The Chemistry Of Some Derivatives Of 2,5-diphenyl-1,4-dithiin. Part A. Kinetics Of Methylation Of Substituted Anilines And Thioanisoles In Acetonitrile By 1-methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborates. Part B. Preparation And Reactions Of Some Dithiin Ring Substituted 1-methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborates. Part C. Methylation Of 2,5-diphenyl-1,4-dithiin-1-oxide.

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THE CHEMISTRY OF SOME DERIVATIVES OF 2,5-DIPHENYL-1,4-DITHIIN

Part A: Kinetics of Methylation of Substituted Anilines and Thioanisoles in Acetonitrile by 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborates

Part B: Preparation and Reactions of Some Dithiin Ring Substituted 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborates

Part C: Methylation of 2,5-Diphenyl-1,4-dithiin-1-oxide

by
Alan R. Oyler

A Dissertation

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

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1973

CERTIFICATE OF PRESENTATION

This dissertation is respectfully submitted to the Graduate Faculty of Lehigh University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Alan R. Oyler

Alan R. Oyler

A CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 20, 1973
Date

Thomas E. Young
Professor in Charge

Special committee directing work of Mr. Alan R. Oyler:

Thomas E. Young
Dr. Thomas E. Young, Chairman

Ned D. Heindel
Dr. Ned D. Heindel

Charles S. Kraihanzel
Dr. Charles S. Kraihanzel

Joseph R. Merkel
Dr. Joseph R. Merkel

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ABSTRACT

The kinetics of methylation of various substituted anilines and thioanisoles by 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate were studied in acetonitrile at several temperatures covering the range from 30° to 70°C. Thermodynamic activation parameters were calculated and the relative reactivities of the two series of nucleophiles compared. At 56.8° aniline was methylated 16 times faster than thioanisole. Application of the Hammett Equation to the data for 56.8° gave rho values of -1.92 ± 0.16 and -1.58 ± 0.16 for the aniline and thioanisole series, respectively.

The methylation and reactions of some bromo and nitro dithiin-ring substituted derivatives of 2,5-diphenyl-1,4-dithiin were studied. 3-Bromo-2,5-diphenyl-1,4-dithiin reacted with methyl iodide-silver tetrafluoroborate to yield 1-methyl-3-bromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate, which was expected to have a potentially labile bromine. However, attempts to effect nucleophilic displacement of the bromine in this salt by diethylamine resulted exclusively in demethylation to the parent bromo-dithiin.

Methylation of 3-nitro-2,5-diphenyl-1,4-dithiin with methyl iodide-silver tetrafluoroborate gave 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate and a compound tentatively characterized as 3-dimethylsulfonium-2,4-diphenyl-5-nitrothiophene tetrafluoroborate. This latter compound was demethylated by triethylamine to produce the corresponding 2,4-diphenyl-3-methylthio-5-nitrothiophene, while the former compound ring-opened to produce

1-phenyl-ethynylthio-2-methylthio-2-nitro-1-phenylethylene. Methylation of this ring-cleavage product gave 1-phenylethynylthio-2-dimethylsulfonium-2-nitro-1-phenylethylene tetrafluoroborate.

Although 3,6-dibromo-2,5-diphenyl-1,4-dithiin could be methylated with methyl iodide-silver tetrafluoroborate, the product, 1-methyl-3,6-dibromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate was obtained in very low yield, while 3-bromo-6-nitro-2,5-diphenyl-1,4-dithiin and 3,6-dinitro-2,5-diphenyl-1,4-dithiin could not be methylated at all with this reagent. The latter two dithiins both yielded an identical compound on thermal decomposition, a process previously reported by Parham who offered no structural assignment for the product. The data provided in the present work show that this product has the composition, $C_{32}H_{20}S_4N_2O_4$, and its structure is tentatively assigned as <u>bis</u>(2,4-diphenyl-5-nitro-3-thienyl)-disulfide.

2,5-Diphenyl-1,4-dithiin-1-oxide reacted with methyl iodide-silver tetrafluoroborate to yield 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate, whose structure was characterized by its infrared and nmr spectra and by its quantitative demethylation to the parent S-oxide with aqueous sodium carbonate solution. The S-methoxy compound, 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate, also underwent thermal decomposition <u>via</u> a novel ring-contraction to yield 2,4-diphenyl-1,3-dithiolium tetrafluoroborate and methyl formate, along with other unidentified products. Authentic 2,4-diphenyl-1,3-dithiolium tetrafluoroborate was also prepared for comparison by an unambiguous route.

IDENTIFICATION OF SYMBOLS AND ABBREVIATIONS

SAM ≡ S-adenosylmethionine
SMM ≡ S-methylmethionine
DPT ≡ dimethyl-β-propiothetin
N^5-FH_4 ≡ N^5-methyltetrahydofolic acid
Met ≡ methionine
k ≡ rate constant
E_{act} ≡ activation energy
R ≡ gas constant
A' ≡ constant
$\Delta H^{\ddagger}$ ≡ enthalpy of activation
$\Delta S^{\ddagger}$ ≡ entropy of activation
$\Delta G^{\ddagger}$ ≡ free energy of activation
T ≡ absolute temperature
$\bar{k}$ ≡ Boltzmann constant
h ≡ Planck constant
range ≡ highest value minus lowest value of a series of repeated determinations

k^{i}_{obs} ≡ mean value of second order rate constants observed at temperature i for a given reaction

k^{i}_{calc} ≡ second order rate constant at temperature i for a given reaction calculated by Arrhenius equation

n ≡ number of temperatures (and rate constants) observed for a given reaction

ρ ≡ Hammett reaction constant

σ_p ≡ Hammett constant for para substituent

σ_m ≡ Hammett constant for meta substituent

G_o ≡ constant dependent only upon the standard chosen reaction

S ≡ concentration of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate

D ≡ concentration of 2,5-diphenyl-1,4-dithiin

N ≡ nucleophile concentration

A ≡ absorbance

ε_S ≡ molar extinction coefficient of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate

ε_D ≡ molar extinction coefficient of 2,5-diphenyl-1,4-dithiin

t ≡ time

PART A

Kinetics of Methylation of Substituted Anilines and Thioanisoles in Acetonitrile by 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate

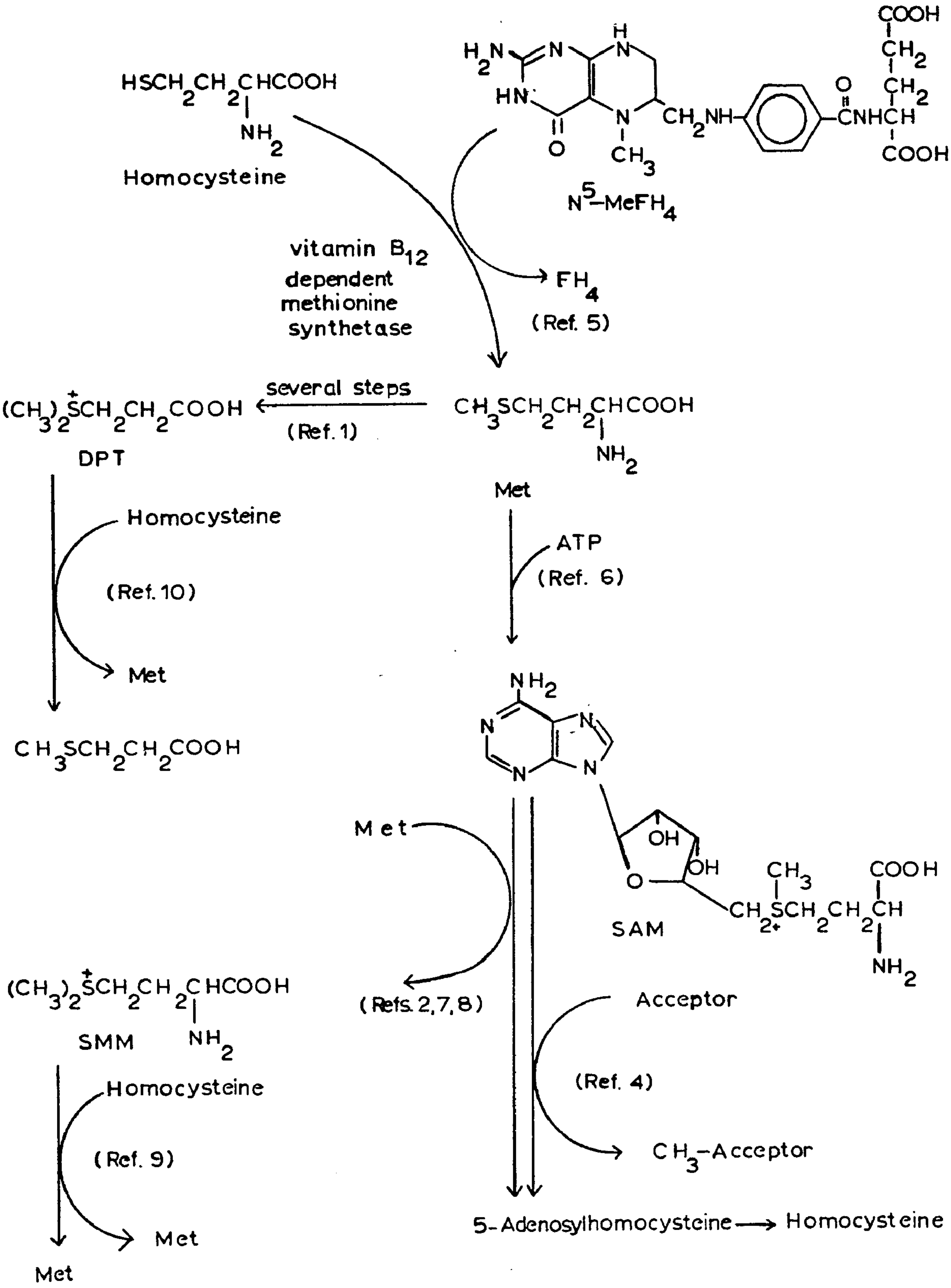
INTRODUCTION

Since there appears to be no direct comparison of substituent effects on the rate of methylation of aromatic amines and sulfides reported in the literature, it was decided to undertake such a study. A sulfonium salt was chosen for this work because agents such as methyl iodide and dimethyl sulfate have been studied extensively. Furthermore, analogies might be made to biological systems in which sulfonium salts play the major role in transmethylations.

At present, there appear to be only three biologically occurring sulfonium salts: S-adenosylmethionine (SAM), S-methylmethionine (SMM), and dimethyl-β-propiothetin (DPT). In contrast to SAM which is of universal importance as a methyl group donor in nearly all biological transmethylation reactions, SMM and DPT are found in a restricted number of organisms, and like betaine, donate their methyl groups only to homocysteine.[1,2,3,4] The methyl group transferred from each of these four methyl group donors was originally derived from N^5-methyltetrahydrofolic acid (N^5-FH_4) via methionine (Met).[4] These biological reactions, some of which will be discussed in more detail, are outlined in Scheme I.

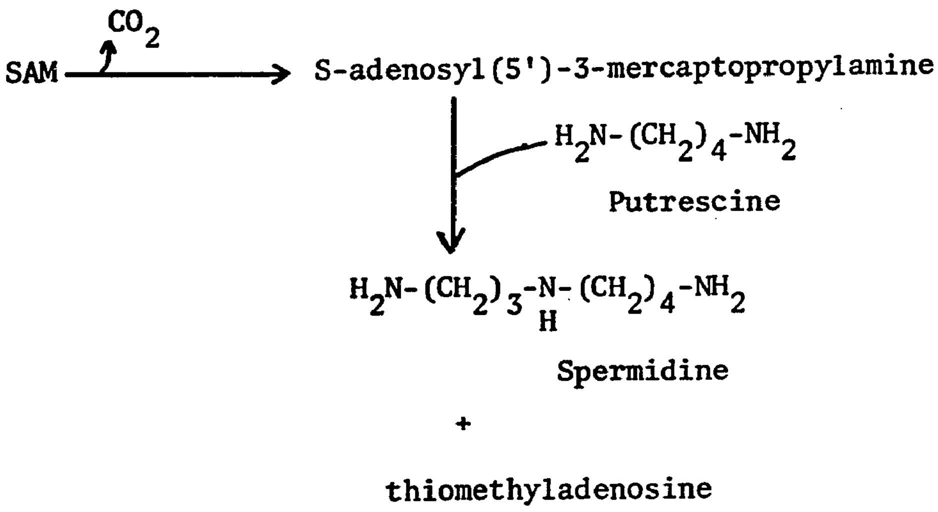
Biological transmethylations do not appear to involve enzyme-bound methyl intermediates[3] except for the special case of methylation of homocysteine by N^5-FH_4.[11] The carboxyl and amino groups of SAM are involved in binding to methyl-transferases, but the sulfonium group itself does not appear to be a major factor

Scheme I


HSCH2CH2CHCOOH
NH2
Homocysteine
N5-MeFH4
vitamin B12 dependent methionine synthetase
FH4
(Ref. 5)
(CH3)2S+CH2CH2COOH
DPT
several steps
(Ref. 1)
CH3SCH2CH2CHCOOH
NH2
Met
Homocysteine
(Ref. 10)
Met
CH3SCH2CH2COOH
ATP
(Ref. 6)
SAM
Met
(Refs. 2,7,8)
(CH3)2S+CH2CH2CHCOOH
SMM
NH2
Homocysteine
(Ref. 9)
Met
Met
Acceptor
(Ref. 4)
CH3-Acceptor
5-Adenosylhomocysteine
Homocysteine

in attachment of SAM to these enzymes.[12] A transalkylation of SAM involving a transfer of a propylamino group, rather than a methyl group, to putrescine is shown in scheme II.[13,14] Williams-Ashman et al.[14] have suggested that the decarboxylated SAM may not be a free intermediate.

SCHEME II



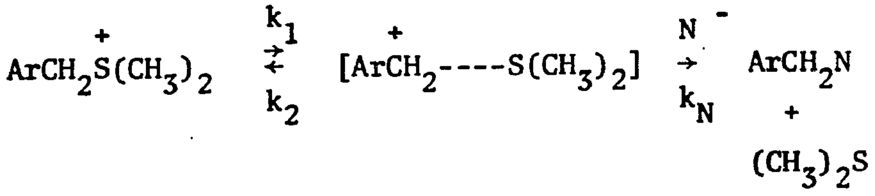
Some of the substrates that are methylated by SAM include pyridines, guanidines, amines, imidazoles, purines, sulfides (Met only), thiols, and phenols.[3] Although aniline is not a natural substrate for SAM, a methyltransferase has been isolated from rabbit lung which does catalyze the methylation of this and other foreign molecules.[15]

Dimethyl-β-propiothetin has only been found in certain marine algae.[1] Greene,[7] using labeled methionine, found that the methyl groups and sulfur of DPT are derived from the methyl group and sulfur of methionine and that the carboxyl group of DPT arises from the α-carbon of methionine. He therefore concluded that methionine is probably converted to DPT by deamination, decarboxylation, oxidation, and methylation (order not known). There was no incorporation of radioactivity from labeled SMM into DPT, but since the experiments were performed on intact organisms, methylation by SMM is not conclusively ruled out. Recently Ishida and Kadota[10] showed that a certain unicellular alga grown in $^{35}SO_4^{--}$ accumulates a large portion of the ^{35}S in DPT. A thetin-homocysteine methyltransferase was isolated from this alga.

