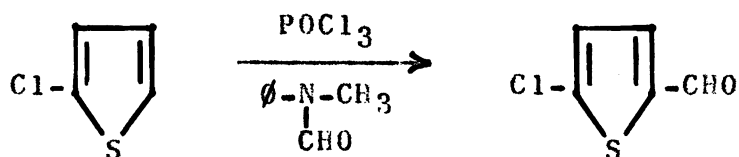


treated with tertiary butyl chloride and sulfuric acid, but a 93 and 81% recovery respectively of starting sulfones I and II was obtained.

Since the alpha hydrogens of the sulfones are acidic, a study of the Knoevenagel reaction was made on I and II. Prout (118) published an excellent article on the use of various catalysts in this condensation. Using the method of Prout and coworkers (119), the reaction of I and II with 2-butanone and various catalysts was studied. In all cases, except the reaction using piperidine as catalyst, a good recovery of starting sulfone was realized. One difficulty with the reaction is that it is an equilibrium reaction (54) and the water formed must be removed. A Barrett-type water extractor was used to effect this,

but in heating the reaction mixture to the reflux temperature of benzene, I dissociated. The use of lower boiling solvents reduced the amount of dissociation but only starting material was obtained.

King and Nord (120) have run formylation reactions with thiophenes in good yield. The procedure is to mix *N*-methylformanilide with phosphorus oxychloride to obtain a red solution. Addition of thiophene causes a vigorous reaction. When I was added to the red solution of *N*-methylformanilide and phosphorus oxychloride, no



signs of a reaction resulted. The low recovery of I (48%) might have resulted from washing the organic layer with saturated sodium bicarbonate solution in which I is soluble.

An acylation reaction using the procedure of Allen and coworkers (121) was attempted. The use of pyridine and acetyl chloride and I gave a 99% recovery of starting sulfone.

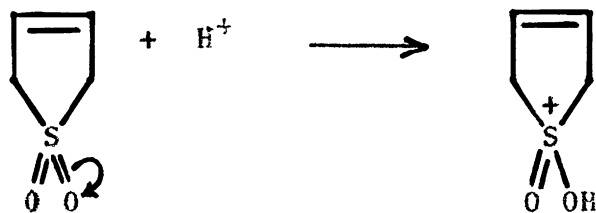
In all cases no condensation, alkylation or acylation reactions were detected with either I or II. Due to the

thermal instability of I, the temperature at which such reactions are performed, could not be employed in the case of I. Although II is thermally stable, the direct conjugation of the double bond with the sulfone group may decrease the acidity of the alpha hydrogens.

F. Interpretation of the Reactions Studied in A - E

The results of the studies with I and II bring out the general fact that nucleophilic addition and substitution reactions readily occur while electrophilic reactions do not. From these results a better picture of the structure of these cyclic sulfones can be gained.

The addition of hydrogen halides to a double bond occurs via an electrophilic attack of a proton at the site of high electron density. It is of interest to note that no evidence for any such addition to I or II was obtained. Considering a resonance form of I, the



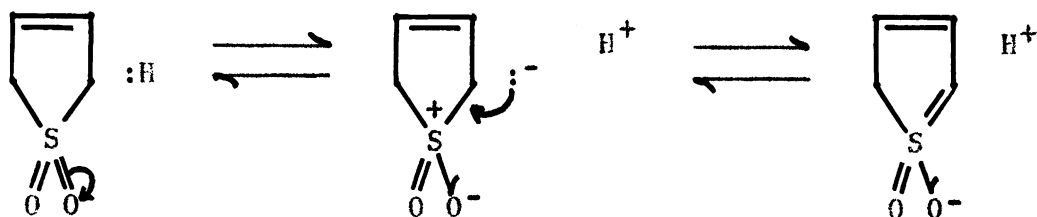
proton could add to the oxygen of the sulfone group. This would make the sulfur positive and by an inductive effect decrease the availability of the π electrons for addition. This would also explain why no evidence for acid catalyzed condensation, alkylation or acylation reactions was obtained. It is significant that hydrogen halides have been added to 3-methyl-2,5-dihydrothiophene 1,1-dioxide (XXVII) (88). In this case, the presence of

the methyl group in the 3-position would, via hyperconjugation and an inductive effect, facilitate addition to the double bond and thus overcome the electron withdrawing effect of the sulfone group.

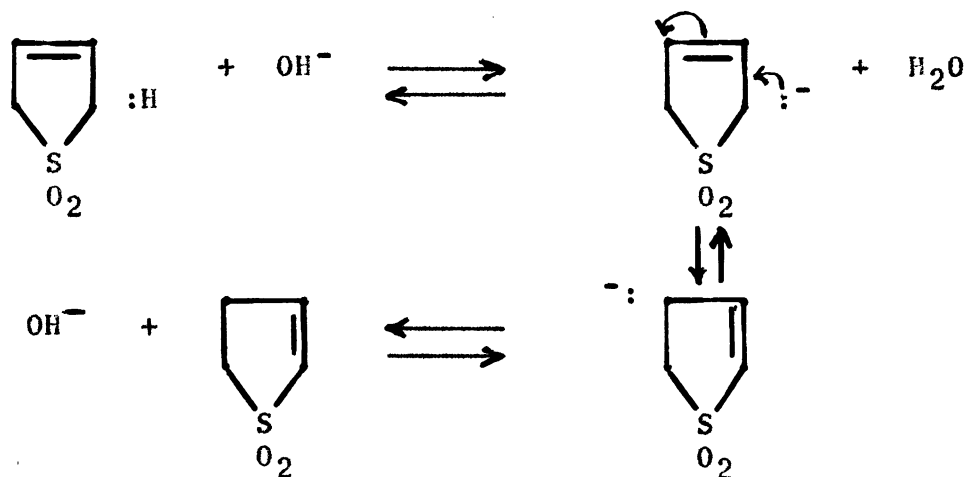
The base catalysed or nucleophilic addition and substitution reactions should be aided by the inductive effect of the sulfone group. In nucleophilic addition reactions, the attacking reagent is seeking a center of low electron density and the inductive effect due to the sulfone group would produce such a center.

Bromine would be expected to add to the double bond in the β -position with little trouble since the reaction involves the addition of a non-acid electrophile in a non-acid medium. However, it was found that the double bond in the α -position is deactivated sufficiently to retard addition of bromine in non-aqueous media. Thus the reaction occurs probably via a nucleophilic attack.

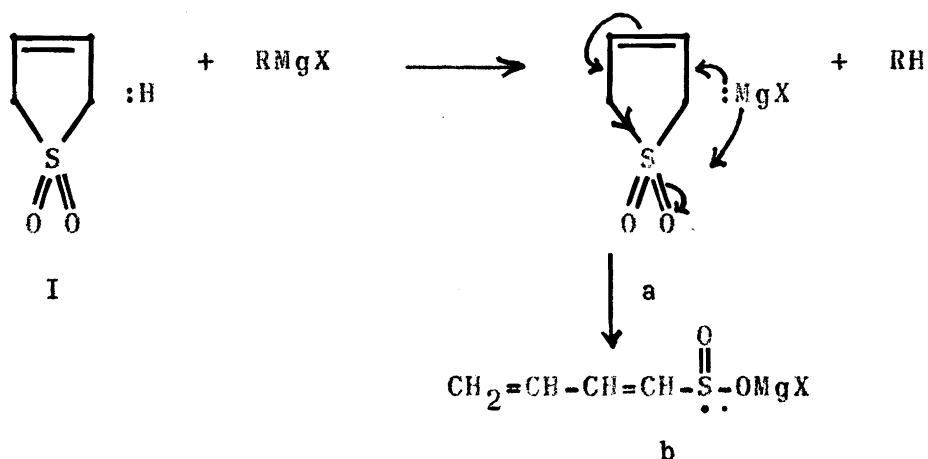
One of the resonance forms postulated for I reveals the acidity of the α -hydrogens. This acidity was supported by the actions of Grignard reagents on I. The



ease of the elimination of hydrogen bromide from the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) to form 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) further supports the acidity attributed to the α -hydrogens. The isomerization of I to II also occurs by the same mechanism (18). It is seen that solvolysis occurs here.



The Grignard reactions show that two moles of Grignard reagent react with one mole of I although the gas data reveals only one acidic hydrogen. The second mole of Grignard reagent could add either 1,4 or 1,6 to b.



In the presence of β -alanine and glacial acetic acid, the Knoevenagel reactions of I and II failed. Although β -alanine (118) has been used successfully with numerous other compounds, it may not have been strong enough to bring about ionization of the α -hydrogen. Amines could not be used in this reaction since they add to the double bonds.

The free-radical-type reactions of halogenating agents gave only addition to the double bond and no substitution products were isolated. According to the generally accepted free-radical mechanism (97) attack occurs at a center of high electron density. The sulfone group by an inductive effect decreases the electron density at the alpha carbons and so addition rather than substitution occurred.

EXPERIMENTAL

A. Formation of the Isomeric Dihydrothiophene
1,1-Dioxides¹

2,5-Dihydrothiophene 1,1-Dioxide (I). The procedure followed was a modification of the method described by Grummitt, Ardis and Fick (16). A 500-ml. stainless steel reaction vessel² was precooled to -78° using a dry-ice acetone bath. To this vessel was added 1.6 g. (0.008 mole) of hydroquinone (2% by weight of 1,3-butadiene), 81.1 g. (1.50 moles) of liquid 1,3-butadiene³ (The Matheson Co., Inc.) and 192.2 g. (3.00 moles) of liquid sulfur dioxide (The Matheson Co., Inc.). The reaction vessel was closed tightly, allowed to warm to room temperature and checked

¹ In the following experimental parts all reported melting and boiling points are uncorrected and all temperatures are expressed in degrees centigrade. All solids were identified by mixture melting points from authentic samples unless otherwise stated. Microanalyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

² This cylindrical vessel (2 3/8" O.D., 2" I.D. x 9 1/2") was made by Mr. F. Hayes of the Virginia Institute for Scientific Research, Richmond, Virginia. The head was equipped with a Hoke valve and pressure guage. The bomb was pressure tested to 500 p.s.i.

³ The butadiene and sulfur dioxide gases were liquified by passing them through a spiraled copper coil maintained at -50 to -60° in a dry-ice acetone bath.

for leaks. It was then inserted in an electrically-heated oil bath and heated to 100-105° for four hours.¹

The vessel was allowed to come to room temperature and the excess sulfur dioxide was removed by venting the gas through 500 ml. of 6N NaOH solution.

The contents of the bomb were dissolved in hot water and decolorized with Norit. One crystallization yielded 166 g. (93%) of pure sulfone melting at 64-65° [Lit. (16) 64.5-65°] .

2,3-Dihydrothiophene 1,1-Dioxide (II). A solution of 50 g. (0.42 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) in 1 l. of 0.5N potassium hydroxide was irradiated at room temperature with ultraviolet light for 20 hours. The resulting solution was submitted to continuous extraction with chloroform for two days. Evaporation of the chloroform solution gave 35.4 g. of light brown oil. This oil was heated to 180° at 15-20 mm. to remove unchanged I. The crude oil was purified by distillation at reduced pressure. The yield of pure II was 24.6 g. (49%), b.p. 116°/0.043 mm., m.p. 49-50° [Lit. (18) b.p. 106-8° (cathode vacuum), m.p. 48.5-49.5°] .

¹ With runs of this size the pressure usually reached 250-300 p.s.i.

B. Addition Reactions to the Isomeric Dihydrothiophene 1,1-Dioxides: Ionic and Free Radical

3,4-Dibromomotetrahydrothiophene 1,1-Dioxide (V).

A solution of 254 g. (2.15 moles) of 2,5-dihydrothiophene 1,1-dioxide (I) in 500 ml. of dry chloroform was placed in a three-necked, round-bottomed flask, fitted with a Hershberg stirrer, a dropping funnel and a condenser to which was attached a calcium chloride filled tube. During a period of two hours, 344 g. (2.15 moles) of bromine dissolved in 200 ml. of dry chloroform was added at room temperature. After twelve hours 32 g. (0.20 mole) of bromine in 50 ml. of dry chloroform was added and the mixture was stirred for an additional 4 hours. The solid was then filtered and washed with chloroform to give white plates. The chloroform washings and the original filtrate were combined and the chloroform was removed to give an additional amount of the product. A total of 567 g. (95%) of pure V was obtained, m.p. 141-142° [Lit. (29) 141.0-141.8°].

3-Bromo-4-Hydroxytetrahydrothiophene 1,1-Dioxide (VI).

The procedure used was that of Backer and Blaas (38). A solution of 24 g. (0.21 mole) of I in 500 ml. of water was added to a flask containing 38 g. (0.24 mole) of bromine in 100 ml. of acetic acid. The mixture was stirred

while cooled with an ice bath. After standing overnight the resulting solid was filtered to give 34 g. of a mixture of V and VI. Hot benzene dissolved the dibromo compound (V), and the yield of VI was 9 g. (20%), m.p. 186-187° [Lit. (38) 187-189°].

2,5-Dihydrothiophene 1,1-Dioxide (I) with Cyanogen Bromide. A solution of 35.4 g. (0.30 mole) of I in 300 ml. of dry benzene was added drop-wise to 35 g. (0.33 mole) of cyanogen bromide in 250 ml. of dry benzene with stirring over a period of one hour. There was no visible sign of a reaction. The solution was stirred overnight and then 200 ml. of 10% hydrochloric acid was added. The benzene solution was separated and washed with 2-25 ml. portions of water and dried over magnesium sulfate. Removal of the benzene gave a solid which was identified as 2,5-dihydrothiophene 1,1-dioxide (I); recovery 21 g. (62%).

Attempted Addition of Anhydrous Hydrogen Bromide to 2,5-Dihydrothiophene 1,1-Dioxide (I).

a. In Anhydrous Benzene. Anhydrous hydrogen bromide (The Matheson Co., Inc.) was passed through a dispersion tube into a solution of 29.5 g. (0.25 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) dissolved in 250 ml. of dry benzene for 5 hours. After the benzene was removed at reduced pressure, a solid was isolated. Purification of

the crude solid gave a quantitative recovery of starting material (I).

b. With Aluminum Chloride as Catalyst. The reaction was run in benzene as solvent using 44 g. (0.33 mole) of aluminum chloride for 35.4 g. (0.30 mole) of I. The anhydrous hydrogen bromide was passed through the solution for 8 hours. The recovered 2,5-dihydrothiophene 1,1-dioxide (I) weighed 32 g. (91%).

c. With Zinc Bromide as Catalyst. To a flask containing 72.7 g. (0.5 mole) of zinc bromide in 60 ml. (0.5 mole) of 48% hydrobromic acid was added 23.6 g. (0.20 mole) of 2,5-dihydrothiophene 1,1-dioxide. The solution was stirred and heated in an oil bath to 50° and anhydrous hydrogen bromide was passed through the solution for 1½ hours. The mixture was stirred at 45-50° for 14 hours. After this time the solution was diluted with 200 ml. of water and extracted with chloroform. Removal of the chloroform gave 13 g. (55%) of a solid identified as starting material (I).

d. With Benzoyl Peroxide as Catalyst. To 175 ml. of dry benzene in a flask was added 23.6 g. (0.20 mole) of 2,5-dihydrothiophene 1,1-dioxide and 2.4 g. (0.01 mole) of benzoyl peroxide. The solution was stirred and heated in an oil bath to 68-73°, while anhydrous hydrogen bromide

was passed into the solution for 13 hours. Removal of the benzene gave 20 g. (86%) of starting 2,5-dihydrothiophene 1,1-dioxide (I).

Potassium Bromide and Ammonia with 2,5-Dihydrothiophene 1,1-Dioxide (I). A solution of 11.8 g. (0.10 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) and 40 g. (0.34 mole) of potassium bromide in 75 ml. of ammonium hydroxide and 50 ml. of water was allowed to stand at room temperature for 5 days. The solution was extracted with ten 30-ml. portions of chloroform and removal of the chloroform gave 6.8 g. (58%) recovery of I. The raffinate was evaporated to dryness and the residue was extracted with hot acetone to give 4.8 g. of oil. The oil was treated with hot ethanol, but no solid was obtained. The oil was vacuum distilled, but no solid was obtained. A qualitative analysis of the oil showed that sulfur was present but halogens and nitrogen absent¹.

Anhydrous Hydrogen Chloride and 2,5-Dihydrothiophene 1,1-Dioxide (I). To 135 ml. (1.58 moles) of hydrochloric acid 136 g. (1.0 mole) of zinc chloride was added with cooling. After all of the zinc chloride dissolved 23.6 g. (0.20 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) was added to

¹ see ref. 51, Chapter V.

the solution. The flask was warmed to 50° and hydrogen chloride was passed into the solution for 4 hours. The solution was stirred and heated for 7 hours and treated with hydrogen chloride for an additional hour. After this period the solution was diluted with water and extracted with six 50-ml. portions of chloroform. Removal of the chloroform at reduced pressure gave some crude solid which was recrystallized from ethanol to give 14 g. (60% recovery) of starting material.

Potassium Chloride and Ammonia with 2,5-Dihydrothiophene 1,1-Dioxide (I). A solution of 11.8 g. (0.10 mole) of I and 40 g. (0.67 mole) of potassium chloride in 150 ml. of 1:1 ammonium hydroxide solution was warmed to 40-50° for 28 hours and allowed to stand at room temperature for 5 days. The solution was then evaporated to dryness and the resulting solid was extracted with hot acetone. Removal of the acetone at reduced pressure gave 11.0 g. of crude oil. The oil was treated with hot ethanol, but failed to crystallize, so it was vacuum distilled. There was obtained 3.5 g. (30%) of material b.p. 75-89°/0.240-0.370 mm. which solidified and had a m.p. of 63-64°. A mixture melting point with I gave no depression¹.

¹ This is the first report of the distillation of I and is surprising in view of its thermal instability.

A portion of the solid was brominated to give the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) identified by mixture melting point. There was some charring in the flask, probably due to decomposition. Qualitative analysis of the remaining oil showed sulfur present and halogens and nitrogen absent¹.

Attempted Addition of Hydriodic Acid to 2,5-Dihydrothiophene 1,1-Dioxide (I). To 60 ml. of 45% hydriodic acid (0.3 mole) was mixed 11.8 g. (0.10 mole) of (I) in a stoppered flask. The yellow solution was allowed to stand for 6 days in the dark and 1 day in the light. Extraction of the solution with six 25-ml. portions of chloroform gave 10.6 g. (91%) recovery of starting material (I).

Preparation of Tetrahydrothiophene 1,1-Dioxide (IV)². The procedure used was that of Backer and Bolt (20). The palladium catalyst was prepared by adding 0.25 g. (0.0014 mole) of palladium (II) chloride and 0.25 g. of gum arabic to 125 ml. of boiling water. While the solution cooled to room temperature hydrogen was passed into it.

A solution of 11.8 g. (0.10 mole) of 2,5-dihydrothiophene, 1,1-dioxide (I) in 125 ml. of water was added to the palladium catalyst and hydrogen was passed into the

1 See ref. 51, Chapter V.

2 See Appendix IV for the infrared spectrum of IV.

solution for three hours. The mixture was extracted with five 50-ml. portions of chloroform. Removal of the chloroform gave 12 g. of crude light yellow oil. This oil was distilled at reduced pressure to give 9.4 g. (78%) of pure IV, b.p. 122-124^o/6mm., m.p. 29-30^o [Lit. (44) b.p. 141-142^o/11 mm., m.p. 29^o].

Reaction of N-Bromosuccinimide with 2,5-Dihydrothiophene 1,1-Dioxide (I). In a 1-liter, three-necked, round-bottomed flask, fitted with a stirrer and condenser, was placed 47.2 g. (0.40 mole) of 2,5-dihydrothiophene 1,1-dioxide (I), 71.2 g. (0.40 mole) of N-bromosuccinimide (Arapahoe Chemicals, Inc.), 4.8 g. (0.02 mole) of benzoyl peroxide and 750 ml. of dry chloroform. The mixture was heated in an oil bath and at 70^o it turned bright red and clear. After 2 hours, the solution turned a clear, yellow color. It was heated for a total of 14 hours and allowed to cool to room temperature. Removal of 300 ml. of chloroform by distillation followed by cooling in the refrigerator caused succinimide to crystallize and float to the top of the solution. Successive removal of chloroform and cooling produced 27.4 g. (69%) of succinimide. The remaining oil was dissolved in ethanol and decolorized using Norit. There was obtained 38.5 g. (69.2% yield on the basis of 0.2 mole of I for 0.4 mole of N-bromosuccinimide) of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V).

There was also obtained 9 g. of white solid, m.p. 108-109°, which contained only nitrogen and bromine by qualitative analysis. The remaining dark thick oil on further treatment did not produce any other identifiable material¹.

Reaction of 1,3-Dibromo-5,5-Dimethylhydantoin with 2,5-Dihydrothiophene 1,1-Dioxide (I). In a 1-liter, three-necked, round-bottomed flask, fitted with a stirrer and condenser was placed 47.2 g. (0.40 mole) of 2,5-dihydrothiophene 1,1-dioxide (I), 114.4 g. (0.40 mole) of 1,3-dibromo-5,5-dimethylhydantoin (Arapahoe Chemicals, Inc.), 4.8 g. (0.02 mole) of benzoyl peroxide and 600 ml. of dry chloroform. The mixture was stirred at room temperature for 5 hours and the liquid phase had a light orange-brown color. The mixture was heated to reflux for 12 hours. The color became lighter, but still some solid was present which dropped to the bottom of the flask². The mixture was heated to 75-80° for 12 additional hours to give a light

¹ Experiments were performed at room temperature and at 45-50°, but these could not be worked-up, since the unreacted benzoyl peroxide decomposed on heating with ethanol.

² Apparently some 1,3-dibromo-5,5-dimethylhydantoin was undissolved, since it is more dense than chloroform, while the 5,5-dimethylhydantoin floats.

yellow colored solution. Upon cooling to room temperature solid appeared at the surface of the solution. The reaction mixture was treated similarly to that from the N-bromosuccinimide reaction and 40.9 g. (80%) of 5,5-dimethylhydantoin was obtained. Work-up of the oil gave 1.3 g. (27%) recovery of benzoyl peroxide and 22.8 g. (21%) yield of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V). The remaining oil did not give any other solid on further attempted purification.

3-Methoxytetrahydrothiophene 1,1-Dioxide XXVI. The procedure used was described in a British patent (57). In a 500-ml., three-necked, round-bottomed flask, equipped with stirrer and condenser was placed a solution of 0.5 g. (0.009 mole) of potassium hydroxide in 25 ml. (0.6 mole) of methyl alcohol. Then 23.6 g. (0.20 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) was added in portions at room temperature, while the solution was stirred. After all of I was added, the solution was then acidified to congo red paper with concentrated sulfuric acid. An excess of potassium carbonate was then added and the separated salts removed by filtration. The excess methanol was distilled, and the residual oil was vacuum distilled. There was obtained 19.5 g. (65%) of pure 3-methoxytetrahydrothiophene 1,1-dioxide (XXVI), b.p. 103-105°/less than

1 mm., n_D^{24} 1.4837 [Lit. (59) b.p. 113-115°/0.1 mm.,
 n_D^{24} 1.4830].

2,3-Dibromotetrahydrothiophene 1,1-Dioxide (VII).

In a 125 ml. Erlenmeyer flask was placed a solution of 13 g. (0.11 mole) of 2,3-dihydrothiophene 1,1-dioxide (II) in 50 ml. of water. To this was added 25.6 g. (0.16 mole) of bromine and the solution was allowed to stand at room temperature for three days. During this time solid precipitated. The yellow solid was removed by filtration and recrystallized from ethanol to give 17.4 g. (57%) of pure, 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII), m.p. 116-117° [Lit. (23) 112-115°].

Anhydrous Hydrogen Chloride with 2,3-Dihydrothiophene 1,1-Dioxide (II). In a 200-ml., three-necked, round-bottomed flask, equipped with a stirrer, gas dispersion tube and condenser was placed 68 g. (0.5 mole) of zinc chloride in 65 ml. (0.8 mole) of concentrated hydrochloric acid. After the zinc chloride dissolved 9.4 g. (0.079 mole) of 2,3-dihydrothiophene 1,1-dioxide (II) was added and the flask warmed to 50°. While the flask was maintained at 50°, hydrogen chloride was passed into the solution for 4 hours. The solution was kept at 50° for an additional 8 hours and then diluted with water. Extraction of the solution with chloroform gave 5.9 g. (63% recovery) of starting II.