S-methylmethionine has been found in plants and yeast.[2] Its biological synthesis, involving SAM and methionine,[2,7,8] represents the only known methylation of a sulfide by SAM. Karr et al.[8] isolated SAM:Met methyltransferase from wheat germ and found it to require Zn^{++} or Mn^{++}. Other methyltransferases are known which require divalent cations,[16] but such a requirement does not appear to be a general property of this group of enzymes.[3] A S-methylmethionine:homocysteine methyltransferase has been isolated from jack bean meal by Abrahamson and Shapiro.[9]

Sulfonium salts have a pyramidal structure[17] with a C-S-C bond angle of 103° in trimethylsulfonium iodide[18]. Like sulfoxides[19] and sulfonium ylides,[20] they are capable of exhibiting optical activity. However, sulfoxides[19] undergo pyrimidal inversion to form racemic mixtures, usually at high temperature, while sulfonium salts[21-25] and sulfonium ylides[20] invert much more readily at lower temperatures. Nucleophilic substitution reactions on methylsulfonium salts may show S_N2-type behavior,[26,27] with nearly quantitative inversion demonstrated for the reaction of optically active dimethyl-1-phenylethylsulfonium iodide with azide.[28] Coward and Sweet[27] found that phenyldimethylsulfonium perchlorates behaved much like methyl iodide upon attack by a wide variety of nucleophiles. Alternatively, nucleophilic decomposition of sulfonium salts, especially those containing groups such as t-butyl[29] or benzyl,[30] may be described by an "ion pair" mechanism as proposed by Sneen[30] (Scheme III) for the decomposition of p-methoxybenzyl- and benzyldimethylsulfonium nitrate in water in the presence of added nucleophile. (For the case where $k_N >> k_2$ and k_1 becomes rate determining, this model corresponds to the traditional S_N1 mechanism.)[31] Darewish,[23] likewise, invoked this model to explain the

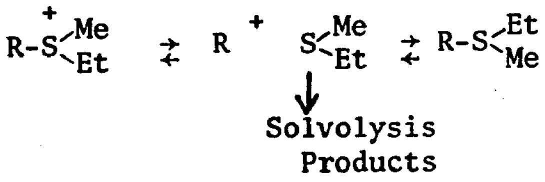
SCHEME III



$$ArCH_2\overset{+}{S}(CH_3)_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\overset{+}{ArCH_2}----S(CH_3)_2] \xrightarrow[k_N]{N^-} ArCH_2N + (CH_3)_2S$$

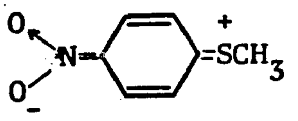
unusually fast rate of solvolysis and racemization of p-methoxybenzylethylmethylsulfonium perchlorate (Scheme IV).

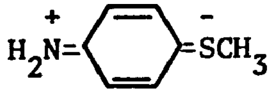
SCHEME IV



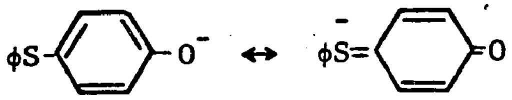
$$R-\overset{+}{S}{<}^{Me}_{Et} \rightleftarrows \underset{\substack{\downarrow \\ \text{Solvolysis} \\ \text{Products}}}{R^{+} \;\; S{<}^{Me}_{Et}} \rightleftarrows R-S{<}^{Et}_{Me}$$

X-ray data on p-tolylsulfide and p-bromophenylsulfide show the C-S bond distance to be 1.75 Å, which is approximately midway between 1.82 Å for a C-S single bond and 1.61 Å for a C-S double bond.[32] Orbital overlap between sulfur and a phenyl ring involves donor 2p and acceptor 3d orbitals.[33] For example, dipole moment measurements on compounds such as p-nitrophenyl- and p-aminophenylthioanisole are consistent with resonance structures, such as those shown below, making significant contributions to the ground state.[34] Hyne and Greidanus[35] in a recent review





concluded that transmission of electronic effects in diarylsulfides by an extended π-electron system could be of sufficient magnitude to influence the physical and chemical properties in some of these molecules. The increased acidity of p-phenylmercaptophenol over its m-isomer is considered to be due to 3d-orbital resonance



interaction.[36]

Romm, et al.[37] measured the pπ-conjugation of aromatic amines, ethers, and sulfides by a method of complexation. These workers demonstrated by uv spectroscopy that the interaction of these molecules with strong electron acceptors, such as aluminum bromide, resulted in breaking up of pπ-conjugation between the heteroatom and the aromatic ring. They therefore reasoned that the pπ-conjugation energy, E_c, was equal to the difference between

ΔH for the formation of the complex with the aromatic compound and the mean ΔH for the same complexation with aliphatic counterparts. The results, which are presented in Table I, indicate that pπ-conjugation energy in aromatic sulfides is probably not a great deal less than in the corresponding amines and ethers.

TABLE I[37]

E_c (Kcal/mol)
25° C

	Acceptor[a]		
Donor	$AlBr_3$	$AlCl_3$	$GaCl_3$
Anisole	7.8	7.3	6.5
Thioanisole	4.4	5.3	6.2
N,N-Dimethylaniline	8.1	7.6	9.0
Diphenyl ether	11.3	11.2	10.9
Diphenylsulfide	7.3	8.5	7.8
N-methyldiphenylamine	14.9	14.8	17.0

[a] The authors considered the $AlBr_3$ data to be the most reliable.

Pearson, et al.[38], have tabulated a large number of nucleophilic reactivity constants toward methyl iodide in methanol at 25°C. The portion of their data that is relevant here is presented in Table II. Comparison of structurally equivalent sulfides and amines in Table II shows that the amines react roughly 40-80 times faster than the corresponding sulfide at 25°C.

TABLE II[38]

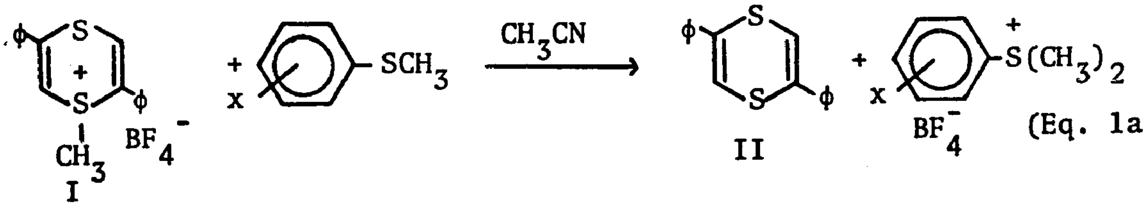
$$Y + CH_3I \xrightarrow{k_2} \overset{+}{Y}CH_3 + I^-$$

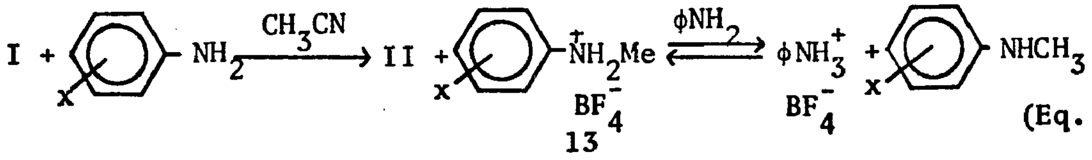
Y	$10^4 k_2$ l/mol-sec	n_{CH_3I}[a]
CH_3OH	0.0000013	0.00
C_6H_5SH	0.64	5.70
Et_2NH	12	7.0
$(CH_2)_5S$	0.342	5.42
Piperidine	26	7.30
$(CH_2)_4S$	0.587	5.66
Pyrrolidine	22	7.23
$C_6H_5NH_2$	0.52	5.70
$C_6H_5NMe_2$	0.562	5.64
Me_2S	0.452	5.54
$(C_6H_5CH_2)_2S$	0.09	4.84

[a] $n_{CH_3I} = \log(k_{2Y}/k_{2CH_3OH})$

RESULTS

The kinetic studies of reactions of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) with thioanisoles and anilines (equation 1a,b) were carried out under pseudo-first order conditions


(Eq. 1a)


(Eq. 1b)

with the nucleophile present in vast excess. A preparative scale reaction of the dithinium salt I with aniline in 16.5 fold excess showed the products to be 2,5-diphenyl-1,4-dithiin (II) and N-methylaniline.* Reaction of I with thioanisole likewise yielded II and dimethylphenylsulfonium tetrafluoroborate.* The absence of any dependence of the second order rate constant on the nucleophile concentration is illustrated by Table III.

TABLE III

Reaction of I with Thioanisole[a]

[I]	24.19×10^{-5}	38.19×10^{-5}	34.68×10^{-5}
$[C_6H_5SMe]$	1.0138	0.8685	0.5018
10^4k_2 l/mol-sec[b]	2.32±0.03	2.43±0.02	2.39±0.04

[a] Temperature, 65.3±0.3°

[b] Average of two runs

The rate data for equation 1 for various nucleophiles at different temperatures is presented in Table IV and the corresponding Arrhenius plots are shown in Figures 1-12. The activation parameters, Arrhenius equation variables, and rate constants at 330°K calculated from the Arrhenius plots are found in Table V. Hammett plots[39] (Figure 13) gave ρ values of -1.92 ± 0.16 (correlation coefficient 0.998) and -1.58 ± 0.16 (correlation coefficient 0.999) for the aniline and thioanisole series respectively.**

---

* See experimental section for details.

** Hammett equation: $\log_{10}k^X = \rho\sigma + \log_{10}k^H$ where ρ is a constant for the particular reaction, σ is the constant for each meta and para substituent, k^X is the rate constant for the reaction involving the substituted reactant, and k^H is the rate constant for the reaction involving the unsubstituted reactant.

TABLE IV

Effect of Temperature on the Rate of Methylation of Nucleophiles by I

Temp, ± 0.3°C	10^4k_2,l/mol-sec[a]
Aniline	
37.1	2.85 ± 0.06
44.8	5.62 ± 0.11
54.0	13.0 ± 0.3
62.2	26.5 ± 0.5
m-Chloroaniline	
41.1	0.855 ± 0.017
48.9	1.85 ± 0.13
56.7	3.73 ± 0.21
63.4	7.04 ± 0.13
p-Toluidine	
31.5	3.85 ± 0.02
40.3	9.37 ± 0.02
49.3	22.9 ± 0.5
56.9	43.3 ± 0.6
p-Anisidine	
39.0	12.7 ± 0.5
44.7	22.5 ± 0.4
47.9	28.2 ± 1.1
56.9	56.3 ± 0.9
59.5	72.0 ± 0.9
α,α,α-Trifluoro-m-Toluidine	
43.8	0.693 ± 0.023
49.8	1.14 ± 0.04
56.7	2.21 ± 0.05
63.4	4.02 ± 0.05
65.3	4.71 ± 0.05
m-Toluidine	
37.4	3.81 ± 0.04
44.8	8.01 ± 0.13
51.4	15.3 ± 0.5
59.2	30.4 ± 0.5
N-Methylaniline	
40.2	6.70 ± 0.13
48.6	15.8 ± 0.6
53.7	23.0 ± 0.7
59.0	39.1 ± 3.1

	N,N-Dimethylaniline	
36.8		4.63 ± 0.17
40.0		6.03 ± 0.04
48.6		14.5 ± 0.2
56.6		26.0 ± 0.02
	Thioanisole	
50.0		0.535 ± 0.014
54.6		0.890 ± 0.060
59.6		1.38 ± 0.04
65.3		2.40 ± 0.05
	p-Methylthioanisole	
48.7		0.964 ± 0.023
54.6		1.72 ± 0.04
60.5		3.07 ± 0.03
67.0		5.45 ± 0.09
	p-Chlorothioanisole	
54.5		0.389 ± 0.009
59.6		0.638 ± 0.010
64.3		0.976 ± 0.019
69.9		1.67 ± 0.02
	p-Methoxythioanisole	
49.3		1.28 ± 0.01
54.8		2.46 ± 0.05
60.1		4.00 ± 0.03
67.0		7.44 ± 0.22