Reaction of N-Bromosuccinimide with 2,3-Dihydrothiophene 1,1-Dioxide (II). In a 500-ml., three-necked, round-bottomed flask was placed 11.8 g. (0.10 mole) of 2,3-dihydrothiophene 1,1-dioxide (II), 17.8 g. (0.1 mole) of N-bromosuccinimide (Arapahoe Chemicals, Inc.), 1.2 g. (0.005 mole) of benzoyl peroxide and 350 ml. of dry chloroform as solvent. The above mixture was heated to reflux and after a few minutes the solution turned a deep red color. After 20 hours of heating and stirring the solution turned a straw-yellow color and was heated for two more hours. The solution was allowed to cool to room temperature and succinimide floated to the surface. The succinimide was filtered and the remaining volume was reduced in half by distillation of the chloroform. Cooling of the resulting solution caused succinimide to crystallize and float on the top of the solution. This procedure was continued until no more succinimide came out of the solution. A total of 7.8 g. (88%) of succinimide was obtained. There was also obtained 1.7 g. of solid, m.p. 142-143°, which contained only nitrogen and bromine by qualitative tests. The solvent was removed from the remaining solution and 18.2 g. of crude oil was obtained which failed to crystallize upon repeated attempts. A forced, vacuum distillation gave two fractions. The first fraction of 2 g. (17%) proved to be recovered II by a

mixture melting point. The other fraction of 12.6 g. (55%) was identified as the 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII). There was about 3.6 g. of material lost due to charring in the distillation flask.

Reaction of 1,3-Dibromo-5,5-Dimethylhydantoin with 2,3-Dihydrothiophene 1,1-Dioxide (II). A mixture of 57.2 g. (0.20 mole) of 1,3-dibromo-5,5-dimethylhydantoin (Arapahoe Chemicals, Inc.), 23.6 g. (0.20 mole) of 2,3-dihydrothiophene 1,1-dioxide (II), 2.4 g. (0.01 mole) of benzoyl peroxide and 400 ml. of dry chloroform was placed in a 1-liter, three-necked, round-bottomed flask fitted with stirrer and condenser. The mixture was heated to reflux and after 15 minutes the solution was clear and dark red. The solution was then heated for 17 hours, during which time it changed color to a light orange-brown and solid appeared at the surface. The flask was cooled and some more 1,3-dimethylhydantoin floated to the top. This was removed by filtration and subsequent distillation of half of the chloroform followed by cooling produced a total of 25.6 g. (87%) yield of pure 1,3-dimethylhydantoin. Removal of all solvent by distillation gave 48 g. of crude yellow oil. This oil failed to crystallize and was subjected to a forced, vacuum distillation. A total of 31.2 g. (56%) yield of 2,3-dibromotetrahydrothiophene

1,1-dioxide (VII) was isolated and about 17 g. of material was lost by charring and tar formation.

C. Elimination Reactions of the Isomeric
Dibromotetrahydrothiophene 1,1-Dioxides
and Some Displacement Reactions

5-Bromo-2,3-Dihydrothiophene 1,1-Dioxide (XVIIc).

In a 100-ml., round-bottomed flask was placed a solution of 8.3 g. (0.03 mole) of 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII) in 50 ml. of dry acetone¹. To this solution was added 4.6 g. (0.058 mole) of dry pyridine¹ and the system was protected with a calcium chloride filled tube. The solution was warmed to 50° for 15 minutes and then allowed to stand at room temperature during which time crystals of pyridine hydrobromide formed. After 42 hours the mixture was filtered to give 2.7 g. of pyridine hydrobromide. The filtrate was acidified with concentrated hydrochloric acid and the resulting solution was extracted with six 25-ml. portions of chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate. Removal of the chloroform gave 5.8 g. of crude solid. The crude solid was recrystallized from hot ethanol to give 4.3 g. (73%) of pure XVIIc, m.p. 74.5-75.0°.

Anal. Calc'd. for $C_4H_5SO_2Br$:

C, 24.38; H, 2.56; S, 16.27; Br, 40.55

Found: C, 24.36; H, 2.51; S, 16.43; Br, 40.35.

¹ The dry acetone and dry pyridine were prepared according to the method of Fieser, ref. 50.

A sample of XVIIc was hydrogenated in an attempt to prepare the 2-bromotetrahydrothiophene 1,1-dioxide (XVIII), a known compound. However, using palladium as catalyst and passing hydrogen through the solution for two hours caused hydrogenolysis of the carbon bromine bond.

Another sample of XVIIc was heated with sodium iodide in dry acetone but there was no reaction.

3-Bromo-2,3-Dihydrothiophene 1,1-Dioxide XIII. In a 1-liter, round-bottomed flask was placed a solution of 60 g. (0.22 mole) of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) in 250 ml. of dry acetone. To this solution was added 33 g. (0.42 mole) of dry pyridine and the system was protected with a calcium chloride filled tube. Within 20 minutes, at room temperature, crystals of pyridine hydrobromide began to appear. After 14 hours the mixture was filtered to give 35.4 g. of pyridine hydrobromide. The filtrate was acidified with concentrated hydrochloric acid and the resulting aqueous phase removed. The acetone rich phase was subjected to reduced pressure to remove the acetone. The residual oil and small amount of water were extracted with 50 ml. of benzene from which 24.7 g. of a white solid was obtained. Extraction of the combined aqueous phases with three 25-ml. portions of benzene gave an additional 12.3 g. of white solid. The solids were combined and purified by recrystallization from ethanol to

give 33.1 g. (78%) of pure XIII, m.p. 63-64° [Lit. (38) 64.5-65°] .

3-Iodo-2,3-Dihydrothiophene 1,1-Dioxide (XIX). To a solution of 9.9 g. (0.05 mole) of 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) in 50 ml. of dry acetone was added a solution of 11.3 g. (0.075 mole) of sodium iodide in 50 ml. of dry acetone. A precipitate formed immediately and the solution turned a light yellow color. After 15 minutes the solution began to darken and the solid was filtered. The solid, 4.8 g. (94%), was sodium bromide and was found to be free from iodide ion¹. The filtrate was shaken with a saturated solution of sodium thiosulfate and was dried over magnesium sulfate. The acetone was removed at room temperature under reduced pressure and the residue (oil plus a small amount of water) was extracted with chloroform. Removal of the chloroform gave 9.9 g. of crude oil which solidified upon standing. Recrystallization from methanol-petroleum ether gave 6.5 g. (53%) of pure XIX, m.p. 72.0-72.5°.

Anal. Calc'd. for C₄H₅SO₂I:

C, 19.68; H, 2.06; S, 13.14

Found: C, 19.67; H, 2.05; S, 12.58

3-Chloro-2,3-Dihydrothiophene 1,1-Dioxide XX. To 3.9 g. (0.016 mole) of 3-iodo-2,3-dihydrothiophene 1,1-

¹ A qualitative test for bromine and iodine was made using the method in Shriner and Fuson (51). Bromine was found to be present and iodine was absent.

dioxide (XIX) in 50 ml. of hot, absolute ethanol¹ was added a solution of 4.4 g. (0.016 mole) of mercuric chloride in 50 ml. of hot, absolute ethanol. The resulting solution was allowed to stand overnight at room temperature protected with a calcium chloride filled tube. The solution was then heated to reflux for 8 hours. Distillation of about two-thirds of the ethanol caused the precipitation of 2 g. of mercuric iodide² which was removed by filtration. The removal of the remainder of the ethanol gave a mixture of mercuric iodide, mercuric chloride and 3-chloro-2,3-dihydrothiophene 1,1-dioxide (XX). Fractional crystallization of this mixture from ethanol gave 1.0 g. (42%) of pure XX, m.p. 82.5-83.0°.

Anal. Calc'd. for $C_4H_5SO_2Cl$:

C, 31.48; H, 3.30; S, 21.01

Found: C, 31.30; H, 3.33; S, 20.95

Attempted Preparation of 3-Fluoro-2,3-Dihydrothiophene 1,1-Dioxide (XXI). A mixture of 9.9 g. (0.050mole) of 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII), 4.4 g.

1 The absolute ethanol was prepared using the method of Lund and Bjerrum (52).

2 The solid was proven to be mercuric iodide by its melting point, 125-126° Lit. (53) 127° .

(0.075 mole) of potassium fluoride and 50 ml. of diethylene glycol was stirred and heated to 80° for five hours. During this time 3.3 g. of polymer, containing sulfur but no halogens was formed. The solid was removed by filtration and the solution diluted with 100 ml. of water. The water solution was extracted with seven 25-ml. portions of chloroform. Removal of the chloroform gave 1.4 g. (14% recovery) of starting material (XIII).

Attempted Preparation of 3-Cyano-2,3-Dihydrothiophene 1,1-Dioxide (XXII).

a. Aprotic Medium. A mixture of 9.9 g. (0.05 mole) of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII), 4.5 g. (0.05 mole) of copper (I) cyanide and 200 ml. of dry benzene was heated to reflux for four hours. The solution was filtered hot to remove the solid. Removal of the benzene at reduced pressure gave 9.6 g. (97% recovery) of XIII.

b. Aqueous Solution. To a solution of 175 ml. of 95% ethanol and 75 ml. of water was added 19.7 g. (0.10 mole) of XIII and 13.0 g. (0.20 mole) of potassium cyanide. The mixture was warmed to 55° to effect solution of the solids and then allowed to stand for one day at room temperature. A solid was obtained which did not melt up to 300° and contained sulfur but no nitrogen or bromine.

Removal of the solvent at reduced pressure gave only 2 g. of crude, red oil, which could not be purified.

c. Dry Medium. A mixture of 4.3 g. (0.022 mole) of XIII and 2.4 g. (0.026 mole) of copper (I) cyanide was heated at 120-130° for four hours. The mixture became very dark during this time and a black tar was formed.

d. Via 3-Iodo-2,3-Dihydrothiophene 1,1-Dioxide XIX. The 3-iodo-2,3-dihydrothiophene 1,1-dioxide (XIX) was prepared in situ by dissolving 11.7 g. (0.060 mole) of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) in 50 ml. of dry acetone and adding a solution of 13.5 g. (0.090 mole) of sodium iodide in 50 ml. of dry acetone. Sodium bromide was formed immediately and was filtered. To the filtrate was added 6.5 g. (0.10 mole) of potassium cyanide in 350 ml. of methanol. This solution which was allowed to stand at room temperature overnight turned dark red. The solvent was removed at reduced pressure and the resulting oil and solid extracted with chloroform. Removal of the chloroform gave 3.4 g. of crude, dark red oil which could not be purified.

Attempted Preparation of the 3-Bromo-4-Cyanotetrahydrothiophene 1,1-Dioxide (XVI).

a. Methanol Solution. A solution of 55.6 g.

(0.20 mole) of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) and 13.0 g. (0.20 mole) of potassium cyanide in 325 ml. of methanol was heated to reflux for 11 hours. The mixture was filtered hot to remove the inorganic material. There was obtained 31.3 g. (56% recovery) of starting V and 7.7 g. of solid insoluble in water or organic solvents and contained sulfur, but no halogens. There was also obtained about 1 g. of solid identified by mixture melting point as the dehydrobrominated product, the 3-bromo-2,3-dihydrothiophene 1,1-dioxide.

b. Dry Medium. A mixture of 55.6 g. (0.20 mole) of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) and 18 g. (0.20 mole) of copper (I) cyanide were heated to 145-150° for 32 hours. The material became very dark and was extracted with chloroform leaving 23.5 g. of solid not soluble in organic solvents. Removal of the chloroform at reduced pressure gave 34.8 g. (61 % recovery) of V.

D. Metalation Reactions with the Isomeric
Dihydrothiophene 1,1-Dioxides and
Various Halogen Derivatives

Preparation of 3-Ethoxytetrahydrothiophene 1,1-Dioxide

XXV. In preparation for some alkylation work using sodium ethoxide a blank run was made. In a 500-ml., three-necked, round-bottomed flask with stirrer, condenser and addition funnel was placed 100 ml. of absolute ethanol¹. Then 2.3 g. (0.10 gram atom) of sodium in small pieces was added. After all the sodium reacted 11.8 g. (0.10 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) in 75 ml. of absolute ethanol was added to the solution. After 10 minutes 9.8 g. (0.10 mole) of ammonium bromide was added. The solution was stirred for 30 minutes and the inorganic solid removed by filtration. Removal of the ethanol at reduced pressure left an oil. Vacuum distillation of the oil gave 9.2 g. (57%) of XXV, b.p. 110-116°/1mm., m.p. 27-30° [Lit.² (57) 30°].

Attempted Alkylation of 2,5-Dihydrothiophene 1,1-Dioxide (I) using Sodium Amide. The method used to prepare the sodium amide was that of Vaughn, et al. (58). In a 500-ml., three-necked, round-bottomed flask surrounded by

1 Absolute ethanol prepared by the method of Lund and Bjerrum (52).

2 The method used in ref. 57 to prepare XXV involved the treatment of I with potassium hydroxide and ethanol.

a dry-ice bath and equipped with a mercury-sealed stirrer, condenser and addition funnel was placed 350 ml. of liquid ammonia (Armour Ammonia Division). To this was added 0.05 g. (0.0001 mole) of iron (III) nitrate 9-hydrate and 2.3 g. (0.1 gram atom) of sodium in small pieces, while air was bubbled through the ammonia to start the formation of the sodium amide. The sodium was added at such a rate that the deep blue color did not persist. After the addition of all the sodium, the solution had a blue-gray color.

To the suspension of sodium amide in ammonia 11.8 g. (0.10 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) was added. The addition time was 15 minutes and the solution turned a deep red color. After stirring the above solution for 30 minutes 14.2 g. (0.10 mole) of methyl iodide was added drop-wise over a 15 minute period. The solution was stirred for two hours and then 36 ml. of water was added. The dry-ice bath was removed and the ammonia was allowed to evaporate during one day. The remaining dark red solution was acidified to congo red paper with dilute acetic acid and a red tar, insoluble in chloroform, ether or benzene was formed. The solution was extracted with six 50-ml. portions of benzene, however, removal of the benzene at reduced pressure gave only a few drops of a dark tar.

Use of Sodium Hydride in Metalation Studies of 2,5-

Dihydrothiophene 1,1-Dioxide (I). In a 1-liter, three-necked, round-bottomed flask, fitted with a stirrer and condenser, was placed 23.6 g. (0.20 mole) of I in 200 ml. of dry, thiophene-free benzene. To this solution was added 4.8 g. (0.2 mole) of sodium hydride (Metal Hydride, Inc.) in small amounts. Hydrogen gas came off but the reaction was very slow. After three hours the solution had a slight blue color to it. The mixture was stirred overnight and then warmed to 50° for 4 hours. The mixture was cooled to room temperature and 56.8 g. (0.40 mole) of methyl iodide in 125 ml. of benzene was added drop-wise during one hour. The mixture was stirred for a day at room temperature and then the flask was cooled while dilute sulfuric acid was added until the solution was acidic to congo red paper¹. The benzene layer was separated and the removal of benzene at reduced pressure gave some crude solid. The aqueous layer was extracted with four 50-ml. portions of chloroform and removal of the chloroform also gave some crude solid. The two solid fractions were combined and recrystallized from ethanol to give 10.8 g. (46% recovery) of I.

Use of Finely Divided Sodium in Metalation Studies of

1 Due to the presence of unreacted sodium hydride, the hydrolysis is very violent and should be effected with caution.

2,5-Dihydrothiophene 1,1-Dioxide I. In a 1-liter, round-bottomed flask equipped with stirrer and condenser was placed a solution of 35.4 g. (0.30 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) in 200 ml. of dry benzene. Then 9.2 g. (0.4 gram atom) of sodium dispersion¹ in 200 ml. of dry benzene was added to the above flask. The solution turned a slight green color and a small amount of gas came off. The mixture was heated for two days at 50°, however, a large amount of the sodium remained. An additional 59 g. (0.50 mole) of I in 400 ml. of benzene was added in five equal portions. Upon each addition of I a small amount of gas came off. After two more days of stirring 74.1 g. (0.80 mole) of t-butyl chloride was added, but no external signs of a reaction were observed. The mixture was cooled and acidified to congo red paper using dilute sulfuric acid. Work-up of the reaction gave a quantitative recovery of starting I.

Metalation of the Isomeric Dihydrothiophene 1,1-Dioxides and Halogen Derivatives with Organometallic Reagents. Since it has been shown (18,65,66) that alkyl

1 The Sodium Dispersion was a gift from the Ethyl Corporation, New York. Actually 18.4 g. of material were used, since the sample was 50% sodium in toluene. The average particle size was 9 μ and had a size range of 1 μ to 20 μ .

magnesium halides will react with some cyclic and acyclic sulfones to give the sulfone Grignard reagent and liberation of the corresponding alkane, a thorough study has been made with the 2,5-dihydrothiophene 1,1-dioxide (I) to see if any substituted compounds could be prepared. In this section four typical examples are given, and the results of other runs are summarized in Appendix II. Included in this section will also be reactions with the 2,3-dihydrothiophene 1,1-dioxide (II) and 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) with Grignard reagents and the use of *n*-butyl lithium (67).

All the alkyl magnesium halides were prepared under nitrogen atmosphere using ether or other solvents in a ratio of 1 liter per mole of Grignard reagent. The entire system of condenser, addition funnel and flask was kept under an atmosphere of nitrogen. After the Grignard reagent was prepared the sulfone was either added to the Grignard reagent ("direct" addition) or the Grignard reagent was added to the sulfone ("inverse" addition) and the amount of gas measured¹. The gas measurements were accomplished by stopping the flow of nitrogen and connecting the rubber tubing leading to the mercury trap

1 See Results and Discussion for the significance of the gas measurements.

exhaust to a Wet-Test meter¹, protected by a dry-ice trap to condense any solvent vapors. Thus the reaction could be followed from the gas data.

The reaction flask used in these experiments was a three-necked, round-bottomed flask, fitted with a Hershberg mercury sealed stirrer, dropping funnel and an Allihn condenser.

a. Reaction of Methylmagnesium Iodide with 3-Bromo-2,3-Dihydrothiophene 1,1-Dioxide (XIII). The Grignard reagent was prepared by reacting 14.2 g. (0.10 mole) of methyl iodide in 100 ml. of dry ether with 2.4 g. (0.10 gram atom) of magnesium. The Grignard reagent was forced into an addition funnel using nitrogen pressure. The methylmagnesium iodide was then added to a solution of 19.7. g. (0.10 mole) of XIII in 100 ml. of dry benzene. A total of 0.64 l. of gas² (29%) was obtained. A tan colored solid³ appeared at this point. The material was stirred for two hours and then 14.2 g. (0.10 mole) of methyl iodide in 50 ml. of ether was added. There was no external sign

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- 1 Precision Wet-Test Meter manufactured by Precision Scientific Co., Chicago.
 - 2 All gas data were corrected to S.T.P. and the percentages are based on the evolution of one mole of gas per mole of sulfone used.
 - 3 This solid is indicative of a sulfone magnesium halide complex (65).

of a reaction. The mixture was stirred for 24 hours at room temperature and then treated with a small amount of hydroquinone¹. Cold dilute sulfuric acid containing a small amount of hydroquinone was added to the congo red end point², while the flask was cooled with an ice-bath. No further gas came off and a large amount of polymer was formed. The organic layer was separated and removal of the ether-benzene mixture at reduced pressure gave a few drops of dark tar. The water layer was extracted with six 50-ml. portions of chloroform. Distillation of the combined chloroform extracts gave no residue.

b. Reaction of Methylmagnesium Iodide with 3,4-Dibromotetrahydrothiophene 1,1-Dioxide (V). The Grignard reagent was prepared by reacting 14.2 g. (0.10 mole) of methyl iodide in 100 ml. of dry ether with 2.4 g. (0.10 gram atom) of magnesium. The methylmagnesium iodide was removed from the flask as previously described and added to a solution of 13.8 g. (0.050 mole) of V in 100 ml. of

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- 1 It was seen from previous Grignard reactions that hydroquinone added to the Grignard mixture and the sulfuric acid reduced the amount of polymer formed in many cases.
 - 2 In all the Grignard work congo red paper was used as an indicator, since it insured the solution was on the acid side.

dry ether. The addition of the Grignard reagent produced 0.86 l. of gas (77%). The solid which was formed had a slight yellow color. The mixture was warmed to 45° for two hours, cooled, and 14.2 g. (0.10 mole) of methyl iodide in 50 ml. of ether added. There was no external sign of reaction. The mixture was stirred two hours and then hydrolyzed with dilute sulfuric acid, as before with hydroquinone present. A small amount of polymer was formed. The organic layer was separated and removal of the ether-benzene at reduced pressure gave a solid which upon purification, gave 3 g. (22% recovery) of V. The water layer was extracted with chloroform, but removal of the chloroform gave only a few drops of oil.

c. Reaction of *n*-Butyl Lithium with 2,5-Dihydrothiophene 1,1-Dioxide (I). The method used for the preparation of the *n*-butyl lithium was that of Gilman (68). In the apparatus previously described for the preparation of the Grignard reagent was placed 12.4 g. (1.8 gram atoms) of lithium ribbon (Lithium Corporation of America, Inc.) cut in small pieces in 200 ml. of dry ether. The flask was cooled to -20° using a dry-ice acetone bath and then about 30 drops of a solution of 123.3 g. (0.90 mole) of *n*-butyl bromide in 200 ml. of dry ether was added, while the mixture was stirred under nitrogen. After the reaction

started¹ the remainder of the n-butyl bromide solution was added during a three hour period. After the addition was complete the reaction mixture was allowed to warm to 10° and stirred for two hours longer. The excess lithium was filtered under nitrogen atmosphere and the n-butyl lithium solution was added to 35.4 g. (0.30 mole) of I in 250 ml. of dry benzene. A total of 2.82 l. of gas (42%) was evolved during the addition, and a white solid formed with the solution having a slight green color. After the mixture was stirred for an additional hour 78.5 g. (1.00 mole) of acetyl chloride in 100 ml. of dry benzene was added. A vigorous reaction occurred and the mixture turned a dark brown. Hydroquinone was added and the mixture hydrolyzed with cold dilute sulfuric acid. Another vigorous reaction occurred and a black solid formed. Separation of the organic layer and removal of the ether-benzene gave 38 g. of black tar. From the flask 20 g. of a solid, black polymer was obtained.

d. "Inverse" Grignard Reactions with the 2,5-Dihydrothiophene 1,1-Dioxide (I).

1. Use of equal molar amounts of Grignard reagent and I. The Grignard reagent was prepared by reacting 21.8 g. (0.20 mole) of ethyl bromide in 200 ml. of

1 Clouding of the solution and the appearance of bright spots on the lithium indicated that the reaction had started.

dry ether with 4.9 g. (0.20 gram atom) of magnesium. The Grignard reagent was removed from the flask as previously described and added to a solution of 23.6 g. (0.20 mole) of I in 250 ml. of dry benzene. A total of 4.3 l. of gas (96%) was evolved. A white solid appeared and the mixture warmed to 40-55° for two hours. The flask was cooled to room temperature and 8.8 g. (0.20 mole) of acetaldehyde in 250 ml. of benzene was added. There was no sign of an exothermic reaction and the mixture was stirred at room temperature overnight. The flask was cooled in an ice-bath, while the solution was hydrolyzed with cold, dilute sulfuric acid with hydroquinone present. An additional 0.09 l. of gas (2%) came off this time. The organic layer was separated. Reduction of the volume of solvent produced a solid, which upon recrystallization polymerized. The remainder of the organic solution was placed in the refrigerator at the time and it also polymerized and sulfur dioxide was evolved.

2. Use of a 2:1 mole ratio of Grignard reagent and I. Prepared 0.50 mole of methylmagnesium chloride by reacting 50.5 g. (1.0 mole) of methyl chloride¹ in 650 ml.

1 Methyl chloride has a b.p. of -24° and so an excess had to be used. The methyl chloride-ether solution was prepared by dissolving methyl chloride gas in ether and the gain in weight gave the amount of methyl chloride present. The time to prepare the Grignard reagent was 9 hours.

of dry ether with 12.2 g. (0.50 gram atom) of magnesium. The methylmagnesium chloride was removed as previously described and added to a flask containing 23.6 g. (0.20 mole) of I in 200 ml. of dry ether. A total of 4.92 l. (88% on 1:1 basis) of gas was obtained. This was a blank run so the flask was cooled in an ice-bath, while dilute sulfuric acid was added to the congo red end point. There was obtained 1.13 l. (20.2%) of gas at this point. The ether layer was separated and dried over anhydrous sodium sulfate. Removal of the ether at reduced pressure gave about 20 g. of a light yellow, plastic type of solid. This solid would not dissolve in the usual organic solvents. Extraction of the water phase with chloroform failed to produce any further material.

e. "Direct" Grignard Reactions with the 2,5-Dihydrothiophene 1,1-Dioxide (I).