[a] Error = ± range/2

Figure 1

Arrhenius Plot: Aniline

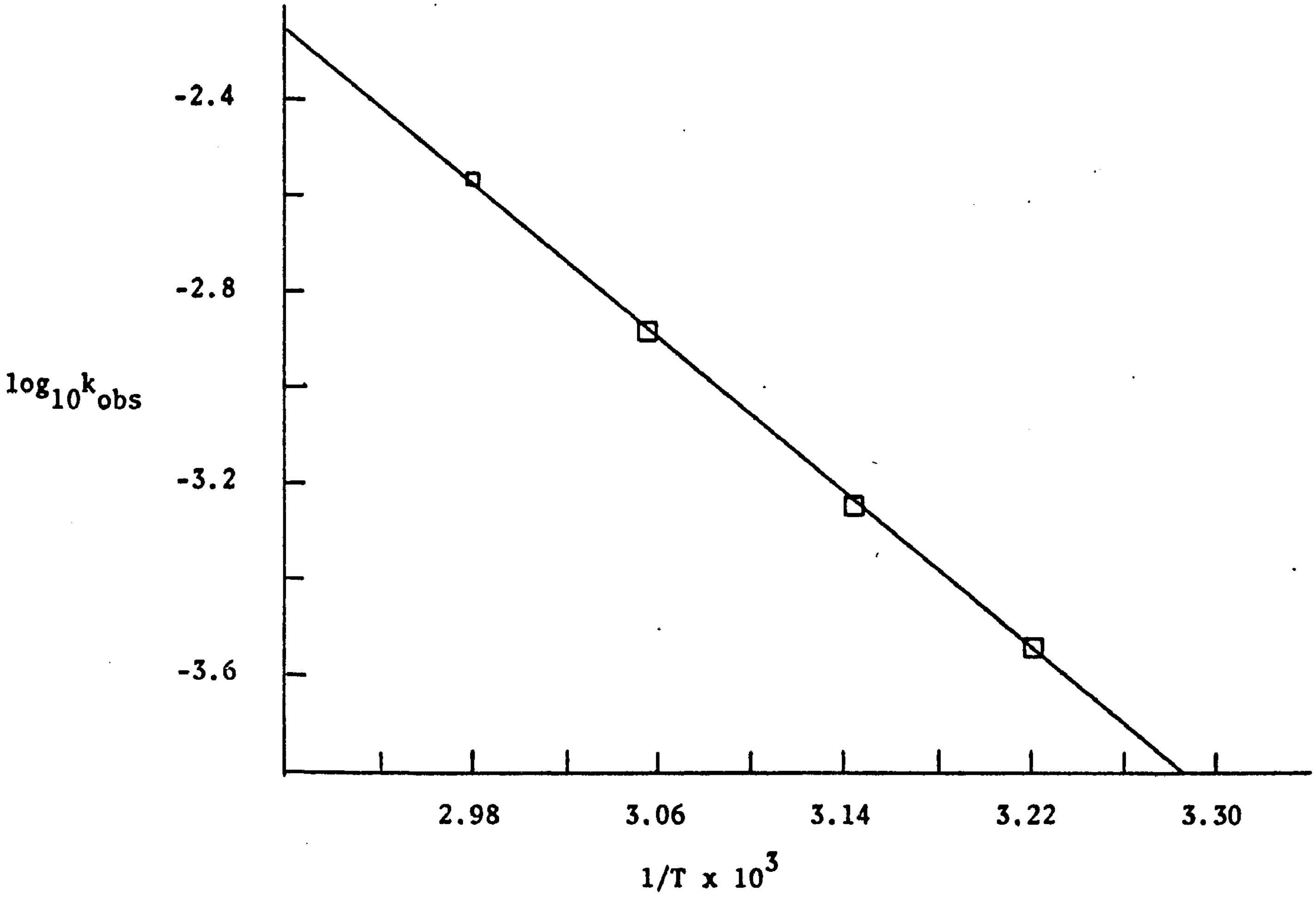


Figure 2

Arrhenius Plot: m-Chloroaniline

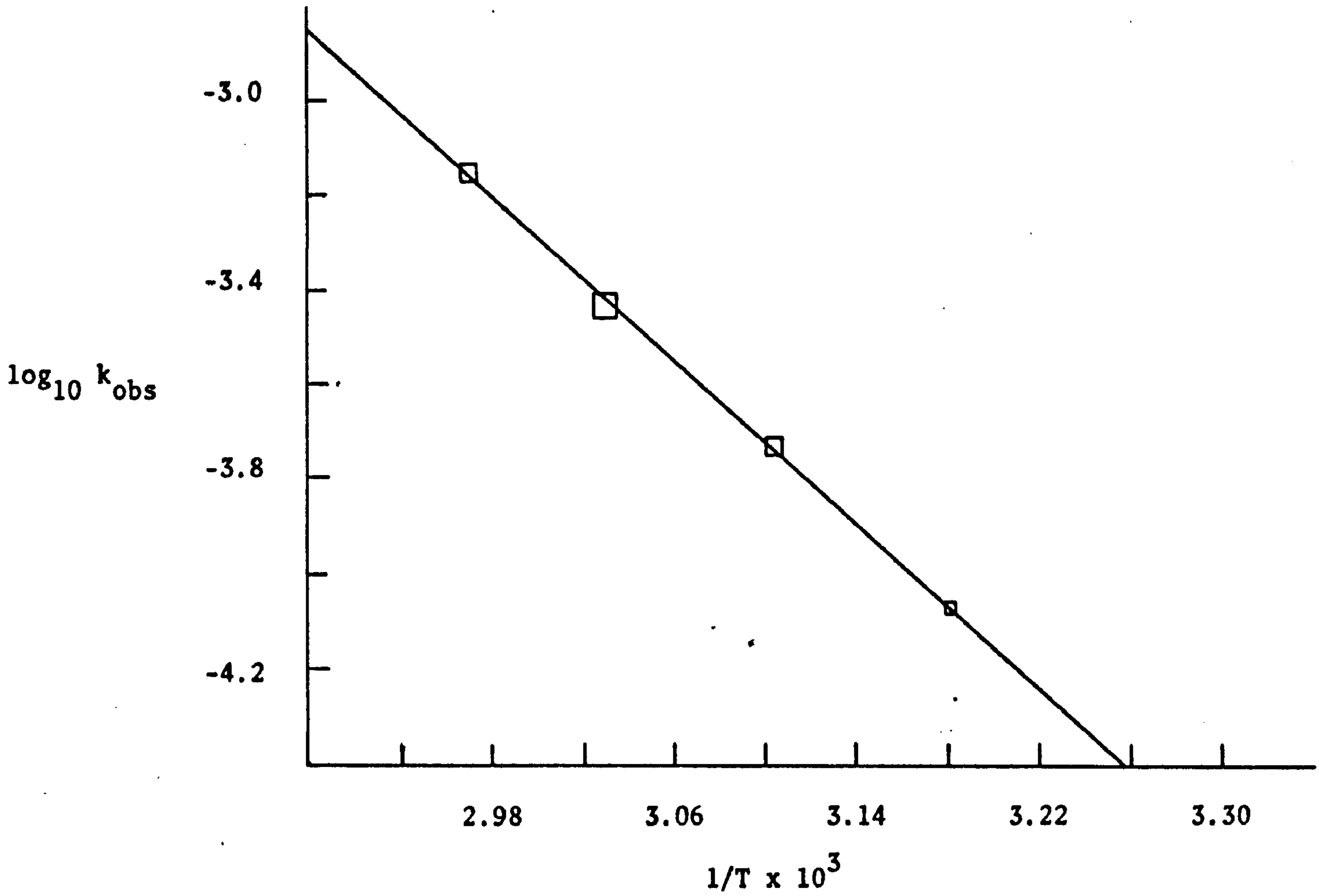


Figure 3

Arrhenius Plot: p-Toluidine

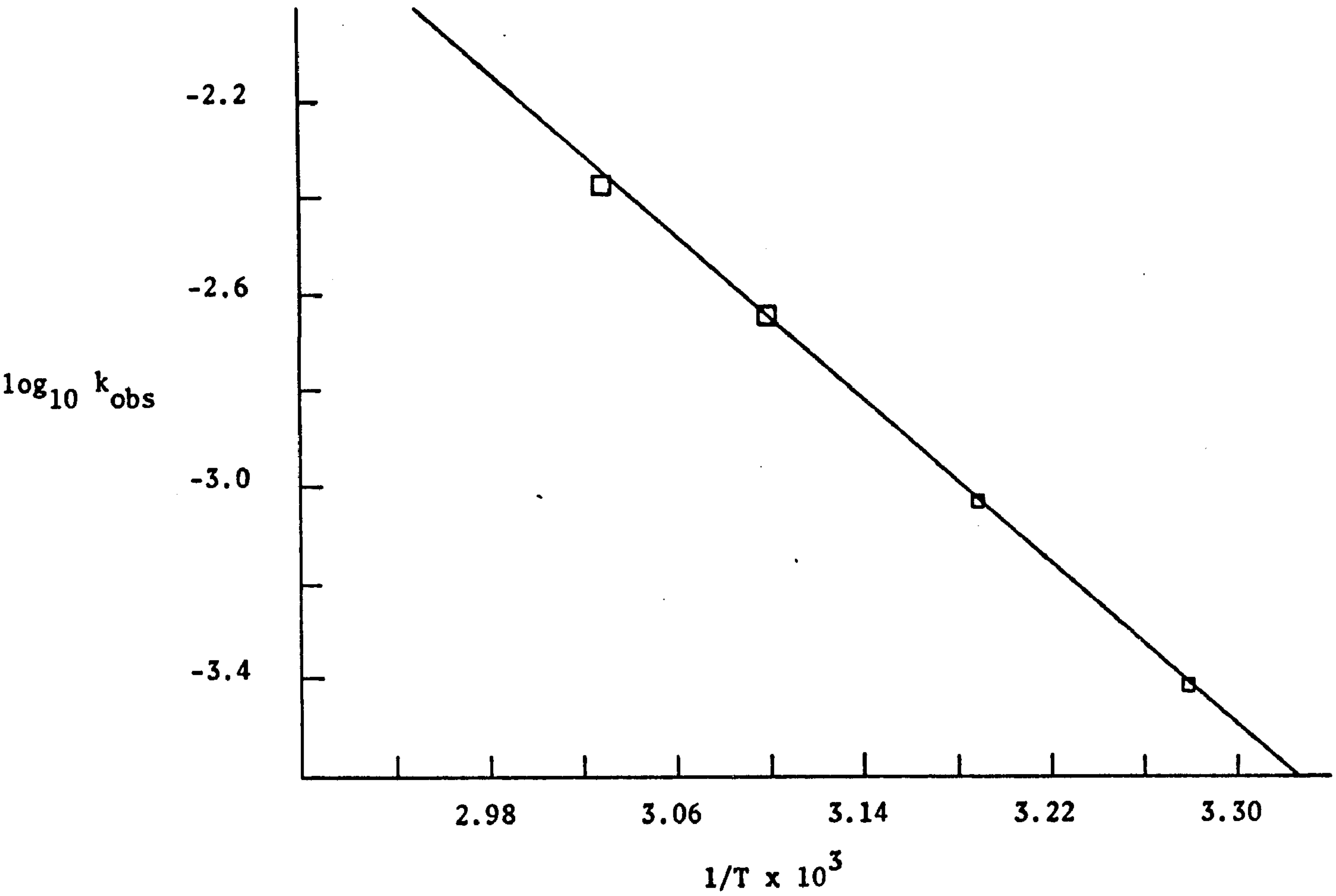


Figure 4

Arrhenius Plot: p-Anisidine

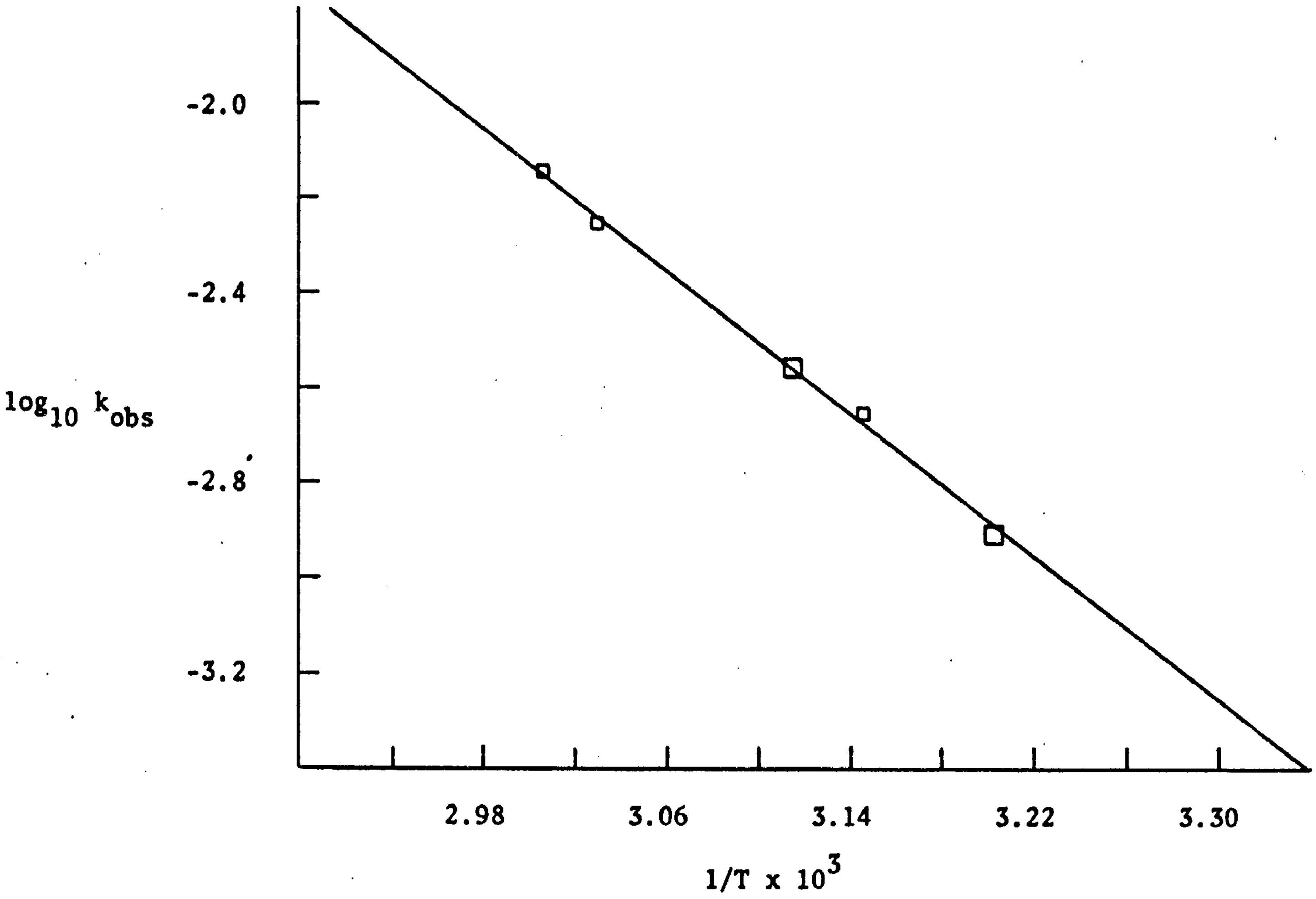


Figure 5

Arrhenius Plot: α,α, α-Trifluoro-m-toluidine

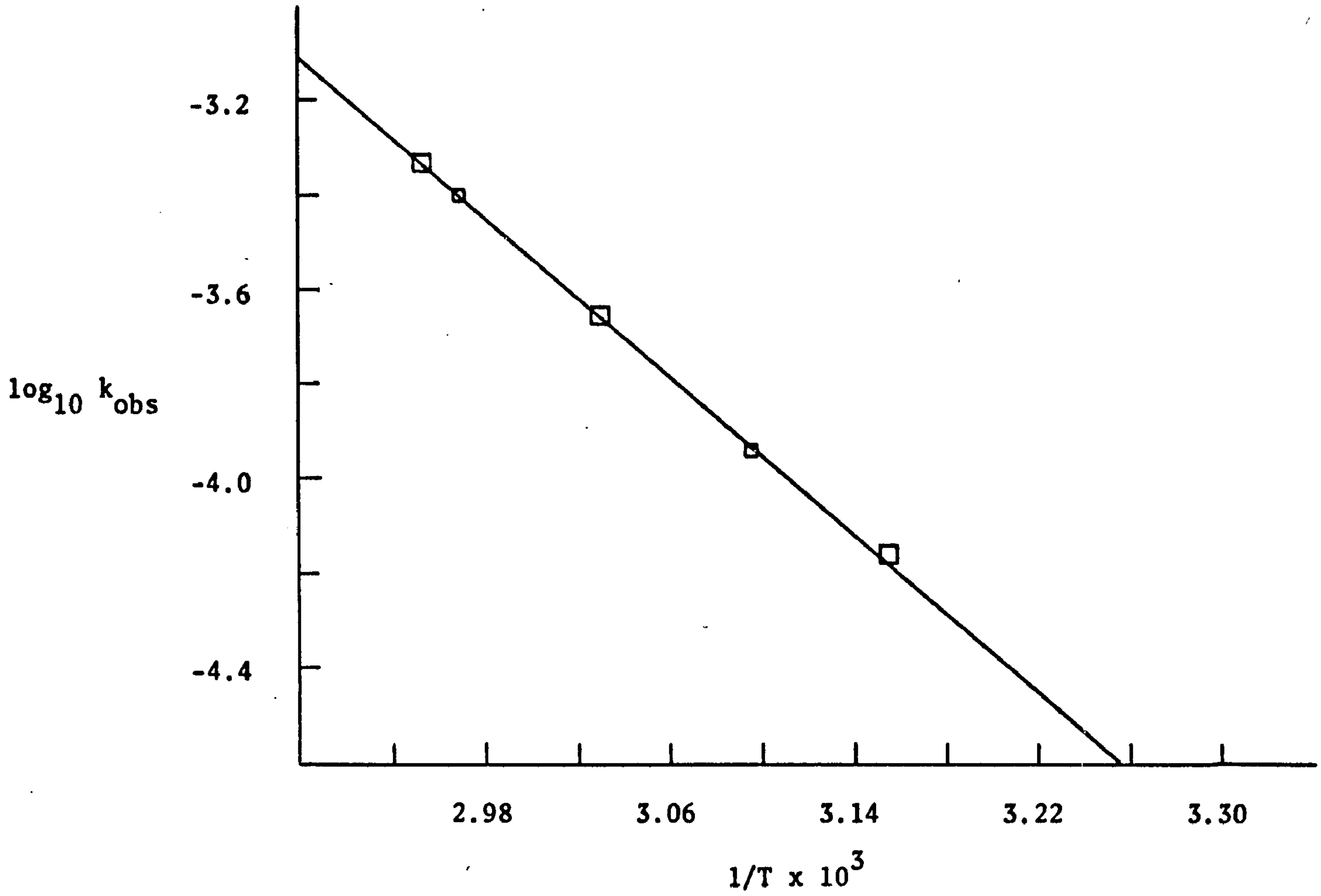


Figure 6

Arrhenius Plot: m-Toluidine

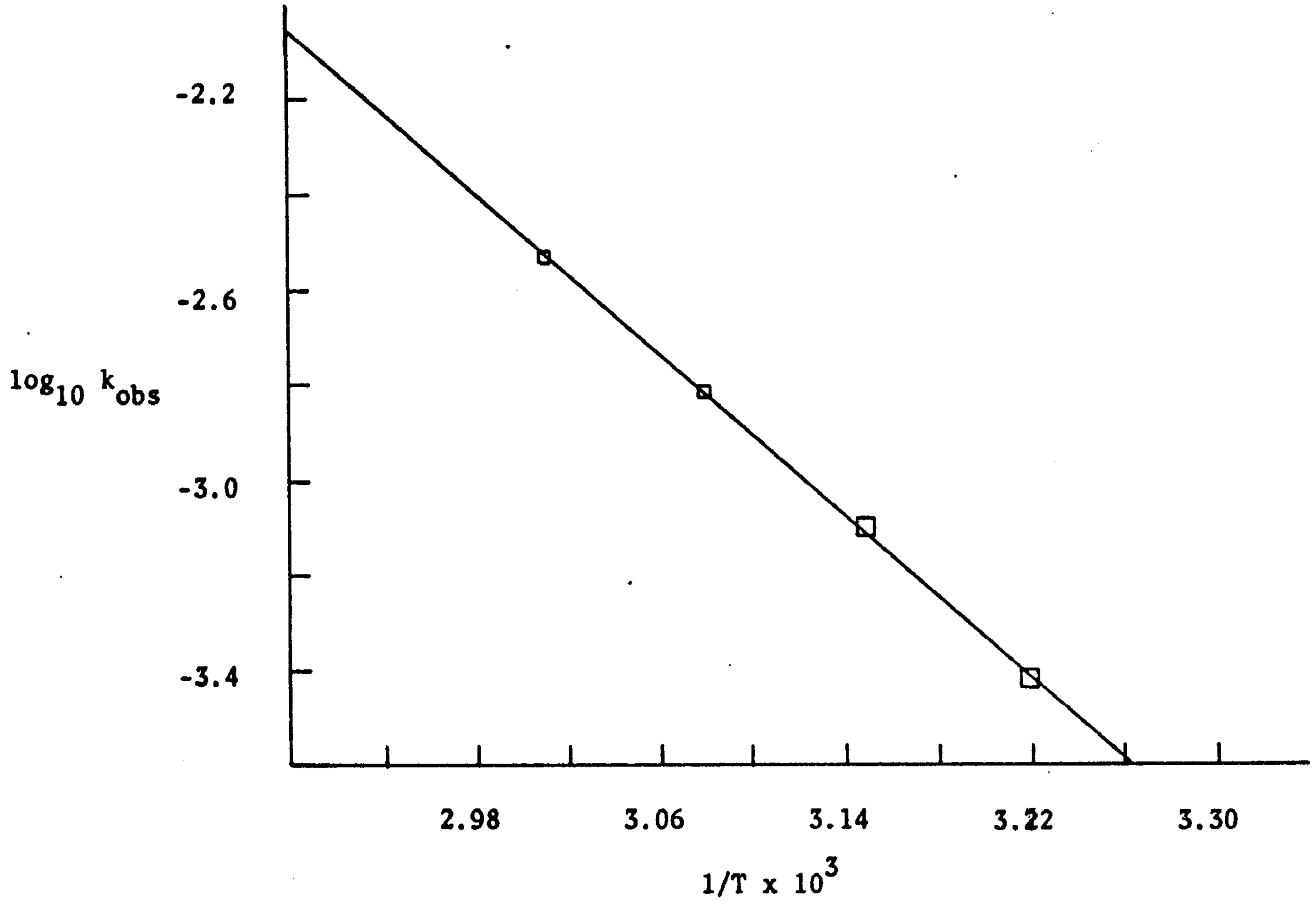


Figure 7

Arrhenius Plot: N-Methylaniline

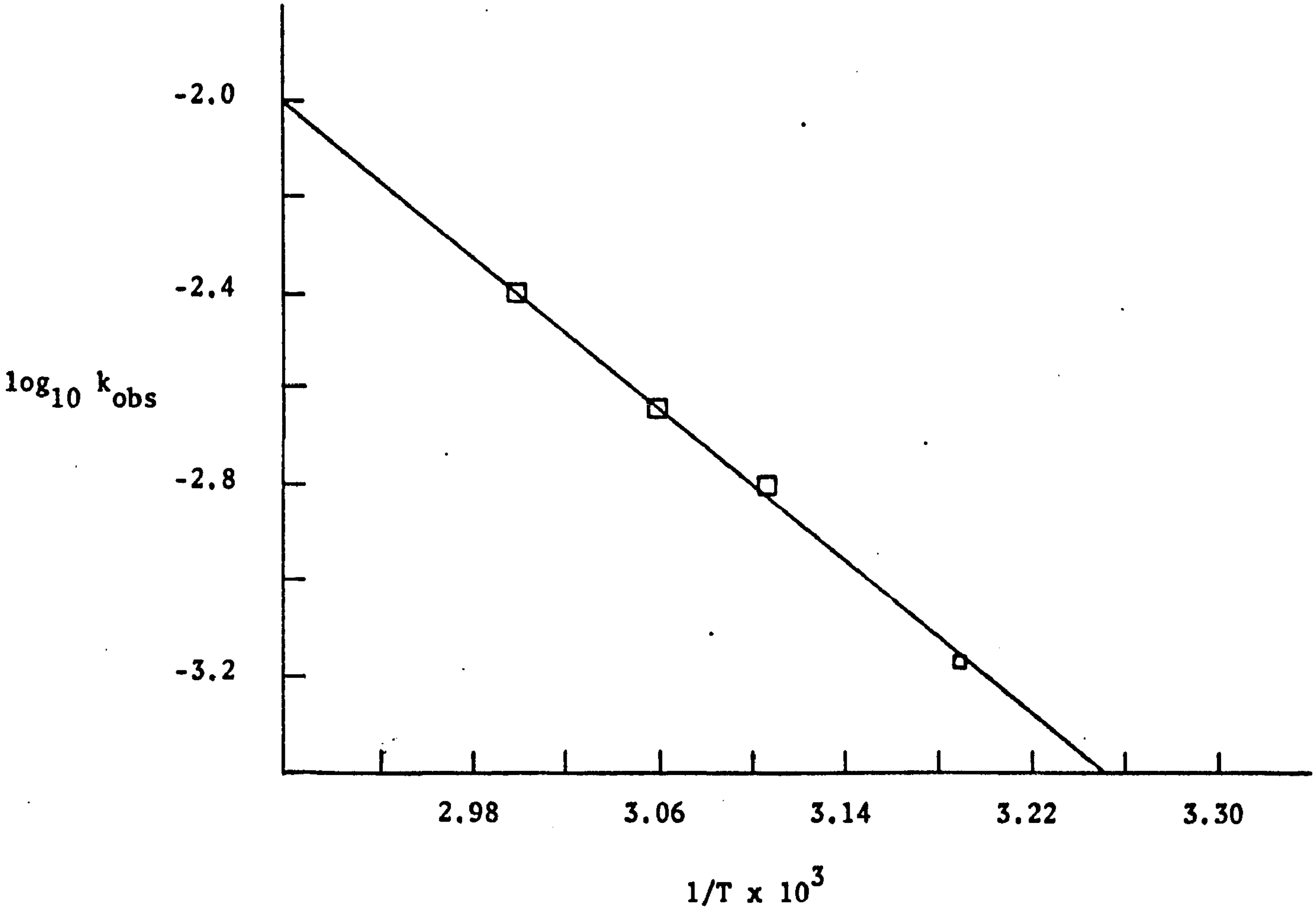


Figure 8

Arrhenius Plot: N,N-Dimethylaniline

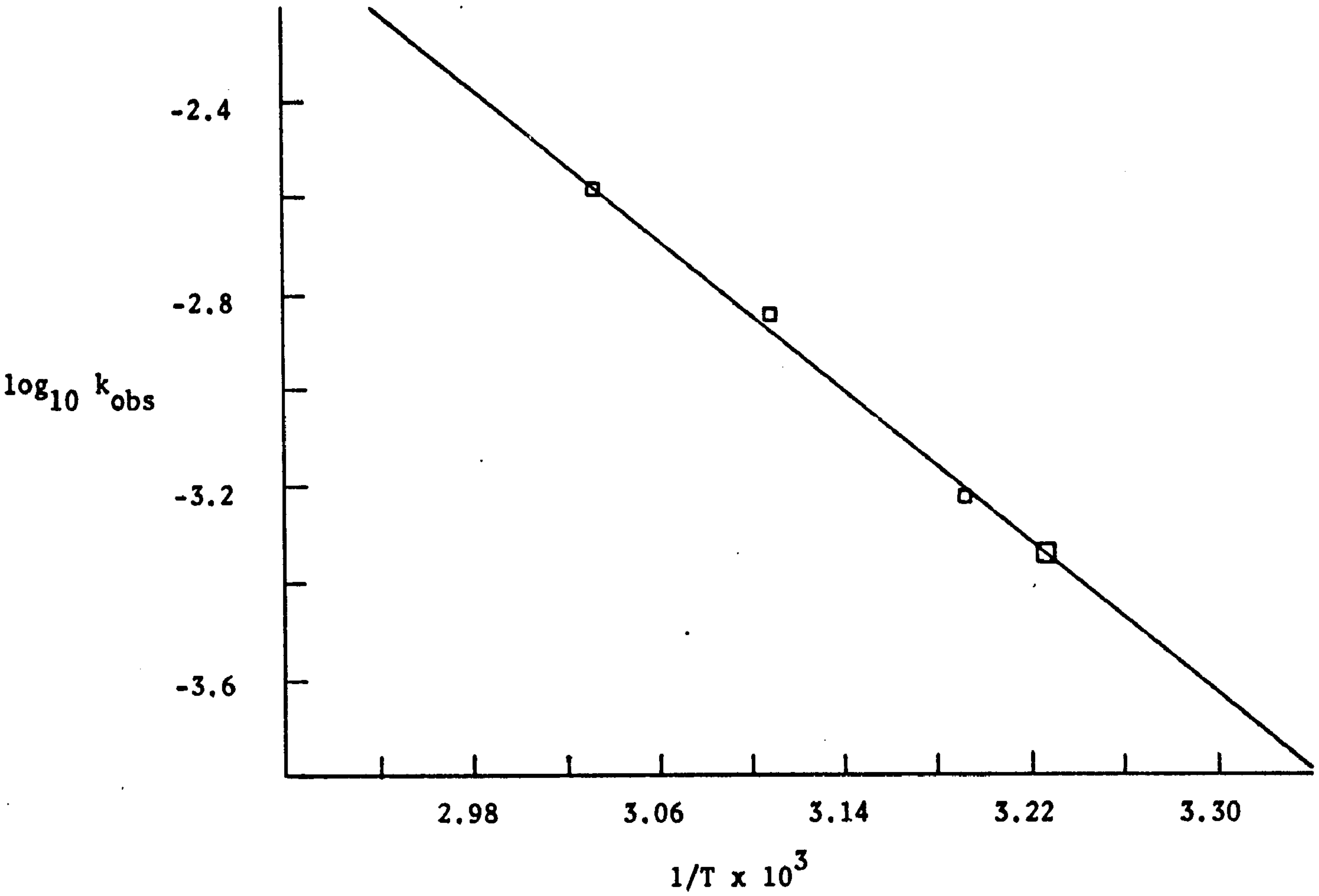


Figure 9

Arrhenius Plot: Thioanisole

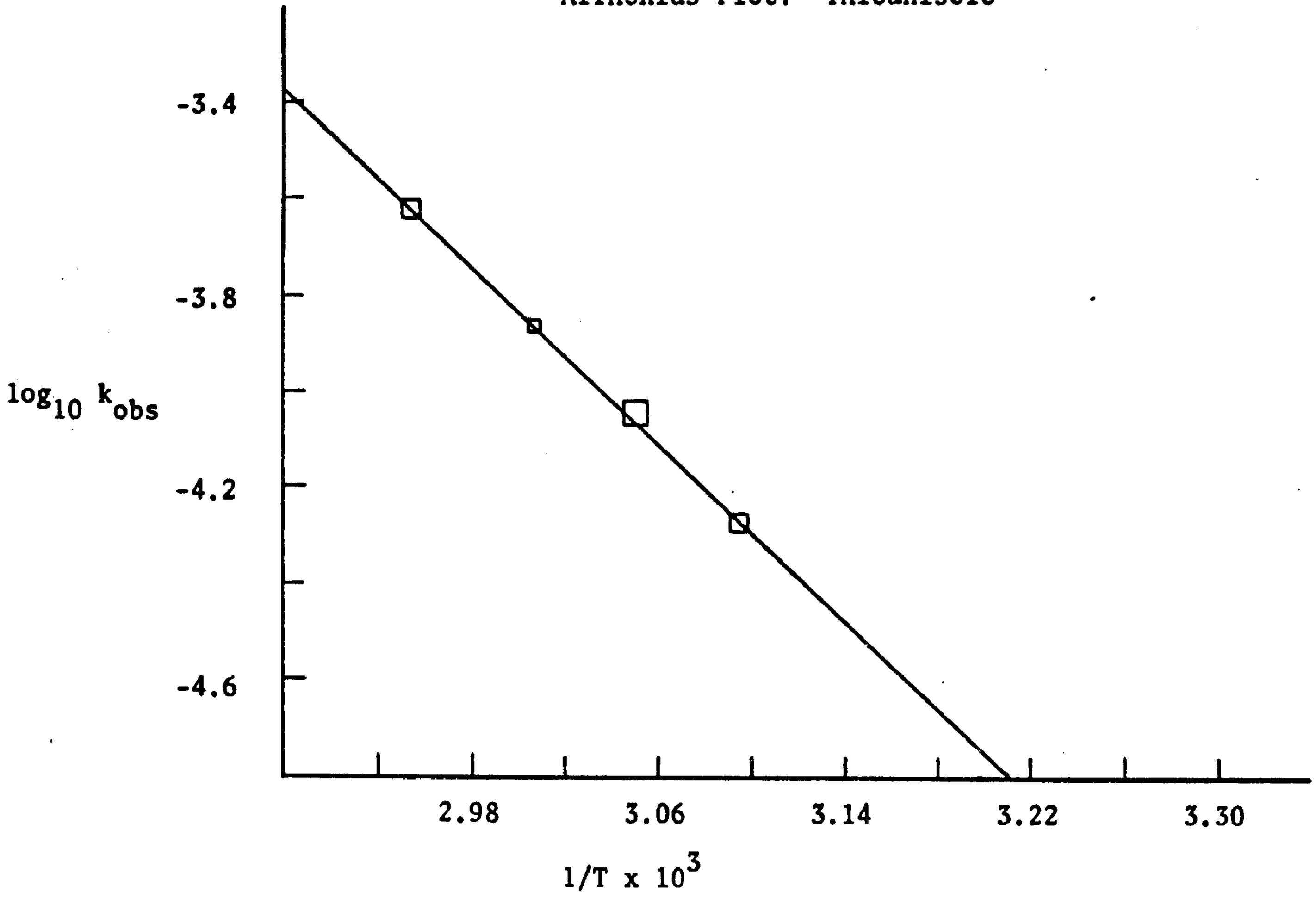


Figure 10

Arrhenius Plot: p-Methylthioanisole

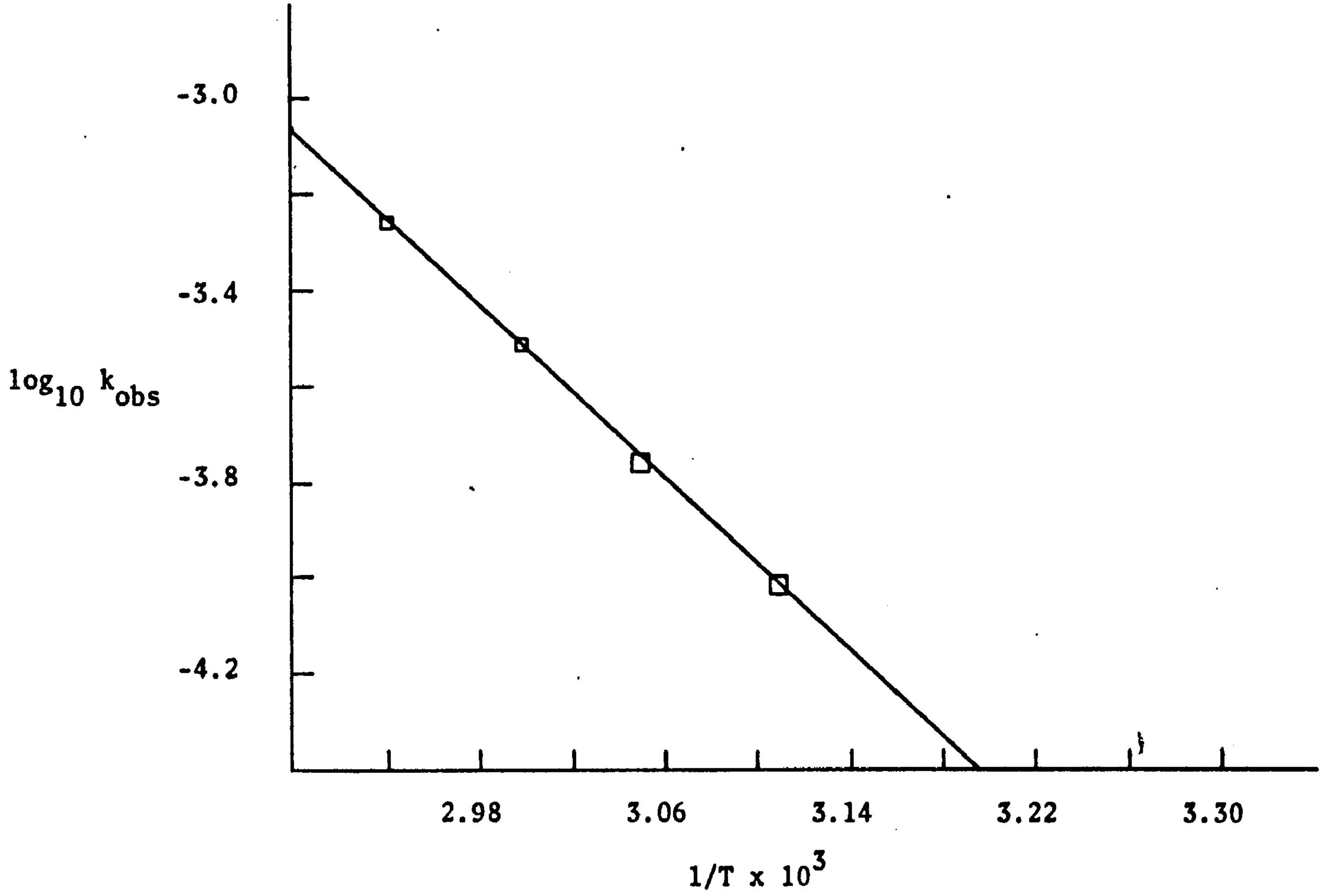


Figure 11

Arrhenius Plot: p-Chlorothioanisole

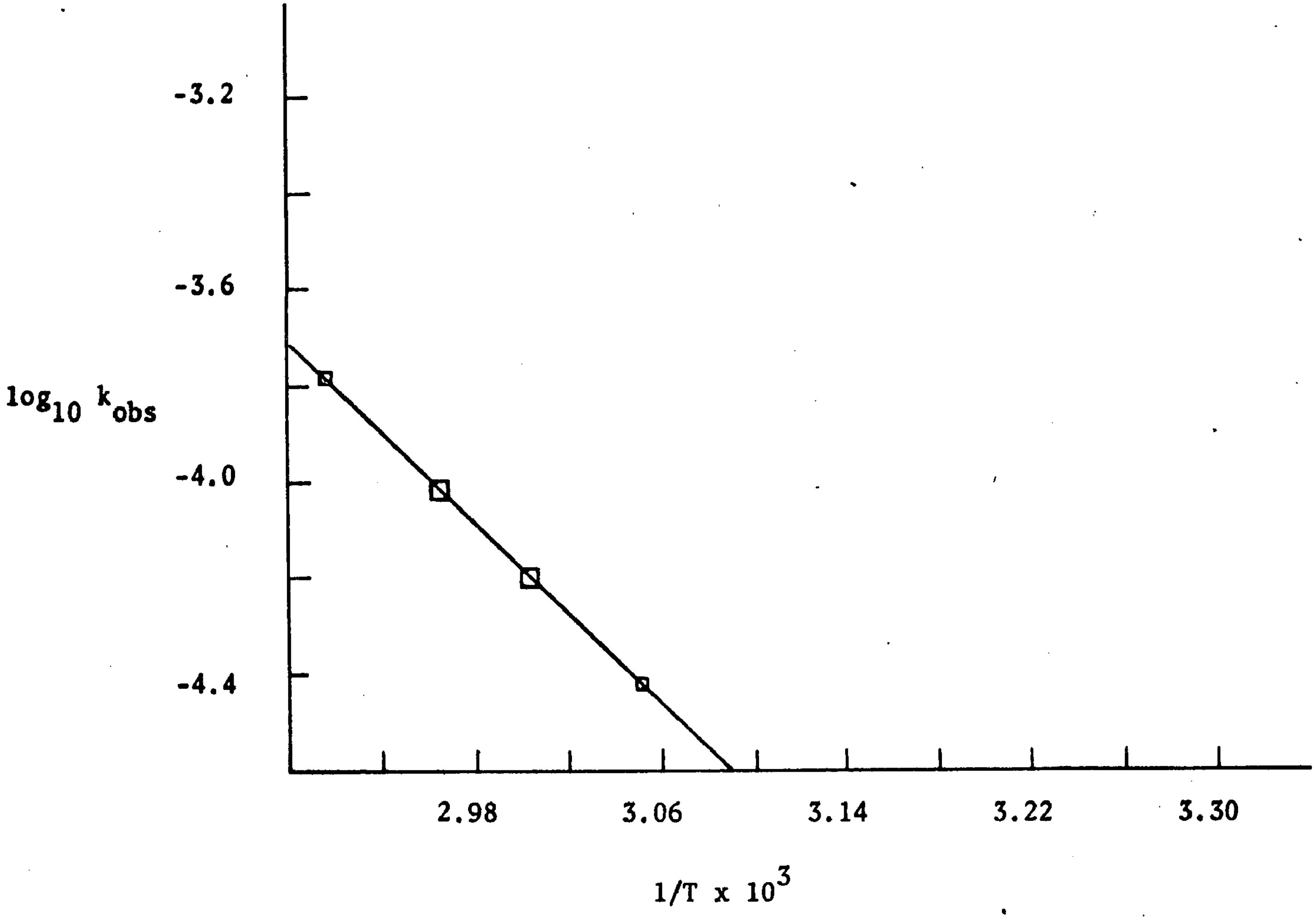