1. Use of a 1:1 mole ratio of Grignard reagent and I. A solution containing 0.18 mole of ethyl magnesium bromide¹ was prepared by reacting 21.8 g. (0.20 mole) of ethyl bromide in 150 ml. of dry ether with 4.9 g. (0.20

1 The exact amount of Grignard reagent was determined using the method of Gilman, et al., ref. 69 for the quantitative determination of Grignard reagents by titration with standard acid.

gram atom) of magnesium. To this solution 21.2 g. (0.18 mole) of I dissolved in 156 ml. of dry benzene was added. After about 41% of I had been added no further gas was given off. At this point 1.42 l. (35%) of gas was obtained. The remainder of the sulfone was added and the mixture stirred overnight. The usual white solid was formed. The flask was cooled in an ice-bath and hydroquinone was added. The reaction mixture was then hydrolyzed with cold dilute sulfuric acid. A total of 0.34 l. (8%) of gas was given off at this time and very little polymer was formed. The organic layer was separated and the solvent removed at reduced pressure to give some crude solid. The water solution was extracted with six 30-ml. portions of chloroform, and the removal of the chloroform gave more crude solid. The two solid fractions were combined and recrystallized from ethanol to give 9.8 g. (46%) recovery of starting I. Nothing else was isolated.

2. Use of a 2:1 mole ratio of Grignard Reagent and I. The Grignard reagent was prepared by adding a solution of 98.1 g. (0.90 mole) of ethyl bromide in 800 ml. of dry ether to 21.9 g. (0.90 gram atom) of magnesium. After the reaction was completed 47.2 g. (0.40 mole) of I in 300 ml. of benzene was added to the ethylmagnesium bromide solution and the reaction was very exothermic. The

usual gray solid was formed. A solution of 113.5 g. (0.90 mole) of methyl sulfate in 125 ml. of ether was added over a 30 minute period and the reaction was exothermic. The pH of the reaction mixture was checked and found to be 8. The mixture was heated to 40-45° for 12 hours and then cooled and hydrolyzed in the usual manner. Very little polymer was formed. The organic phase was separated and removal of the ether and benzene at reduced pressure gave 31 g. of dark thick oil. The water phase was extracted with six 50-ml. portions of chloroform, and the removal of the chloroform gave 15.7 g. of dark, red oil.

The 15.7 g. of red oil was subjected to a vacuum distillation and 5.3 g. of a light yellow oil, b.p. 40°/0.008 mm., n_D^{27} 1.5298, was obtained. The remainder charred in the distillation flask. Qualitative analysis of the distilled oil showed sulfur present and halogens¹ absent.

Quantitative analysis gave:

C, 52.10; H, 7.85; S, 23.26.

Calculated on the basis of $C_{12}H_{22}S_2O_3$:

C, 51.76; H, 7.96; S, 23.03.

¹ See ref. 51, chapter V.

The molecular weight of the above sample was determined using the Rast method¹.

Calc'd: 278.4 Found: 262

221

230

The material readily decolorized a bromine-chloroform solution to give an oil which could not be purified.

A sample of the distilled oil on standing in the open at room temperature decomposed. From the above information there was the possibility that the oil was an unsaturated sulfinic anhydride².

A sample of the distilled oil was treated with aniline employing a method that Knoevenagel (70) used with the diphenyl sulfinic anhydride. A white solid was obtained which was recrystallized from ethanol, but failed to melt when heated to 300°. A sample of aniline sulfate was purified and found to melt with decomposition at 190-193°.

An attempted alkylation was run with the distilled oil using the method of Otto (71) for sulfinic acids. The

1 See ref. 51, pg. 50.

2 For further information on the structure of this compound see the section on Results and Discussion.

oil was mixed with sodium hydroxide solution and methyl sulfate, but only a dark tar was obtained.

Using the method of Hinsberg (72) of reacting a sulfinic acid with benzaldehyde, the purified oil was treated the same way, but only a dark tar was obtained.

The distilled oil was hydrogenated following the procedure previously described for the 2,5-dihydrothiophene 1,1-dioxide (I) but again only a dark tar was obtained.

Pickholz (73) reported that sulfinic acids will react with *p*-quinone to give a stable sulfone, but here also the only material isolated was a dark tar.

"Inverse" Grignard Reaction with 2,3-Dihydrothiophene 1,1-Dioxide (II). The Grignard reagent was prepared using 2.4 g. (0.10 gram atom) of magnesium and 14.2 g. (0.10 mole) of methyl iodide in 100 ml. of dry ether. The methylmagnesium iodide was removed from the flask as previously described and added to a solution of 11.8 g. (0.10 mole) of II in 100 ml. of dry benzene. A white solid was obtained and 1.05 l. (47%) of gas was evolved. The material was warmed to 45° for 6 hours, and 14.2 g. (0.10 mole) of methyl iodide in 50 ml. of ether was added. The mixture was stirred an additional 3 hours, but no sign of a reaction occurred. The mixture was then hydrolyzed as previously described and 1.30 l. (58%) of gas evolved and

a polymer formed. The organic layer was separated and washed with saturated sodium bisulfite solution. Removal of the ether and benzene gave a few drops of dark oil. The water layer was extracted with six 50-ml. portions of chloroform and removal of the chloroform also only gave a few drops of dark oil.

"Direct" Grignard Reaction with 2,3-Dihydrothiophene 1,1-Dioxide (II). A 0.334 mole solution¹ of ethylmagnesium bromide was prepared by reacting 43.6 g. (0.40 mole of ethyl bromide in 500 ml. of ether with 9.7 g. (0.40 gram atom) of magnesium. After the Grignard reagent was formed a solution of 19.6 g. (0.166 mole) of II in 150 ml. of dry benzene was added slowly. It was observed that the amount of gas evolved was not equivalent to the amount of sulfone added. There was obtained 1.17 l. (31.4%) of gas and the usual solid appeared. The mixture was stirred for 2 hours and then 42.1 g. (0.334 mole) of methyl sulfate was added. The reaction was exothermic and 1.34 l. (36%) of gas was given off. There was, however, no change in the appearance of the white solid. The mixture was hydrolyzed in the usual manner and 3.19 l. (85.8%) of gas came off and some polymer was formed. The organic

1 The amount of Grignard reagent determined accurately using the method of Gilman, et al. (69).

layer was separated, and the removal of the ether and benzene at reduced pressure gave 4.7 g. of crude oil. The water layer was extracted with ten 50-ml. portions of chloroform and removal of the chloroform gave 8.6 g. of crude, yellow oil. The oils were combined and vacuum distilled at $81-86^{\circ}/0.056-0.060$ mm. to give 9.8 g. of clear oil. There was about 3.5 g. lost due to charring and tar formation in the distillation flask. The oil was treated with ethanol and 1.5 g. (8%) of II was obtained. The ethanol was removed and a portion of the remaining 8.3 g. of oil was treated with bromine-water and gave a solid, m.p. $115-116^{\circ}$, identified as 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII). Thus a 50% recovery of II was effected¹.

1 It was noted that a very small amount of impurity in many cases hindered the crystallization of the 2,3-dihydrothiophene 1,1-dioxide (II).

E. Alkylation, Condensation and Acylation
Studies of the Isomeric Dihydrothiophene
1,1-Dioxides

Attempted Alkylation of 2,5-Dihydrothiophene 1,1-Dioxide (I).

a. Friedel-Crafts Reaction. In a 1-liter, round-bottomed flask was added 29.5 g. (0.25 mole) of (I) in 150 ml. of s-tetrachloroethane and 46.3 g. (0.50 mole) of t-butyl chloride. A solution of 106.8 g. (0.80 mole) of aluminum chloride in 400 ml. of s-tetrachloroethane was then added to the flask while it was cooled in an ice-bath. The reaction mixture turned a dark brown color and hydrogen sulfide was detected. The material was stirred at room temperature for two days and then hydrolyzed by pouring the mixture onto ice. The organic layer was separated, washed with saturated sodium bicarbonate and dried over anhydrous sodium sulfate. Removal of the solvent gave only a dark tar.

b. Isobutane and Sulfuric Acid. In a 200-ml. three-necked, round-bottomed flask fitted with a Hershberg stirrer, gas dispersion tube, thermometer and condenser were placed 59 g. (0.50 mole) of 2,5-dihydrothiophene 1,1-dioxide (I) in 225 g. (2.3 moles) of sulfuric acid. Into this solution 44.8 l. (2.0 moles) of isobutane¹ was passed

¹ The isobutane was measured using a "Precision" Wet-Test Meter manufactured by Precision Scientific Co., Chicago.

during six hours. There was no evidence of a reaction. The solution was poured onto ice and then extracted with six 50-ml. portions of chloroform. Removal of the chloroform gave 56.1 g. (95% recovery) of I.

c. t-Butyl Chloride and Sulfuric Acid. To a stirred solution of 92.6 g. (1.0 mole) of t-butyl chloride in 49 g. (0.5 mole) of sulfuric acid was added 59 g. (0.50 mole) of 2,5-dihydrothiophene 1,1-dioxide in solid form while the reaction flask was kept at $10^{\circ} \pm 2^{\circ}$ in an ice-bath. Hydrogen chloride was given off during this addition. The solution was stirred for 10 hours and then hydrolyzed by pouring onto ice. There was obtained 36.5 g. of crude solid. The water was extracted with six 50-ml. portions of chloroform. Removal of the chloroform gave an additional 27.5 g. of crude solid. The solids were purified by recrystallization from alcohol and 54.9 g. (93%) of I was recovered¹.

d. Chloromethylation. In a 100-ml., round-bottomed flask 24.8 g. (0.21 mole) of I was dissolved in 60 ml. of glacial acetic acid. The flask was cooled to 0° and 17.4 g. (0.21 mole) of chloromethyl methyl ether was added. The

¹ An experiment was performed in which t-butyl chloride was added to I and sulfuric acid. This also gave a nearly quantitative recovery of I.

solution was stirred for 2 hours at 0° and then allowed to warm to 10° and stirred for an additional 2 hours. The solution was poured onto ice and then extracted with chloroform. Removal of the chloroform gave a crude solid which was recrystallized from ethanol to give 22.7 g. (91.5% recovery) of starting I.

Attempted Alkylation of 2,3-Dihydrothiophene 1,1-Dioxide with *t*-Butyl Chloride and Sulfuric Acid. In a 100 ml. round-bottomed flask 11.8 g. (0.10 mole) of 2,3-dihydrothiophene 1,1-dioxide (II) was mixed with 9.8 g. (0.1 mole) of sulfuric acid. The flask was cooled to 10° and 18.5 g. (0.20 mole) of *t*-butyl chloride was added drop-wise with stirring. The solution was stirred overnight at room temperature and then poured onto ice. The solution was extracted with chloroform, and the removal of the chloroform gave a crude solid. The solid was recrystallized from ethanol to give 9.5 g. (81% recovery) of starting II.

Attempted Knoevenagel Reactions with 2,5-Dihydrothiophene 1,1-Dioxides.

a. β -Alanine and Benzene as Solvent. In a 500-ml. round-bottomed flask was placed 0.2 g. (0.002 mole) of β -alanine, 23.6 g. (0.20 mole) of 2,5-dihydrothiophene 1,1-dioxide (I), 17.3 g. (0.24 mole) of 2-butanone, 4 ml. of

glacial acetic acid and 75 ml. of dry benzene¹ as solvent. A Barrett-type water extractor² and a condenser were attached to the flask and the solution heated to reflux for 35 hours. Since sulfur dioxide was detected, the reaction was stopped. There was formed 1.4 ml. of water (theoret. 3.6 ml.). Removal of the solvent gave 19.1 g. (81% recovery) of I.

b. Piperidine and Acetic Acid. The set-up used was that described in a. A mixture of 18 g. (0.18 mole) of piperidine, 63 ml. of glacial acetic acid, 23.6 g. (0.20 mole) of I, 34.6 g. (0.48 mole) of 2-butanone and 75 ml. of dry benzene was heated to reflux for 3 days. There was no water formed and the solution became very dark and thick, due to the formation of piperidinium acetate.

c. β -Alanine and Diisopropyl Ether as Solvent. The set-up used was that described in a. To a 500-ml. round-bottomed flask was added 36 g. (0.30 mole) of I, 26 g. (0.36 mole) of 2-butanone, 0.3 g. (0.003 mole) of β -alanine, 6 ml. of glacial acetic acid and 300 ml. of diisopropyl ether as solvent. The solution was heated to

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- 1 Dry benzene was prepared by treating a good grade of benzene with sodium ribbon.
 - 2 Vilter (54) showed that the removal of water is essential.

reflux for 75 hours during which time only 0.5 ml. of water separated. Sulfur dioxide was detected, and the work-up of the reaction mixture gave 23 g. (66% recovery) of I.

d. β -Alanine and Methyl Acetate as Solvent. A Barrett-type water separation apparatus was used as in previous reactions. A solution of 36 g. (0.30 mole) of I, 26 g. (0.36 mole) of 2-butanone, 0.3 g. (0.003 mole) of β -alanine, 6 ml. of glacial acetic acid and 250 ml. of methyl acetate were heated to reflux for 24 hours. No water was obtained, and the work-up of the solution gave 31 g. (90% recovery) of I.