Figure 12

Arrhenius Plot: p-Methoxythioanisole

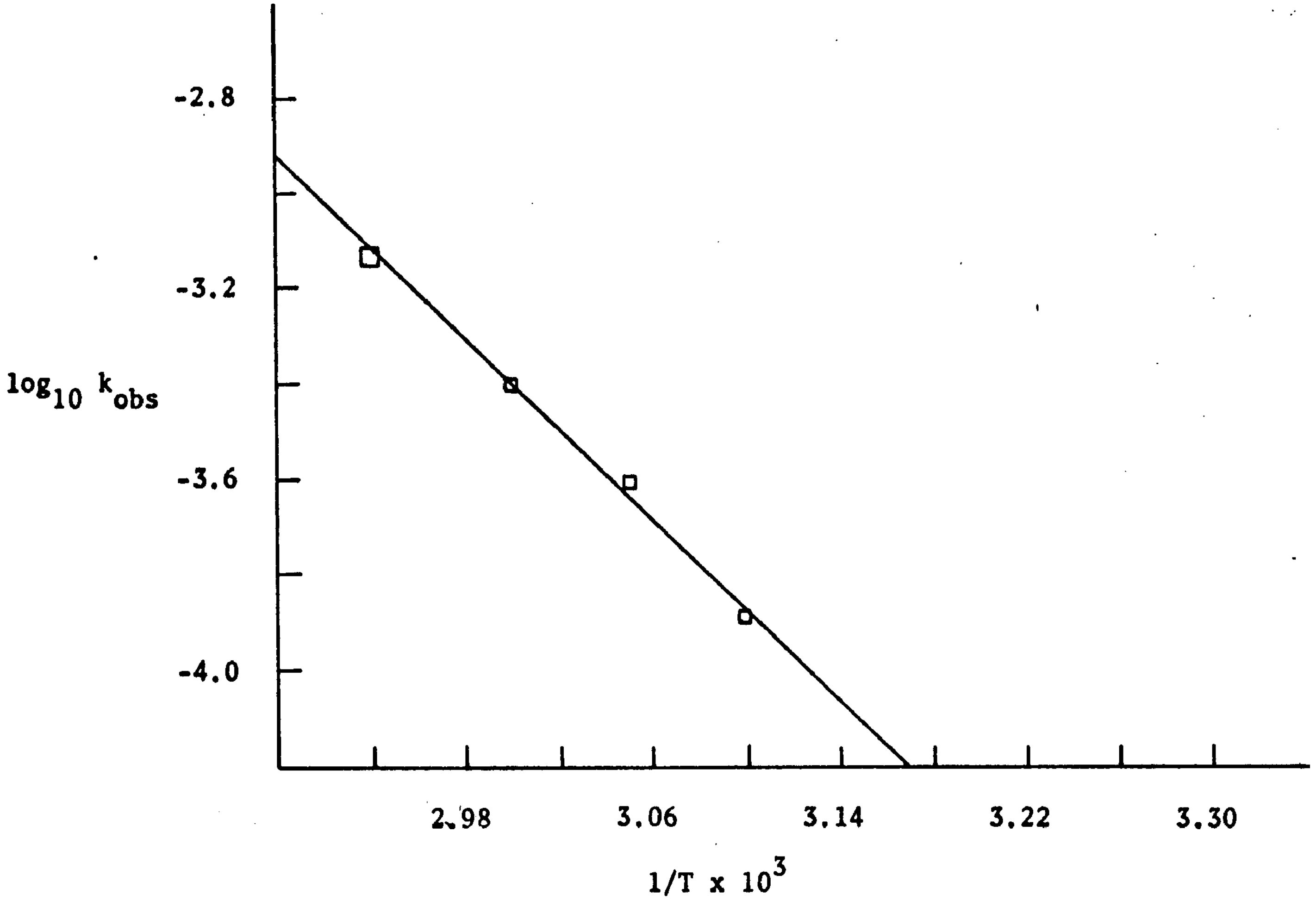


TABLE V

Activation Parameters and Rate Constants at 330°K

Compound	$\frac{E_{act}}{2.303R}$ [a] $\times 10^{-3}$	$\mathrm{Log}_{10}A'$ [a]	k, $\underline{M}^{-1}\,\mathrm{sec}^{-1}$ [b,f] $\times 10^{4}$	E_{act} [b,f] Kcal/mole	$\Delta H^{\ddagger}$ [c,f] Kcal/mole	$\Delta G^{\ddagger}$ [d,f] Kcal/mole	$\Delta S^{\ddagger}_{eu}$ [e,f]	σ [g,h]
Aniline	4.029	9.433	16.7±0.7	18.4±0.7	17.8±0.7	23.58±0.03	-17.6±2.2	0
m-Chloroaniline	4.319	9.674	3.86±0.26	19.8±1.2	19.1±1.2	24.54±0.05	-16.5±3.8	+0.373±0.02
p-Toluidine	4.186	10.329	44.0±1.6	19.2±0.6	18.5±0.6	22.94±0.02	-13.5±1.9	-0.170±0.02
p-Anisidine	3.722	9.041	57.9±3.7	17.0±1.2	16.4±1.2	22.76±0.04	-19.4±3.9	-0.268±0.02
α,α,α-Trifluoro-m-Toluidine	4.202	9.086	2.27±0.13	19.2±1.1	18.6±1.1	24.89±0.03	-19.2±3.4	+0.467±0.071[h]
m-Toluidine	4.281	10.368	24.9±0.9	19.6±0.7	18.9±0.7	23.32±0.02	-13.3±2.1	-0.069±0.02