Attempted Knoevenagel Reactions with 2,3-Dihydrothiophene 1,1-Dioxide (II).

a. β -Alanine and Benzene as Solvent. A solution of 11.8 g. (0.10 mole) of 2,3-dihydrothiophene 1,1-dioxide (II), 8.7 g. (0.12 mole) of 2-butanone, 0.3 g. (0.003 mole) of β -alanine, 6 ml. of glacial acetic acid and 100 ml. of benzene was heated to reflux for 4 days. Although 1 ml. of water was formed, only 11.1 g. (92% recovery) of II was obtained.

b. Ammonium Acetate and Benzene as Solvent. A solution of 11.8 g. (0.10 mole) of II, 8.7 g. (0.12 mole) of 2-butanone, 6.2 g. (0.08 mole) ammonium acetate, 4.6 ml.

of glacial acetic acid and 100 ml. of dry benzene was heated to reflux for 35 hours. There was formed 5.5 ml.¹ of water, but the work-up of the reaction mixture gave only 10.1 g. (86% recovery) of II.

Attempted Condensation of 2,5-Dihydrothiophene 1,1-Dioxide (I) using Zinc Chloride. In a 300 ml. round-bottomed flask, fitted with a condenser, was placed 35.4 g. (0.30 mole) of I, 52.3 g. (0.90 mole) of dry acetone, 46 g. (0.45 mole) of acetic anhydride and 40 g. (0.3 mole) of zinc chloride. The mixture was heated to reflux for 30 hours. A quantitative recovery of I was obtained.

Attempted Acylation of 2,5-Dihydrothiophene 1,1-Dioxide (I). To 31.6 g. (0.40 mole) of dry pyridine, 15.7 g. (0.20 mole) of acetyl chloride in 50 ml. of benzene was added. The reaction was exothermic and a white precipitate was formed². However, when 23.6 g. (0.20 mole) of I in 75 ml. of benzene was added, no exothermic reaction occurred. The solution was stirred for 3 hours and a quantitative recovery of I was obtained.

1 The ammonium acetate was not anhydrous and could account for the large amount of water formed during the reaction.

2 This part of the acylation reaction occurred as stated by Allen (55).

Attempted Formylation of 2,5-Dihydrothiophene 1,1-Dioxide (I). To 45.9 g. (0.30 mole) of phosphorus oxychloride was added 40.5 g. (0.30 mole) of N-methylformanilide. The usual color change (ref. 56) to red occurred, but the addition of 38.9 g. (0.33 mole) of I did not cause any apparent reaction. The solution was stirred for 3 days and then poured onto 300 g. of cracked-ice in 125 ml. of water. The solution was extracted with six 50-ml. portions of chloroform and the combined chloroform extracts were washed with saturated sodium bicarbonate, water, and finally dried over anhydrous magnesium sulfate. Removal of the chloroform gave only 18.7 g. (48% recovery) of I.

SUMMARY

1. The preparation of the 2,5-dihydrothiophene 1,1-dioxide (I) and the 2,3-dihydrothiophene 1,1-dioxide (II) has been improved.

2. On the basis of the reactions studied, a clearer picture of the resonance structure of the 2,5-dihydrothiophene 1,1-dioxide (I) is obtained.

3. Various addition reactions were attempted with the dihydrothiophene 1,1-dioxides. There is evidence that the addition of bromine to the 2,3-dihydrothiophene 1,1-dioxide may proceed via nucleophilic attack. No evidence of addition of hydrogen halides to either sulfone was obtained.

4. The dehydrobromination reaction of the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) has been improved to give 20-25% higher yields of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII).

5. A new compound, the 5-bromo-2,3-dihydrothiophene 1,1-dioxide (XVIIc) has been obtained from the dehydrobromination of the 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII).

6. The 3-bromo, 3-chloro and 3-iodo-2,3-dihydrothiophene 1,1-dioxides have been prepared, the latter two for the first time.

7. The free radical attack of brominating agents

gave only addition to the double bonds of I and II to form the corresponding dibromo compounds.

8. The Grignard reaction with the 2,5-dihydrothiophene 1,1-dioxide (I) has been thoroughly studied and a mechanism consistent with the data has been proposed.

9. No evidence for condensation, alkylation or acylation reactions was found with the isomeric dihydrothiophene 1,1-dioxides.

BIBLIOGRAPHY

1. R.C. Morris, E.C. Shokal and W.S. Thornhill, U.S. Pat., 2,393,925 (Shell Development Co.), Jan. 29, 1946; C.A., 40, 3220 (1946).
2. G.W. Hooker, L.R. Drake and S.C. Stowe, U.S. Pat., 2,402,891 (Dow Chemical Co.), June 25, 1946; C.A., 40, 7229 (1946).
3. G.W. Hooker, L.R. Drake and S.C. Stowe, U.S. Pat., 2,395,050 (Dow Chemical Co.), Feb. 19, 1946; C.A., 40, 3124 (1946).
4. R.C. Morris and H. deV. Finch, U.S. Pat., 2,373,329 (Shell Development Co.), April 10, 1945; C.A., 40, 1534 (1946).
5. H.G. Staaterman, R.C. Morris, R.M. Stager, and G.L. Pierotti, Chem. Eng. Progress, 43, No. 4, Trans. Am. Inst. Engrs., 148 (1947); C.A., 41, 4142 (1947).
6. T.E. Evans and R.C. Morris, U.S. Pat., 2,360,859 (Shell Development Co.), Oct. 24, 1944; C.A., 39, 2163 (1945).
7. E.L. Durrum, U.S. Pat., 2,407,820 (Shell Development Co.), Sept. 17, 1946; C.A., 41, 777 (1947).
8. R.C. Morris and A.V. Snider, U.S. Pat., 2,368,597 (Shell Development Co.), Jan. 30, 1945; C.A., 39, 5138 (1945).
9. G.W. Hooker, S.C. Stowe and L.R. Drake, U.S. Pat., 2,385,704 (Dow Chemical Co.), Sept. 25, 1945; C.A., 40, 185 (1946).
10. F.F. Miller, U.S. Pat., 2,548,169 (B.F. Goodrich Co.), April 10, 1951; C.A., 45, 5975 (1951).
11. N.H. Staudinger, French Pat., 698,857, July 11, 1930.
12. E.J. Crane, Private Communication, Jan. 11, 1955.
13. M.A. Magill, Private Communication, Aug. 16, 1956.
14. C.W. Mortenson, U.S. Pat., 2,460,995 (E.I. duPont de Nemours and Co.), Feb. 8, 1949; C.A., 43, 4514 (1949).

15. A. Sorokin and K.V. Puzitzkii, Sintet. Kouchuk., 6, 12 (1933); C.A., 28, 3339 (1934).
16. O. Grummitt, A.E. Ardis and J. Fick, J. Am. Chem. Soc., 72, 5167 (1950).
17. H.J. Backer and J. Strating, Rec. trav. chim., 53, 525 (1934).
18. E. de Roy van Zuydewijn, Rec. trav. chim., 56, 1047 (1937).
19. J. Boeseken and E. de Roy van Zuydewijn, Proc. Acad. Sci. (amsterdam), 40, 23 (1937).
20. H.J. Backer and C.C. Bolt, Rec. trav. chim., 54, 538 (1935).
21. J. Boeseken and E. de Roy van Zuydewijn, Proc. Acad. Sci. (Amsterdam), 37, 760 (1934).
22. H. Staudinger and B. Ritzenthaler, Ber., 68B, 455 (1935).
23. E. de Roy van Zuydewijn, Rec. trav. chim., 57, 445 (1938).
24. H.J. Backer, J. Strating and C.M.H. Kool, Rec. trav. chim., 58, 778 (1939).
25. K. Alder, H.F. Richert and E. Windmuth, Ber., 71B, 2451 (1938).
26. British Pat., 610,188 (Standard Oil Development Co.), Oct. 12, 1948; C.A., 43, 2216 (1949).
27. F.W. Rose Jr., U.S. Pat., 2,448,053 (Houdry Process Corp.), Aug. 31, 1948; C.A., 43, 663a (1949).
28. S.F. Birch and D.T. McAllan, J. Chem. Soc., 2556 (1951).
29. W.J. Bailey and E.W. Cummins, J. Am. Chem. Soc., 76, 1932 (1954).
30. E. Eigenberger, J. prakt. Chem., (2), 127, 307 (1930).

31. E. Eigenberger, J. prakt. Chem., [2], 129, 312 (1931).
32. E. Eigenberger, J. prakt. Chem., [2], 131, 289 (1931).
33. J.H. Boyd Jr., U.S. Pat., 2,440,671 (Phillips Petroleum Co.), May 4, 1948; C.A., 42, 7341 (1948).
34. R.L. Moore and R.A. Trimble, U.S. Pat., 2,471,077 (Shell Development Co.), May 24, 1949; C.A., 43, 7512 (1949).
35. F.G. Bordwell and W.H. McKellin, J. Am. Chem. Soc., 73, 2251 (1951).
36. S.F. Birch and D.T. McAllan, J. Chem. Soc., 233 (1952).
37. J. Boeseken and E. de Roy van Zuydewijn, Proc. Acad. Sci. (Amsterdam), 39, 31 (1936).
38. H.J. Backer and Th. A.D. Blaas, Rec. trav. chim., 61, 785 (1942).
39. O.E. van Lohuizen and H.J. Backer, Rec. trav. chim., 68, 1137 (1949).
40. T.E. Jordan and F. Kipinis, J. Am. Chem. Soc., 71, 1875 (1949).
41. T.F. Yen, Ph.D. Thesis, Virginia Polytechnic Institute, November, 1955.
42. J.E. Mahan and S.C. Fauske, U.S. Pat., 2,578,565 (Phillips Petroleum Co.), Dec. 11, 1951; C.A., 46, 6672 (1952).
43. French Pat., 847,254 (J.G. Farbenind. A.G.), Oct. 5, 1939; C.A., 35, 5519 (1941).
44. M.W. Farlow, U.S. Pat., 2,233,999 (E.I. DuPont de Nemours & Co.), March 4, 1941; C.A., 35, 3652 (1941).
45. R.C. Morris and E.C. Shokal, U.S. Pat., 2,419,982 (Shell Development Co.), April 15, 1947; C.A., 41, 4813 (1947).

46. R.C. Morris and J.L. Van Winkle, U.S. Pat., 2,504,099 (Shell Development Co.), April 18, 1950; C.A., 44, 6887 (1950).
47. M.S. Kharasch, M. Freiman, and W.E. Urry, J. Org. Chem., 13, 570 (1948).
48. R.C. Morris and N.C. Melchior, U.S. Pat., 2,451,298 (Shell Development Co.), Oct. 12, 1948.
49. E. Sauter, Z. Krist., 83, 340 (1932); C.A., 27, 2362 (1933).
50. L.F. Fieser, "Experiments in Organic Chemistry", 2nd Ed., D.C. Heath & Co., New York, 1941.
51. R.L. Shriner and R.C. Fuson, "The Systematic Identification of Organic Compounds", 3rd Ed., John Wiley and Sons, Inc., New York, 1948.
52. H. Lund and J. Bjerrum, Ber., 64, 210 (1931).
53. N.A. Lange, "Handbook of Chemistry", 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949.
54. E.J. Vilter, M.S. Thesis, DePaul University, Chicago, Illinois, August, 1955.
55. C.F.H. Allen, C.J. Kibler, D.M. McLachlin and C.V. Wilson, Org. Syn., 26, 1 (1946).
56. A.W. Weston and R.J. Michaels, Jr., Org. Syn., 31, 108 (1951).
57. British Pat., 489,974, (Interessengemeinschaft Farbenindustrie Aktiengesellschaft) Jan. 31, 1938.
58. T.H. Vaughn, R.H. Vogt and J.A. Nieuwland, J. Am. Chem. Soc., 56, 2120 (1934).
59. H.J. Backer and J. Strating, Rec. trav. chim., 62, 815 (1943).
60. S.F. Birch and D.T. McAllan, J. Chem. Soc., 3411 (1951).
61. W. Dilthey, E. Graef, H. Dierichs, and W. Josten, J. prakt. chem., 151, 185 (1938).