N-Methylaniline	4.180	10.169	31.9±2.8	19.1±2.1	18.5±2.1	23.15±0.06	-14.2±6.6	---
N,N-Dimethylaniline	3.953	9.419	27.5±1.8	18.1±1.5	17.4±1.5	23.25±0.05	-17.6±4.6	---
Thioanisole	4.603	9.979	1.07±0.07	21.1±1.9	20.4±1.9	25.38±0.05	-15.1±6.0	0
p-Methylthioanisole	4.518	10.023	2.15±0.07	20.7±0.4	20.0±0.4	24.92±0.02	-14.9±1.3	-0.17±0.02
p-Chlorothioanisole	4.592	9.605	0.488±0.15	21.0±0.9	20.4±0.9	25.89±0.02	-16.8±2.8	+0.227±0.02

TABLE V (Continued)

Compound	$\frac{E_{act}}{2.303R}$ [a] X 10^{-3}	$Log_{10}A'$ [a]	k, $\underline{M}^{-1}sec^{-1}$ [b,f] X 10^{4}	E_{act} [b,f] Kcal/mole	$\Delta H^{\ddagger}$ [c,f] Kcal/mole	$\Delta G^{\ddagger}$ [d,f] Kcal/mole	$\Delta S^{\ddagger}_{eu}$ [e,f]	σ [g,h]
p-Methoxythio-anisole	4.691	10.674	2.87±0.17	21.5±1.6	20.8±1.6	24.73±0.04	-11.9±4.9	-0.268±0.02

[a] From least squares analysis of Arrhenius plots.

[b] Calculated by Arrhenius equation: $\log_{10}k = \frac{-E_{act}}{2.3\ R}\ \frac{1}{T} + \log_{10} A'$.