62. J.L. Melles and H.J. Backer, *Rec. trav. chim.*, 72, 314 (1953).
63. S.F. Birch and D.T. McAllan, *Nature*, 165, 899 (1950).
64. C.C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds", Interscience Publishers, Inc., New York, 1946.
65. L. Field, *J. Am. Chem. Soc.*, 74, 3919 (1952).
66. H.E. Faith, U.S. Pat., 2,656,336 (Allied Laboratories, Inc), Oct. 20, 1953; *C.A.*, 48, 10775 (1954).
67. H. Gilman and D.L. Esmay, *J. Am. Chem. Soc.*, 74, 266 (1952).
68. E.G. Jones and H. Gilman, *Org. Reactions*, 6, 352 (1951).
69. H. Gilman, P.D. Wilkinson, W.P. Fishel and C.R. Meyers, *J. Am. Chem. Soc.*, 45, 150 (1923).
70. E. Knoevenagel and L. Folack, *Ber.*, 41, 3323 (1908).
71. K. Otto, *Ber.*, 13, 1272 (1880).
72. O. Hinsberg, *Ber.*, 27, 3259 (1894).
73. S. Pickholz, *J. Chem. Soc.*, 685 (1946).
74. J.W. Baker "Hyperconjugation", Oxford University Press, London, 1952, pg. 24.
75. G.M. Phillips, J.S. Hunter and L.E. Sutton, *J. Chem. Soc.*, 146 (1945).
76. H.P. Koch, *J. Chem. Soc.*, 408. (1949).
77. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1946, pgs. 131 and 167.
78. R.C. Morris and J.L. Van Winkle, U.S. Pat., 2,495,467 (Shell Development Co.) Jan. 24, 1950; *C.A.*, 44, 4509 (1950).

79. D. Delfs, U.S. Pat., 2,219,006 (General Aniline and Film Corp.), Oct. 22, 1940, C.A., 35, 1902 (1941).
80. R.C. Morris and E.C. Shokal, British Pat., 566,930 (Shell Development Co.), Jan. 19, 1945; C.A., 41, 1711 (1947).
81. R.C. Morris and E.C. Shokal, U.S. Pat., 2,452,949 (Shell Development Co.), Nov. 2, 1943; C.A., 43, 2237 (1949).
82. R.C. Morris and J.L. Van Winkle and E.C. Shokal, U.S. Pat., 2,461,339 (Shell Development Co.), Feb. 8, 1949; C.A., 43, 3851 (1949).
83. R.C. Morris and J.L. Van Winkle, U.S. Pat., 2,482,631 (Shell Development Co.), Sept. 20, 1949; C.A., 44, 2033 (1950).
84. R.C. Morris and J.L. Van Winkle, U.S. Pat., 2,494,515 (Shell Development Co.), Jan. 10, 1950; C.A., 44, 3032 (1950).
85. R.C. Morris and A.V. Snider, U.S. Pat., 2,430,821 (Shell Development Co.), Nov. 11, 1947; C.A., 42, 2285 (1948).
86. H.J. Backer and R. Van Der Ley, Rec. trav. chim., 70, 564 (1951).
87. H.J. Backer and G.J. DeJong, Rec. trav. chim., 70, 377 (1951).
88. F.E. Bidot, Private Communication.
89. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York, 1953, pg. 658.
90. J. Reid and W.G. Reid, J. Chem. Soc., 745 (1928).
91. C.K. Ingold and E.H. Ingold, J. Chem. Soc., 2354 (1931).
92. A.H. Klopp and F. Wright, J. Org. Chem., 4, 142 (1939).

93. R.C. Elderfield and H.A. Hageman, *J. Org. Chem.*, 14, 626 (1949).
94. T.D. Waugh, "N-Bromosuccinimide, Its Reactions and Uses", Arapahoe Chem., Inc., Boulder, 1951.
95. H.J. Backer, W. Stevens and N. Dost, *Rec. trav. chim.*, 67, 451 (1948).
96. R.C. Krug and T.F. Yen, *J. Org. Chem.*, 21, 1082 (1956).
97. G.F. Bloomfield, *J. Chem. Soc.*, 114 (1944).
98. M.S. Kharasch, M. Freeman and W.H. Urry, *J. Org. Chem.*, 13, 570 (1948).
99. O.O. Orazi, R.A. Corral and J.D. Bonafede, *Anales asoc. quim. argentina*, 43, 98 (1955); *C.A.*, 50, 10071 (1956).
100. O.O. Orazi and M.H. Giunti, *Anales asoc. quim. argentina*, 39, 84 (1951); *C.A.*, 46, 2528 (1952).
101. M.E. Fondovila, O.O. Orazi and J.F. Salellas, *Anales asoc. quim. argentina*, 39, 184 (1951); *C.A.*, 47, 2709 (1953).
102. O.O. Orazi, J.F. Salellas, M.E. Fondovila, R.A. Corral, N.M.I. Mercere, and E.C. Rakunas de Alvarez, *Anales asoc. quim. argentina*, 40, 61 (1952); *C.A.*, 47, 3244 (1953).
103. W.J. Bailey and E.W. Cummins, *J. Am. Chem. Soc.*, 76, 1936 (1954).
104. E.A. Braude and F.C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York, 1955, pg. 202.
105. G. Stark and F.H. Clarke, *J. Am. Chem. Soc.*, 78, 4619 (1956).
106. H.D. Hartough, "Thiophene and Its Derivatives", Interscience Publishers, Inc., New York, 1952, pg. 131.

107. R.B. Wagner and H.D. Zook, "Synthetic Organic Chemistry", John Wiley and Sons, Inc., New York, 1953, pg. 94.
108. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, 1954, pg. 36.
109. W. von E. Doering and A.K. Hoffmann, J. Am. Chem. Soc., 77, 509 (1955).
110. F. Brody and M.T. Bogert, J. Am. Chem. Soc., 65, 1080 (1943).
111. A. Oppenheim, Ann., 140, 204 (1866).
112. F.W. Hoffmann, J. Org. Chem., 15, 430 (1950).
113. A. Comey, Ber., 17, 790 (1884).
114. F.G. Ciapetta, Ind. and Eng. Chem., 37, 1210 (1945).
115. G. Egloff and G. Hulla, Chem. Rev., 37, 323 (1945).
116. P. Cogniant and M. Cogniant, Bull. soc. chim. France, 713 (1952).
117. L. Schmerling, U.S. Pat., 2,399,512 (Universal Oil Products Co.), April 30, 1946; C.A., 40, 4390 (1946).
118. F.S. Prout, J. Org. Chem., 18, 928 (1953).
119. F.S. Prout, R.J. Hartman, E.P.Y. Huang, C.J. Korpics and G.R. Tichelaar, Org. Syn., 35, 6 (1955).
120. W.J. King and F.F. Nord, J. Org. Chem., 14, 405 (1949).
121. C.F.H. Allen, C.J. Kibler, D.M. McLachlin, and C.V. Wilson, Org. Syn., 26, 1 (1946).
122. O. Hinsberg, J. prakt. chem., 85, 337; C.A., 6, 2403 (1912).
123. E.A. Fehnel and M. Carmack, J. Am. Chem. Soc., 71, 231 (1949).

124. F. Arndt and B. Eistert, Ber., 74, 451 (1941).
125. W.J. Zimmerschied and R.C. Arnold, U.S. Pat., 2,585,292 (Standard Oil Company, Chicago), Feb. 12, 1952.
126. N. Green and F.B. LaForge, J. Am. Chem. Soc., 70, 2287 (1948).
127. L. Field, Abstract of Papers, American Chemical Society, March, 1954, pg. 9N.
128. W.E. Truce and K.R. Buser, J. Am. Chem. Soc., 76, 3577 (1954).
129. H.E. Faith, U.S. Pat., 2,656,336 (Allied Laboratories, Inc.), Oct. 20, 1953.
130. W.E. Truce and M.F. Amos, J. Am. Chem. Soc., 73, 3013 (1951).
131. D.A. Shirley and E.A. Lehto, Abstract of Papers, American Chemical Society, September, 1954, pg. 8-0.
132. H. Gilman and D.L. Esmev, J. Am. Chem. Soc., 75, 298 (1953).
133. E. Eigenberger, J. prakt. chem., [2], 131, 289 (1931).
134. W.B. Wartman, Jr., Private Communication, Feb. 12, 1957.

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APPENDIXES

APPENDIX I

Data From the Preparation of 2,5-Dihydrothiophene
1,1-Dioxides (I)

<u>Time</u>	<u>Temperature °C.</u>	<u>Pressure P.S.I.</u>
0 minutes	23	0
20 "	70	0
30 "	85	100
40 "	100	190
60 "	103	300
70 "	105	150
90 "	105	100
2 hours	105	50
3 "	103	25
4 "	103	25
5 "	103	25
6 "	102	20
12 "	103	20

APPENDIX II

Metalation of 2,5-Dihydrothiophene 1,1-Dioxide

RMgX ¹	Alkylating Agent	Mole ² Ratio	Gas ³		Product
			Obs.	Theo.	
EtMgBr	MeI	1:1:1	2.16	3.36	25 g. of oil; decomposed on distillation.
EtMgBr	MeI	1:1.4:1	2.02	3.36	40 g. of dark oil; polymerized on purification.
MeMgI	MeI	1:1:1	4.23	4.48	7 g. of dark oil. Distillation caused charring.
MeMgCl	Me ₂ SO ₄	1:2:4	No gas data		Polymer; S+, halogen-.
MeMgCl	CoCl ₂	1:2:2.7	No gas data		Polymer; S+, halogen-.
MeMgI	MeI	1:1.2:2.5	4.36	4.48	10-15 g. of dark oil which polymerized.
MeMgCl	Benzaldehyde	1:1.2:1.2	4.26	4.48	Polymer & 95% benzaldehyde

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- 1 All reactions are "inverse" Grignards except where an asterisk (*) appears, which is a "direct" Grignard reaction.
 - 2 Ratio of 2,5-Dihydrothiophene 1,1-dioxide to Organo-metallic Complex to Alkylating agent respectively.
 - 3 All gas calculated at S.T.P. and the theoretical gas calculated on the basis of sulfone used, 22.4 l. per mole.

APPENDIX II (cont.)

<u>RM, gX</u>	<u>Alkylating Agent</u>	<u>Mole Ratio</u>	<u>Gas</u>		<u>Product</u>
			<u>Obs.</u>	<u>Theo.</u>	
EtMgBr	Blank	1:1	3.59	4.48	Solid. Polymerized in refrigerator. Also 1% of I.
EtMgBr	Blank	1:2	4.29	4.48	Polymer
EtMgBr	Blank	1:2	4.81 0.60	4.48 4.48	Polymer and 21 g. crude oil, later polymerized.
EtMgBr	Acetaldehyde	1:1:1	7.53	8.96	Oil. Polymerized in refrigerator.
EtMgBr	Acetaldehyde	1:1:1	4.44	4.48	22 g. of liq.; polymerized on distillation.
EtMgBr	CO ₂	1:1:excess	No gas data		Polymer.
EtMgBr	Blank	1:1	No gas data		Polymer.
EtMgBr ¹	Benzaldehyde	1:1:1	8.94	8.96	Polymer.
EtMgBr	Br ₂	1:1:2	4.80	6.72	Oil.
EtMgBr	Br ₂	1:1.2:2.2	5.65	6.72	Oil.
<u>n</u> -BuLi	EtBr	1:3:3	1.20	6.72	40 g. polymer in flask and 14 g. black tar from organic layer.
EtMgBr	CNBr	1:1:1	6.30	6.72	56 g. oil. Vacuum and steam distillations caused polymerization.

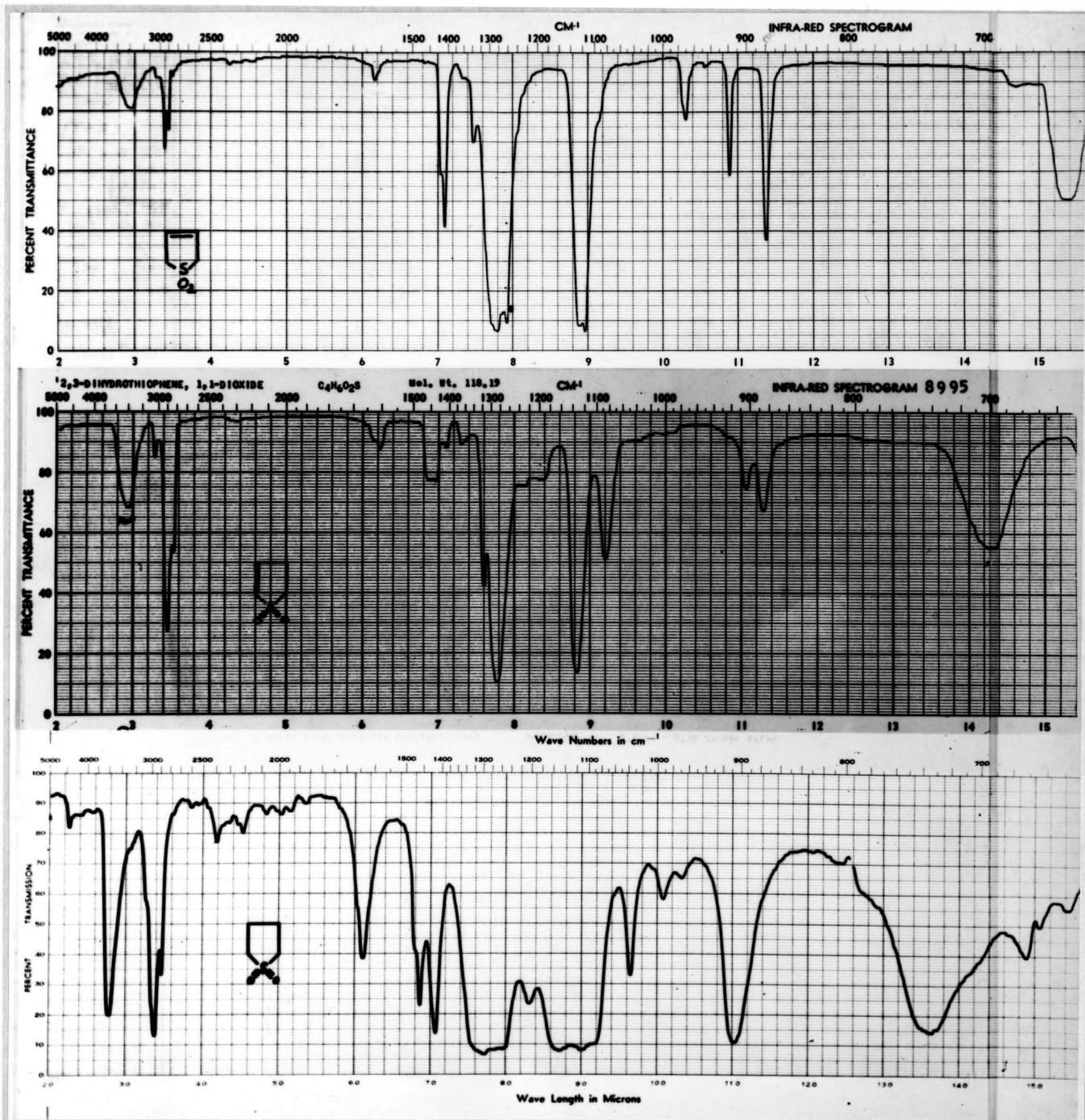
1 Used N-methylmorpholine as solvent in this reaction.

APPENDIX II (cont.)

<u>RM 9X</u>	<u>Alkylating Agent</u>	<u>Mole Ratio</u>	<u>Gas</u>		<u>Product</u>
			<u>Obs.</u>	<u>Theo.</u>	
EtMgBr	MeI	1:1:1.3	5.36	6.72	50 g. oil, which polymerized.
EtMgBr	MeI	1:1:1.3	5.86	6.7	Oil. Treated with maleic anhydride, but polymerized.
MeMgI ¹	MeI	1:1:1	10.4	17.9	11% starting material and polymer.
EtMgBr*	Blank	1:1	1.30	4.48	50% starting material & 8 g. oil, which charred on distillation.
∅-MgBr*	Blank	1:1.1	No gas		30% starting material and 26 g. crude oil which decomposed.
∅-MgBr*	Blank	1:2.2	No gas		91 g. of dark oil.

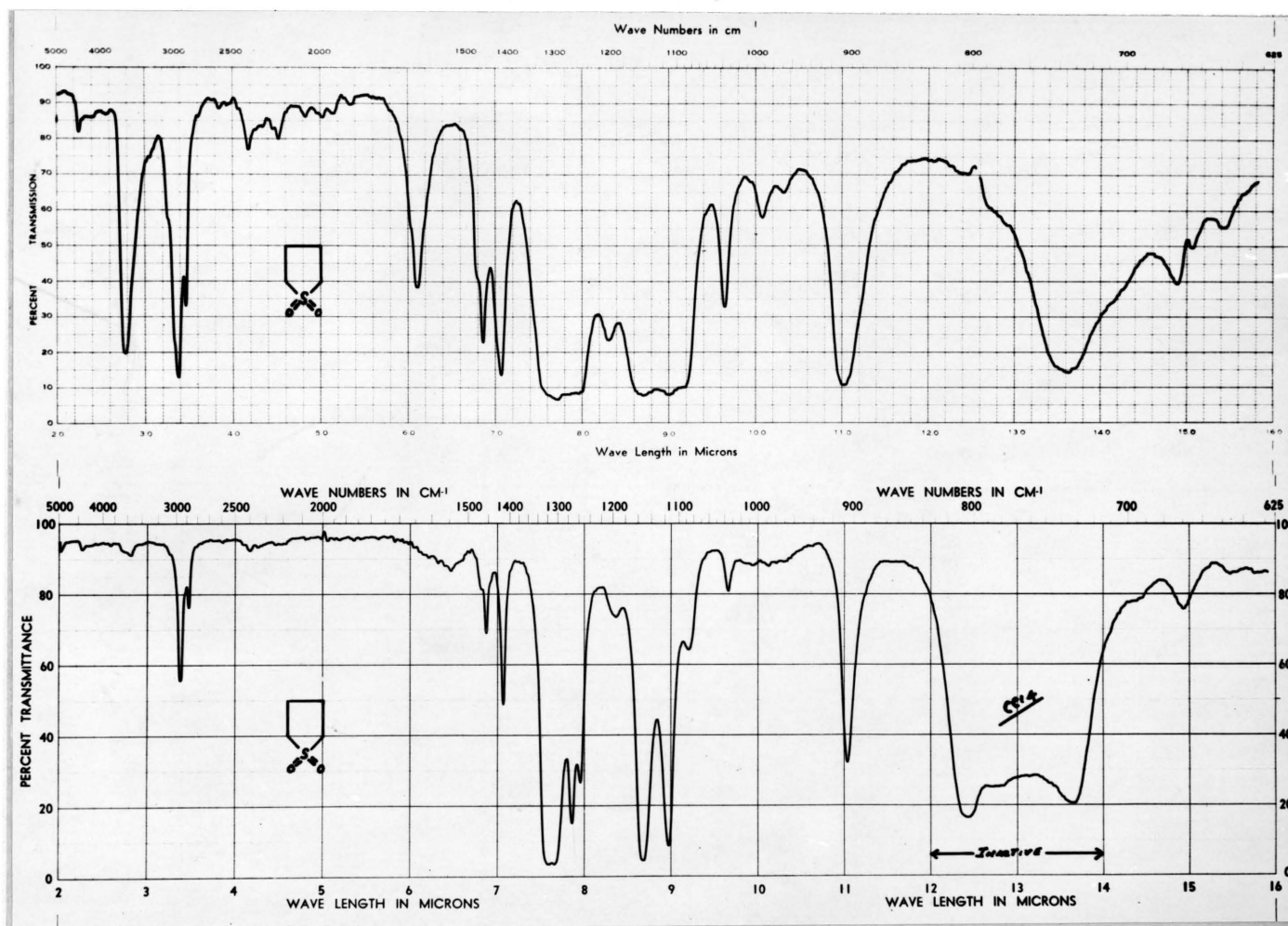
1 This reaction was run at -50° and allowed to come to room temperature slowly.

APPENDIX III



2,5-Dihydrothiophene 1,1-Dioxide (I)
 2,3-Dihydrothiophene 1,1-Dioxide (II)
 Tetrahydrothiophene 1,1-Dioxide (IV)

APPENDIX IV



Tetrahydrothiophene 1,1-Dioxide (No Solvent)
 Tetrahydrothiophene 1,1-Dioxide (CCl₄ Solvent)

The infrared spectra of the tetrahydrothiophene 1,1-dioxide (IV) was obtained from the American Tobacco Company, Richmond, Virginia. A Baird infrared spectrophotometer was used.

ABSTRACT

REACTIONS AND PROPERTIES OF THE
ISOMERIC DIHYDROTHIOPHENE 1,1-DIOXIDES

by

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Thesis submitted to the Faculty of the
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in candidacy for the degree of

DOCTOR OF PHILOSOPHY

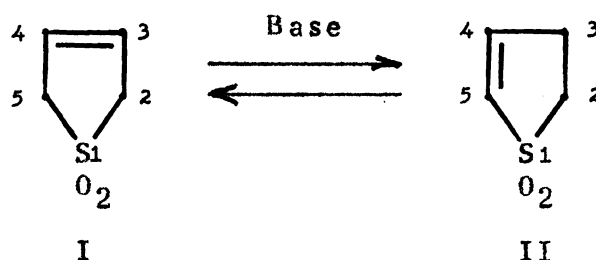
in

Chemistry

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Blacksburg, Virginia

Sulfur dioxide and 1,3-butadiene react to form a five-membered cyclic unsaturated sulfone, the 2,5-dihydrothiophene 1,1-dioxide (I). When treated with a base, I will isomerize to form the 2,3-dihydrothiophene 1,1-dioxide (II). The known procedures for the preparation of I and II have been improved.



The 2,5-dihydrothiophene 1,1-dioxide (I) is the parent member of a large group of five-membered cyclic β -sulfones while the 2,3-dihydrothiophene 1,1-dioxide (II) is the parent member of the corresponding α -sulfones.

Structurally, I contains a carbon-carbon double bond, a sulfone group and two α -methylene groups while II only has one α -methylene group but its carbon-carbon double bond is conjugated with the sulfone group. It is of considerable interest to study the chemical reactions of these two polyfunctional molecules to gain some information concerning the influence of the functional groups upon each other. Of further interest would be to

compare the reactions of I and II since differences in chemical properties are to be expected since the α -sulfones have the double bond conjugated with the sulfone group while the β -sulfones do not.

Bromine adds readily to I in aprotic media to give the 3,4-dibromotetrahydrothiophene 1,1-dioxide (V). The addition of bromine to II only occurs in a water solution to give the 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII). The total lack of evidence of the addition of hydrogen halides to I or II was not expected. The electrophilic attack is hindered by the presence of the sulfone group.

Free radical reactions using N-bromosuccinimide and 1,3-dibromo-5,5-dimethylhydantoin were employed with I and II. The expected allylic substitution of bromine in I at the 2 or 5 position and in II at the 3 position was not obtained but rather addition to the double bond of I and II occurred.

The dehydrobromination reaction of 3,4-dibromotetrahydrothiophene 1,1-dioxide (V) has been improved to give better yields of the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII). A new compound, the 5-bromo-2,3-dihydrothiophene 1,1-dioxide (XVIIc), has been obtained from the dehydrobromination of the 2,3-dibromotetrahydrothiophene 1,1-dioxide (VII).

The 3-bromo, 3-chloro and the 3-iodo-2,3-dihydrothiophene 1,1-dioxides were prepared through a series of reactions, the latter two for the first time. The 3-iodo-2,3-dihydrothiophene 1,1-dioxide (XIX) was prepared by treating the 3-bromo-2,3-dihydrothiophene 1,1-dioxide (XIII) with sodium iodide in acetone. The 3-chloro-2,3-dihydrothiophene 1,1-dioxide (XX) in turn was prepared by reacting the 3-iodo-2,3-dihydrothiophene 1,1-dioxide (XIX) with mercuric chloride in absolute ethanol. The infrared spectra of the above compounds were compared.

Since the alpha hydrogens are acidic in the cyclic unsaturated sulfones, a thorough study of Grignard reagents with the 2,5-dihydrothiophene 1,1-dioxide (I) was made. A compound, believed to be a sulfinic anhydride, was obtained from the action of the 2,5-dihydrothiophene 1,1-dioxide (I) on ethylmagnesium bromide. Some evidence in support of this sulfinic anhydride is offered. A mechanism for the Grignard reactions is proposed from the data obtained.

There was no evidence for condensation, alkylation or acylation reactions with the isomeric dihydrothiophene 1,1-dioxides.

On the basis of the reactions studied, a clearer picture of the resonance structure of the 2,5-dihydrothiophene 1,1-dioxide (I) is obtained.