[c] $\Delta H^{\ddagger} = Eact - RT$

[d] $k = \frac{\bar{K}T}{h}\ e^{-\Delta G^{\ddagger}/RT}$

[e] $\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T}$

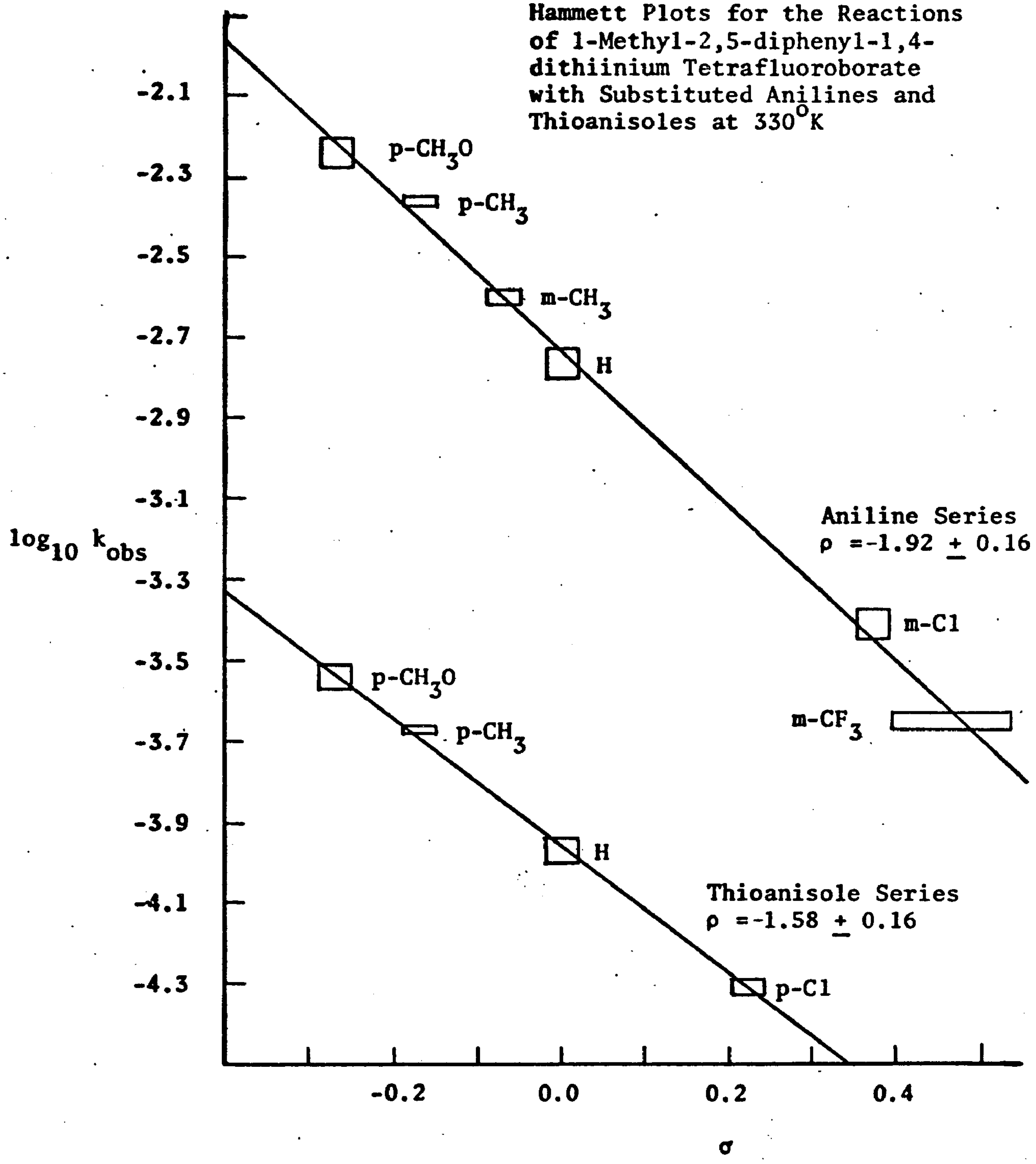
[f] For a discussion of the error calculations see appendix.

[g] All values except CF_3 were taken from D. McDaniel and H. Brown, J. Org. Chem., <u>23</u>, 420 (1958).

[h] H. van Bekkum, P. Verkade, and B. Wepster, Rec. Trav. Chim., <u>78</u>, 815 (1959).

Figure 13

Hammett Plots for the Reactions of 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate with Substituted Anilines and Thioanisoles at 330°K



DISCUSSION

A comparison of the rates of methylation of comparable thioanisoles and anilines is presented in Table VI. At 25° the ratio, $k_{amine}/k_{sulfide}$, is analogous to the ratios that can be obtained from the data of Pearson[38] for methyl iodide and aliphatic amines and sulfides in methanol. Examination of the activation parameters given in Table V shows that the activation energies and enthalpies of the thioanisole series are slightly higher by ca. 2-3 kcal/mol than the aniline series. Within experimental error, the activation entropies are alike. Likewise, experimental error precludes any discussion of relationships between activation parameters within either series.

The Hammett rho measures the susceptibility of a reaction to variation of substituents on a reactant.[39] According to Jaffe[39] there are three factors which determine this susceptibility: a) transmission of electrical effects to the reaction site, b) susceptibility of the reaction to changes of electron density at the reaction site, and c) the reaction conditions (especially temperature and solvent).

In this study the reaction conditions were identical. However, anilines, unlike thioanisoles, are capable of hydrogen-bonding with other aniline molecules and with acetonitrile. The self-association of aniline has been studied by various workers[40,41] and does not appear to be significant at the concentrations used for this study. No quantitative data for the interaction between anilines and

TABLE VI

Rates of Methylation of Comparable Thioanisoles and Anilines[a,b]

Temp, °C		PhSME	$PhNH_2$	PhNHMe	$PhNMe_2$	p-MePhSMe	p-$MePhNH_2$	p-MeOPhSMe	p-$MeOPhNH_2$
25	k	0.0348	0.830	1.41	1.44	0.0739	1.94	0.0870	3.64
	k_a/k_s		23.9	40.5	41.4		26.3		41.8
45.2	k	0.332	5.87	11.0	10.0	0.677	14.8	0.866	22.4
	k_a/k_s		17.7	33.1	30.1		21.9		25.9
56.9	k	1.07	16.7	31.9	27.5	2.15	44.0	2.87	57.9
	k_a/k_s		15.6	29.8	25.7		20.5		20.2
80	k	8.82	106	216	168	16.9	298	24.5	318
	k_a/k_s		12.0	24.5	19.0		17.6		13.0

[a] $k = 10^4 k$, l/mol-sec,
Calculated by
Arrhenius equation

[b] $k_a/k_s = k_{amine}/k_{sulfide}$

acetonitrile appear to be available, but such an interaction definitely exists,[42-45] although it is much weaker than many other hydrogen bonded systems. Apparently this interaction is not of great significance in the methylation reaction since aniline and N,N-dimethylaniline show very similar rates and activation parameters (Table V).

Since the same methylating agent was used for both the aniline and thioanisole series, it may therefore be assumed that the susceptibility of both reactions to changes in the electron density at the reaction site is the same.

There are several possible processes by which electrical effects are transmitted to the reaction site,[46] but only three are of major importance:[47-49] 1) Electric dipole field of polar substituents may influence the reaction site across space (field effect).[46] 2) The pi-electron system may be polarized by resonance interaction with substituents (mesomeric effect)[46], or by repulsion from non-bonded electrons on substituents.[48] 3) There may be mutual conjugation between the substituent and the reaction center (electromeric effect).[46] In the present study no substituents were used which underwent extensive mutual conjugation with the reaction center since all substituents were correlated well with σ_p and σ_m.[50]

Derivation of the Hammett equation using transition state theory leads to equation 2[51] which shows that rho should be inversely proportional to the temperature. Plots of rho versus 1/T are

$$\rho = \frac{G_o}{T}\left(\frac{\partial \Delta G^{\ddagger}}{\partial \sigma}\right)_T \qquad \text{(eq. 2)}$$

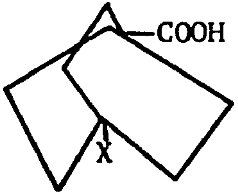
usually linear although in rare cases the slope is in the opposite direction from that expected by equation 2.[39] Table VII and Figure 14 show the temperature dependence of rhos which were calculated from the Arrhenius equations. Better correlations are obtained for temperatures within the range of the actual kinetic determinations. The errors in the individual rho values make definite conclusions about the slopes of the two lines impossible. However, it does <u>appear</u> that the rho values of the two series approach one another with increasing temperature and may coincide at somewhere near 140°C.

TABLE VII

Temperature Dependence of ρ

		Thioanisole Series		Aniline Series	
T,°C	1/T°K	ρ ± std. error	Correl. Coeff.	ρ ± std.error	Correl. Coeff.
25.0	0.003354	-1.55 ± 0.12	0.9946	-2.06 ± 0.08	0.9972
45.2	0.003141	-1.57 ± 0.07	0.9981	-1.97 ± 0.05	0.9988
56.9	0.003030	-1.58 ± 0.05	0.9991	-1.92 ± 0.06	0.9981
80.0	0.002832	-1.60 ± 0.03	0.9997	-1.83 ± 0.11	0.9930

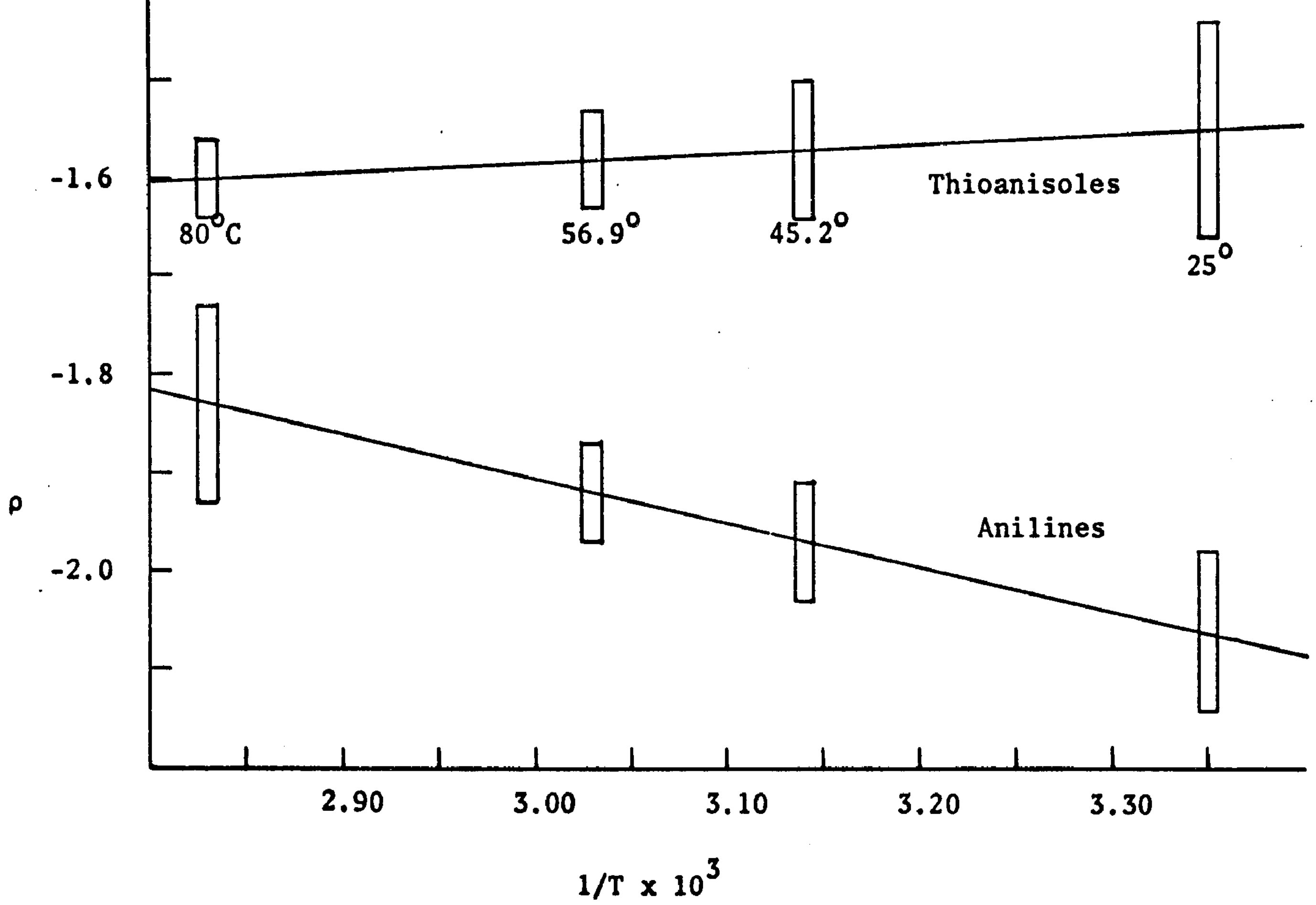
Swain and Lupton[52] have calculated the field and resonance components of substituent constants by making only two quite valid assumptions. The first of these is the assumption that substituent effects on the acidities of 4-substituted-bicyclo-[2.2.2]-octane-1-carboxylic acids (III) are entirely field effects.[52] The substituent



III

Figure 14

Temperature Dependence of Rho for the Reactions of 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate with Substituted Anilines and Thioanisoles



constants derived from this series are designated, F , by these authors.[52] The second assumption is that the trimethylammonium group has no resonance effect.[52] Therefore σ_p can be expressed by equation 3 and substitution of appropriate values for the trimethylammonium group allows the determination of α to be 0.56.[52] Thus (0.56 F) represents the field component of σ_p for each substituent and, $\mathcal{R}$, the resonance component, is simply the remainder.[52]

$$\sigma_p = \alpha\, F + \mathcal{R} \qquad \text{(Eq. 3)}$$

The results for the j th substituent are expressed in equation 4 where σ_F is equal to $\alpha\, F$. It is clear that if two reaction series

$$\sigma_p{}^j = \sigma_F{}^j + \mathcal{R}^j \qquad \text{(Eq. 4)}$$

are correlated well by σ_p, then the proportion of resonance effects to field effects in each series is the same, although the overall susceptibility to both effects may be different. Another way of looking at the situation is to consider the Ehrenson-Brownlee-Taft equation[53,54] (equation 5) in which ρ_{σ_F} and $\rho_{\mathcal{R}}$ are weighting factors that reflect the relative importance of field and resonance effects

$$\log k/k_o = \rho_{\sigma_F}\, \sigma_F + \rho_{\mathcal{R}}\, \mathcal{R} \qquad \text{(Eq. 5)}$$

in a given reaction series. If a reaction series is correlated well by σ_p,then the weighting factors are equal (equation 6). From these

$$\log k/k_o = \rho\sigma_p = \rho(\sigma_F + \mathcal{R}) \qquad \text{(eq. 6)}$$

considerations it may be stated that the rhos determined for the aniline and thioanisole series reflect differences in the susceptibilities of the two reactions to resonance interactions between the reaction site and the substituent. Likewise the two rhos reflect differences in susceptibilities to field interactions. If the interaction of the lone pair on nitrogen of the amino group with the pi-electron system of the phenyl ring was much greater than that of the interaction between the lone pair of sulfur and the ring, it would be expected that the rho for the aniline series would be much larger (i.e., more negative) than that for the thioanisole series. Since the rhos are quite similar it is implied that these interactions are similar. Such a conclusion is consistent with the data of Romm.[37]

Substituent effects for the two reactions reported herein and related series from the literature are presented in Table VIII. All values for literature reactions were recalculated using the σ_p and σ_m values of McDaniel and Brown.[55] It must be emphasized that rho values for reactions in different solvents are not strictly comparable since rho is not solvent independent.[39,56]

The larger rho value for the N,N-dimethylaniline series over that of the aniline series in nitrobenzene may be due to the near planarity of the N,N-dimethylaniline molecule and the corresponding increased resonance interaction[57] in comparison to aniline which is not planar.[58] Such a conclusion is substantiated by the Swain and Lupton[52] $\mathcal{R}$ values of -0.846 and -0.681 for N,N-dimethylaniline and aniline respectively.

TABLE VIII

Comparison of Rho Values for Methylation of Substituted Anilines and Thioanisoles

Methyl Donor	Methyl Acceptor	Solvent	Temperature,°C	ρ[a]	Correlation Coefficient	# Points
CH_3I	$XC_6H_4N(CH_3)_2$	ϕNO_2	80°	-2.45±0.11[b]	0.993	9
CH_3I	$XC_6H_4NH_2$	ϕNO_2	80°	-2.14±0.13[c]	0.993	6
Dithiinium Salt (I)	$XC_6H_4NH_2$	CH_3CN	80°	-1.83±0.10[d]	0.993	6
Dithiinium Salt (I)	$XC_6H_4SCH_3$	CH_3CN	80°	-1.60±0.03[d]	0.9997	4
[39]$(CH_3)_2SO_4$	$XC_6H_4SCH_3$	ϕCH_2OH	45.2°	-1.67±0.06[e]	0.998	6
Dithiinium Salt (I)	$XC_6H_4SCH_3$	CH_3CN	45.2°	-1.57±0.07[d]	0.998	4

[a] Error is standard error.

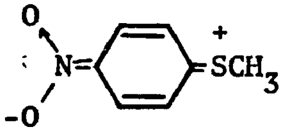
[b] Calculated from the combined data of J. Russell, J. Chem. Soc., 5183 (1963) and K. Laidler, J. Chem. Soc., 1786 (1938).

[c] Calculated from data of P. Randhakrishnamurti and L. Panigrahi, J. Ind. Chem. Soc., 46, 567 (1969).

[d] This work.

[e] V. Gosselck and H. Barth, Z. Naturforshg, 16b, 280 (1961) Does not include p-NO_2. These authors incorrectly reported rho as -1.14.

The Hammett plot (Figure 15) for the reaction of dimethyl sulfate with thioanisole[59] shows a significant deviation for the p-nitro-derivative. Although Gosselck and Barth[59] made no comments about experimental errors, this deviation can possibly be ascribed to enhanced resonance interaction involving the resonance hybrid shown below:



Examination of the data in Tables IX and X shows that in aprotic solvents at temperatures above 25° the dithiinium salt (I) reacts faster than methyl iodide. Furthermore, the activation energy of the methyl iodide reactions are lower but the activation entropy is about two times as negative as the sulfonium salt reactions. This latter fact suggests that the molecules of the transition state in the methyl iodide reactions are more tightly bound than those in the transition state of the sulfonium salt reactions.[60]

A comparison of the rate constants at 45.2° for the methylation of substituted thioanisoles by dimethyl sulfate in benzyl alcohol and by dithiinium salt (I) in acetonitrile (Table XI) shows the dimethylsulfate reaction to be nearly three times faster.

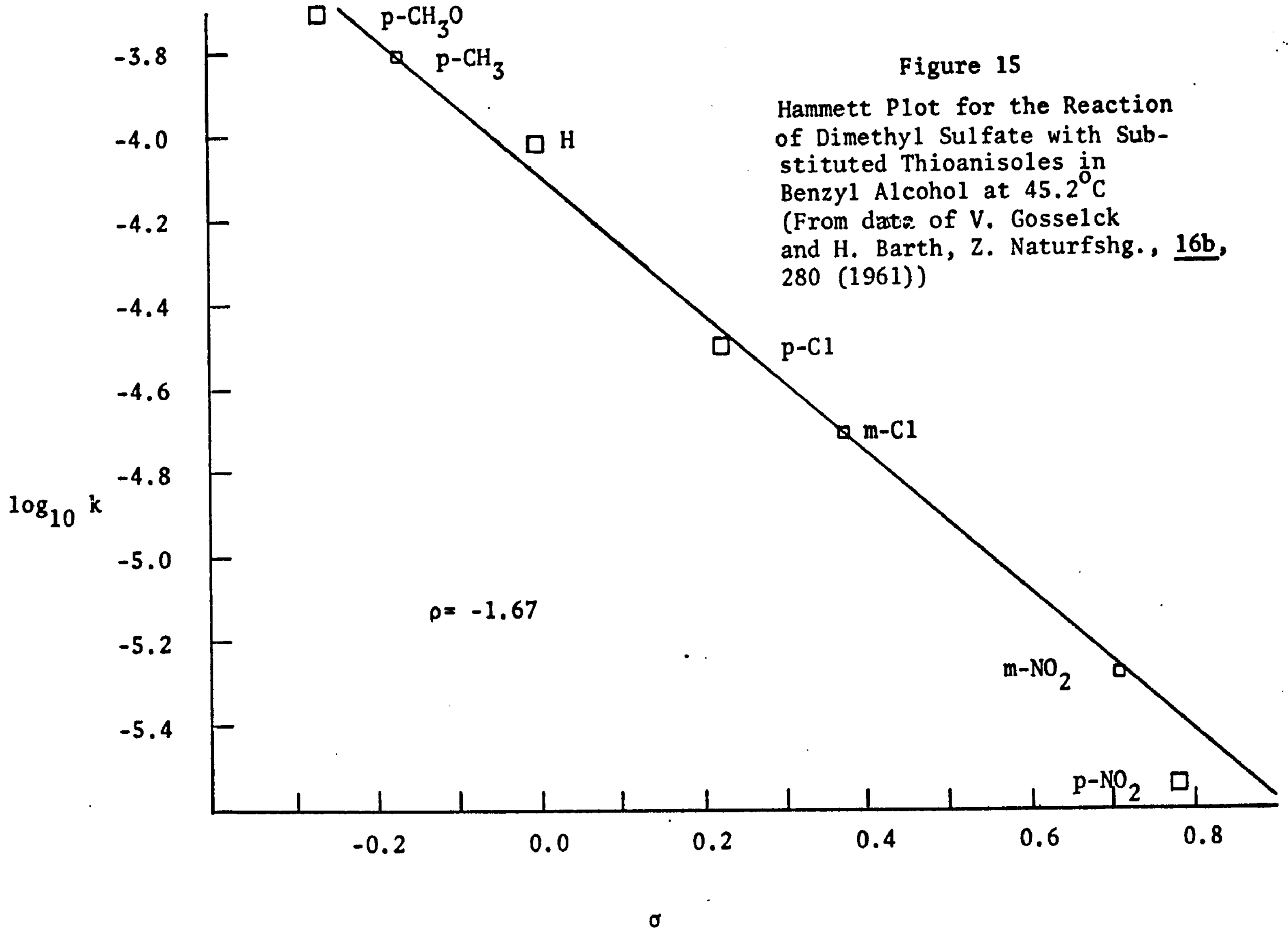


Figure 15

Hammett Plot for the Reaction of Dimethyl Sulfate with Substituted Thioanisoles in Benzyl Alcohol at 45.2°C (From data of V. Gosselck and H. Barth, Z. Naturfshg., <u>16b</u>, 280 (1961))

TABLE IX
Comparison of Kinetic Data for Methylation of Anilines

Methyl Donor	Solvent	N,N-Dimethylaniline. 10^4k_2, ℓ/mole-sec 25°C	35°C	40°C	60°C	80°C	Eact, Kcal/Mole	$\Delta H^{\ddagger a}$ Kcal/Mole @330°K	$\Delta G^{\ddagger a}$ Kcal/Mole @330°K	$\Delta S^{\ddagger a}$ eu @330°K	Reference
CH_3I	CH_3OH	0.562	1.31	1.96^b	8.49^b	31.1^b	15.2	14.5	24.17	-29.3	D. Evans, H. Watson and R. Williams J.Chem.Soc., 1345 (1939)
CH_3I	$(CH_3)_2C=O$	--	1.95	--	--	--	--	--	--	--	R. Benkesser, O. DeBoer, R.Robinson, and D.Sauve,J.Amer. Chem.Soc.,78,682 (1956)
CH_3I	$SO_2(\ell)$	0.126^b	0.323^b	0.477	2.66^b	11.6^b	17.2	16.5	24.94	-25.5	N.Tokura and Y. Kondo, Bull.Chem. Soc. Japan, 36, 200 (1963)
CH_3I	ϕNO_2	0.839	1.83^b	2.10	7.72	23.8	12.8	12.14	24.15	-36.4	K.Laidler, J.Chem. Soc.,1786(1938)
CH_3I	ϕNO_2	1.10	2.13^b	2.86	8.86	27.4	12.15	11.5	24.08	-38.1	J.B.Russell,J. Chem.Soc.,5183 (1963)
CH_3I	ϕNO_2	0.903^b	1.70^b	2.30	7.16	19.3	11.58	10.9	24.25	-40.4	P. Radhakrishnamurti and G. Panigrahi, J.Ind.Chem.Soc., 46,567(1969)
Dithiinium Salt(I)	CH_3CN	1.44^b	3.89^b	6.23^b	35.7^b	168^b	18.1	17	23.25	-17.6	Present work

TABLE IX - Continued

Methyl Donor	Solvent	$10^4\ k_2$, ℓ/mole-sec 25°C	35°C	40°C	60°C	80°C	Eact Kcal/Mole	$\Delta H^{\ddagger a}$ Kcal/Mole @330°K	$\Delta G^{\ddagger a}$ Kcal/Mole @330°K	$\Delta S^{\ddagger a}$ eu @330°K	Reference
				N-Methylaniline							
CH_3I	ϕNO_2	0.685^b	1.42^b	2.02^b	7.55	23.7	13.3	12.7	24.25	-35.0	P.Radhakrishnamurti and G.Panigrahi,J.Ind.Chem.Soc.,46,567(1969) [c]
Dithiinium Salt(I)	CH_3CN	1.41^b	4.03^b	6.64^b	43.0^b	216^b	19.1	18.5	23.15	-14.2	Present work
				Aniline							
CH_3I	ϕNO_2	0.815^b	1.32^b	1.66^b	3.69	9.22	8.77	8.11	24.62	-50.00	P.Radhakrisnamurti and G.Panigrahi,J.Ind.Chem.Soc.,46,567(1969) [c]
Dithiinium Salt(I)	CH_3CN	0.830^b	2.28^b	3.68^b	21.8^b	106^b	18.4	17.8	23.35	-17.6	Present work

[a] Calculated from data in reference cited by using equation presented in Table V.

[b] Calculated from Arrhenius equation

[c] The results from this reference tabulated here were completely recalculated assuming only the rate constants for the first 20% of reaction were correct as presented in reference.

TABLE X

Comparison of Methylation of Substituted Anilines with Methyl Iodide and 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (I).

Substituent	Methyl Iodide[a] 10^4 k, ℓ/mole-sec	I[b] 10^4 k, ℓ/mole-sec[c]	σ[d]
m-CF_3	--	15.4	+0.467 0.071[e]
m-Br	1.94	--	+0.391 0.02
m-Cl	1.57	27.8	+0.373 0.02
p-CI	3.26	--	+0.227 0.02
H	9.22	106	0
m-CH_3	16.0	176	-0.069 0.02
p-CH_3	28.0	298	-0.170 0.02
p-CH_3O	--	318	-0.268 0.02
N-Methylaniline	23.7	216	---
N,N-Dimethyl-aniline	19.3	168	---

[a] P. Randhakrishnamurti and G. Panigrahi, J. Ind. Chem. Soc., <u>46</u>, 567 (1969). Solvent: nitrobenzene.

[b] This work. Solvent: acetonitrile.

[c] Computed by Arrhenius equation.

[d] All values except m-CF_3 from D. McDaniel and H. Brown, J. Org. Chem., <u>23</u>, 420 (1958).

[e] H. van Bekkum, P. Verkade, and B. Wepster, Rec. Trav. Chim., <u>78</u>, 815 (1959).

TABLE XI

Comparison of Methylation of Substituted Thioanisoles with Dimethyl Sulfate and 1-Methyl-2,5-diphenyl-1,4-Dithiinium Tetrafluoroborate (I) at 45.2°C.

Substituent	Dimethyl Sulfate[a] 10^4k ℓ/mole-sec	I[b] 10^4k ℓ/mole-sec[c]	σ[d]
p-NO_2	0.0283	---	+0.778
m-NO_2	0.0520	---	+0.710
m-Cl	0.193	---	+0.373
p-Cl	0.310	0.151	+0.227
H	0.950	0.332	0
p-CH_3	1.59	0.677	-0.170
p-CH_3O	2.03	0.866	-0.268

[a] V. Gosselck and H. Barth, Z. Naturforschg., 16 b, 280 (1961). Solvent: benzyl alcohol. Gosselck and Barth tabulated log k values without specifying time units. However, in another paper in the series (V. Gosselck et al., Ann., 671, 1 (1964)) these workers again presented log k values and specified time units in minutes. Therefore, this table was prepared assuming the time units were minutes.

[b] This work. Solvent: acetonitrile.

[c] Computed from Arrhenius equation.

[d] All values from D. McDaniel and H. Brown, J. Org. Chem., 23, 420 (1958).

CONCLUSIONS

In summary, the following conclusions can be made:

(1) With increasing temperature in the range of 25-80° in aprotic media, the ratio $k_{amine}/k_{sulfide}$ for the methylation of corresponding anilines and thioanisoles decreases from ca. 40 to ca. 10. The activation parameters for these two reactions are very similar.

(2) Anilines show a slightly increased susceptibility to substituent effects over thioanisoles in methylation reactions in the temperature range ca. 25-80° which reflects increased resonance and field interactions between the amine reaction site and the substituent.

(3) In aprotic media at temperatures above 25°, the dithiinium salt (I) reacts faster than methyl iodide. The activation energies of the methyl iodide reactions are slightly less, but the activation entropies are almost twice as negative as the sulfonium salt reactions.

EXPERIMENTAL SECTION

Apparatus

Ultraviolet spectra and kinetic data were obtained with a Perkin-Elmer 402 uv-visible spectrophotometer fitted with a cast iron cell block. Constant temperature (±0.03°C) was maintained by circulating water from a Forma-Temp Jr. constant temperature bath and circulator through a jacketed 1-cm sample cell and the cell block. Reaction temperatures were read (±0.3°C) from a calibrated thermometer in the cell block. Nmr spectra were recorded on a Hitachi-Perkin-Elmer R-20A spectrometer. Vpc analyses were carried out with a Nester-Faust Anakro IA chromatograph fitted with a silicone SE 30 column. Melting points were determined in capillary tubes using a calibrated Mel-Temp apparatus.

Materials

1-Methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) was prepared by the method of Young and Lazarus.[61,62] The amines, which were commercially available, were purified either by distillation under reduced pressure or by recrystallization followed by sublimation. All of the sulfides except p-methoxythioanisole were commercial products purified by distillation under reduced pressure. p-Methoxythioanisole was prepared according to the procedure of Bordwell and Pitt[63] and was distilled under reduced pressure to give pure product with a boiling point in agreement with literature values.[63] Acetonitrile (Fisher Certified) was distilled three times from phosphorus pentoxide.

Acetonitrile solutions of the dithiinium salt (I) were stable indefinitely at room temperature and for at least 24 hr at 66°, which represents the upper limit of temperature for these studies. Solutions of 2,5-diphenyl-1,4-dithiin (II) at 66° likewise showed no ultraviolet absorbance change for at least the several hours necessary to monitor the aniline reactions. Literature reports of failure of amines to react with acetonitrile[64,65] were confirmed by observing no change in the nmr spectrum of a 1.5 M solution of aniline in acetonitrile at 63° overnight. Therefore, competing reactions under the conditions used to study the methylation of anilines are insignificant. In contrast, solutions of the dithiin (II) and thioanisole showed a steady increase in absorbance over a period of hours at 66° which would complicate the study of the slower reacting thioanisoles. Apparently this increase was due to oxidation, since careful flushing of the solutions for the thioanisole kinetics with dry nitrogen eliminated the problem.

Identification of Products

Reaction of I with Aniline

Six g (0.0162 mol) of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) and 25.0 g (0.268 mol) of aniline were heated at 78° for 3 hr. The solution was cooled and the precipitated 2,5-diphenyl-1,4-dithiin (II) was removed by filtration. After it was concentrated on a rotary evaporator, an approximately 0.1 M solution of HCl was added to the filtrate to precipitate the remaining 2,5-diphenyl-1,4-dithiin (II) which was combined with the previous material to give a total yield of 4.15 g (96%). Ammonium hydroxide was then added to separate an amine layer which was extracted into ether and distilled from calcium hydride. Vpc analysis showed the mixture to be aniline and N-methylaniline with only a trace of N,N-dimethylaniline.

Reaction of I with Thioanisole

Five-tenths g (0.00135 mol) of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) and 0.25 g (0.002 mol) of thioanisole in 8 ml of acetonitrile was maintained at 65° for 18 hr. Concentration of the solution led to precipitation of 0.30 g of crude 2,5-diphenyl-1,4-dithiin (II). Addition of ether precipitated 0.24 g (78.6%) of a white solid with m.p. = 131-132.5°. Evaporation of the filtrate to near dryness allowed the collection of another 0.03 g of II to give a total crude yield of 0.33 g (91%), which after one recrystallization from absolute ethanol weighed 0.2 g (55%) with m.p. 114-116° (Lit,[62] m.p. 112-114°). Recrystallization of the hygroscopic white solid from acetonitrile-ether and drying *in vacuo* with phosphorus pentoxide gave analytically pure dimethylphenylsulfonium tetrafluoroborate with m.p. 132.5-133.5°. nmr (CD_3CN) δ3.17 (S, 6, CH_3 's), 7.8 (m, 5, ArH) ppm.

Anal. Calcd for $C_8H_{11}SBF_4$: C, 42.51; H, 4.91; S, 14.18. Found: C, 42.59; H, 4.95; S, 14.11.

Kinetics

The progress of the reactions described herein was followed by observing the decrease in ultraviolet absorbance at 340 nm.

Beer's law plots of the 2,5-diphenyl-1,4-dithiin (II) and 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluorborate (I) were linear and passed through the origin. A least squares computer procedure gave molar extinction coefficients (ε) of 1.05×10^3 and 4.72×10^3 for the dithiin II and the dithiinium salt (I) respectively. Since the reactions were run with an initial dithiinium salt concentration ($S_{t=0}$) of about 20×10^{-5} M and a nucleophile concentration (N) of about 0.01-1.0 M, the integrated rate equation given by equation 7 was applicable:

$$\ln \frac{S_{t_1}}{S_{t_2}} = kN(t_2 - t_1) \qquad \text{(Eq. 7)}$$

Since

$$A_t = \varepsilon_S\, S_t + \varepsilon_D\, D \text{ and } D = S_{t=0} - S_t,$$

$$A_t = S_t\, (\varepsilon_S - \varepsilon_D) + \varepsilon_D\, S_{t=0} \quad \text{or} \quad S_t = \frac{(A_t - \varepsilon_D\, S_{t=0})}{\varepsilon_S - \varepsilon_D}$$

Substitution of this latter equation for S_t into equation 7 gives the final rate equation 8. Pseudo-first order plots of ln

$$\ln \frac{A_{t_1} - \varepsilon_D\, S_{t=0}}{A_{t_2} - \varepsilon_D\, S_{t=0}} = k\, N(t_2 - t_1) \qquad \text{(Eq. 8)}$$

$(A_t - \varepsilon_D\, S_{t=0})$ versus time were linear to 2-4 half-lives and both the aniline and thioanisole reactions were found to go essentially to completion. Any absorbance due to the nucleophiles was cancelled by placing in the reference beam a solution of nucleophile of exactly the same concentration as that in the reaction solution. All kinetic determinations were made in triplicate with agreement usually better than ±5%.

Stock solutions of the dithiinium salt I and the nucleophile were prepared in the bath. The reaction was started by pipetting a known volume of the dithiinium salt solution into a 10 ml volumetric flask and diluting to the mark with the stock nucleophile solution. In the case of the thioanisole series reactions, dry nitrogen was slowly bubbled through the stock solutions cooled in an ice bath for ca. 20 min. and through the reaction solution for about 10 min. before placing it in the sample cell. The nucleophile concentrations were typically 0.01-0.20 M for the aniline series reactions and 0.2-1.0 M for the thioanisole series reactions. In the case of the aniline series the 5-fold ordinate expansion system of the spectrophotometer was used and the calculated rate constant was usually based on the first 15-30% of the reaction. The normal ordinate plot was used for the thioanisole series and the rate constants were based on approximately the first 75% of the reaction.

APPENDIX

Error Calculations for Data Reported in Table V

The errors reported in Table V were calculated by procedures similar to those of R. Peterson et al. (J. Amer. Chem. Soc., <u>83</u>, 3819 (1961)) and represent estimates of the "maximum possible error." These calculations take into consideration the reproducibility of individual runs and deviation of points of the Arrhenius plot from the least squares line.

The equation used to calculate the rate constants and the corresponding errors (denoted Z) is given by:

$$\log_{10} k_{calc} \pm \text{error} = \frac{-E_{act}}{2.3Rt} + \log_{10} A' \quad \pm Z$$

$$\text{where } Z = \sqrt{\frac{\sum_{i} (\log_{10} k^{i}_{obs} - \log_{10} k^{i}_{calc})^{2}}{n-1}} \quad + \sqrt{\frac{\sum_{i} [\log_{10} (k^{i}_{obs} + \frac{\text{range}}{2}) - \log_{10} k^{i}_{obs}]^{2}}{n-1}}$$

The reported activation energies and errors (denoted $\text{error}_{E_{act}}$) were calculated by:

$$\text{Reported } E_{act} \pm \text{error}_{E_{act}} = E_{act} \pm \left| E_{act} - 2.3R \frac{-(\log_{10} k^{2}_{calc} + Z) - (\log_{10} k^{1}_{calc} - Z)}{\frac{1}{T_2} - \frac{1}{T_1}} \right|$$

where the superscripts 1 and 2 denote the values for the lowest and highest temperatures observed, respectively. Since $\Delta H^{\ddagger} = E_{act} - RT$ the errors reported for activation enthalpies will be the same as those reported for activation energies ($\text{error}_{E_{act}}$).

The reported activation free energies and errors (denoted by $\text{error}_{\Delta G^{\ddagger}}$) were calculated by:

$$\text{Reported } \Delta G^{\ddagger} \pm \text{error}_{\Delta G^{\ddagger}} =$$

$$\Delta G^{\ddagger} \pm \left| 2.3RT\left[\left(\log_{10}\frac{\bar{k}T}{h} - \log_{10} k_{calc}\right) - \left(\log_{10}\frac{\bar{k}T}{h} - \log_{10} k_{calc} - Z\right)\right]\right| = \Delta G^{\ddagger} \pm 2.3RT\ Z$$

The reported activation entropies and errors were calculated by:

$$\text{Reported } \Delta S^{\ddagger} \pm \text{error} = \Delta S^{\ddagger} \pm \left| \Delta S^{\ddagger} - \frac{(\Delta H^{\ddagger} + \text{error}_{E_{act}}) - (\Delta G^{\ddagger} - \text{error}_{\Delta G^{\ddagger}})}{T} \right|$$

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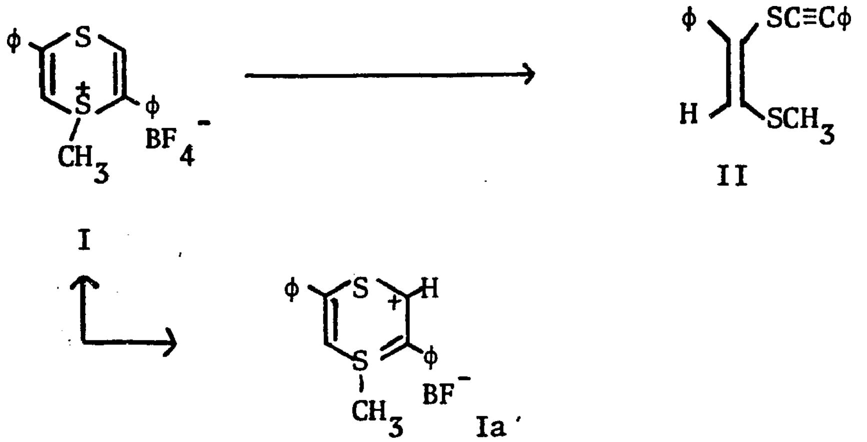
PART B

Preparation and Reactions of Some Dithiin Ring Substituted 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborates

INTRODUCTION

In order to obtain data more closely related to biological systems, it was decided to investigate the reactions of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) with biological molecules in aqueous media. Unfortunately, however I was found to undergo ring cleavage in pH 6.8 phosphate buffer at 37° to give 1-phenylethynylthio-2-methylthio-1-phenylethylene (II) which was previously obtained by Lazarus[1a,b] when I reacted with sodium hydride.



Since the β proton of α,β-unsaturated sulfonium salts is significantly deshielded with respect to the β proton of the corresponding sulfide,* it has been concluded that (p-d)-π bonding is important in these compounds.[1a,b,2] Thus structure Ia would be expected to contribute to the ground state of I. The facile ring opening of the dithiinium salt I, described above, would seem to substantiate this reasoning.

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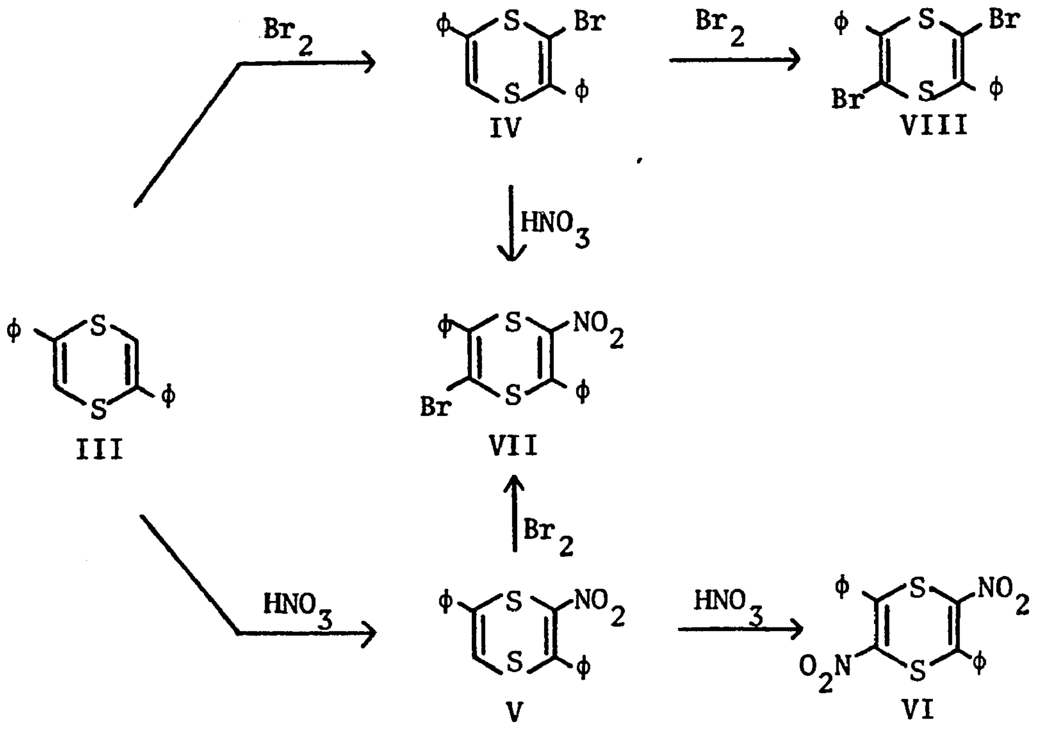
* Lazarus[1a,b] reported that the nmr spectrum (d_6-DMSO, TMS) of 2,5-diphenyl-1,4-dithiin (III) showed the vinyl protons at δ 6.98 and the aromatic protons at 7.58 ppm, while the nmr spectrum (d_6-DMSO, TMS) of 1-methyl-2,5-diphenyl-1,4-dithiinium 2,4,6-trinitrobenzenesulfonate showed a vinyl proton (H-3) at δ 8.75, a vinyl proton (H-6) at 6.90, and the aromatic protons at 7.68 ppm.

With these facts at hand, it becomes apparent that 3-substituted analogs of I would circumvent the ring opening problem for biochemical studies and would provide molecules for additional kinetic studies to yield quantitative data that is relevant to (p-d)-π bonding. A 3-nitro derivative of I would be especially desirable since it should have greater reactivity and water solubility than I itself.

Parham and co-workers[3,4,5] prepared various bromo and nitro derivatives of 2,5-diphenyl-1,4-dithiin (III), which appear to be the only known dithiin ring substituted derivatives of III. Lazarus[1a,b] was able to methylate 3-bromo-2,5-diphenyl-1,4-dithiin (IV)

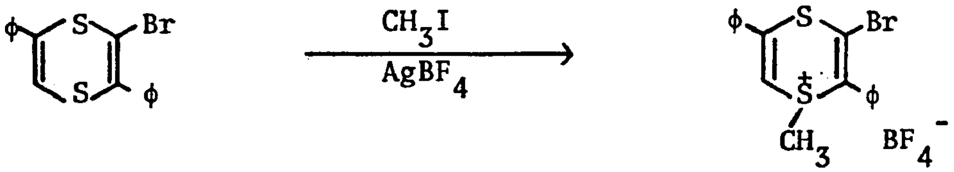


with methyl iodide and silver perchlorate to form 1-methyl-2,5-diphenyl 1,4-dithiinium perchlorate, but reported that methylation of 3-nitro-2,5-diphenyl-1,4-dithiin (V) with methyl iodide and silver 2,4,6-trinitrobenzenesulfonate yielded a yellow compound which was too unstable to isolate.

This section describes a completion of the study, begun by Lazarus,[1b] of the methylation of the bromo and nitro derivatives of 2,5-diphenyl-1,4-dithiin (III) originally prepared by Parham[3,4,5] and some interesting related reactions. Unfortunately, no compounds were isolated with substantial water solubility that did not undergo ring cleavage in aqueous media and no compounds were isolated that were suitable for the proposed kinetic studies.

RESULTS AND DISCUSSION

1-Methyl-3-bromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (IX) was prepared in good yield from the bromo dithiin IV using methyl iodide and silver tetrafluoroborate.

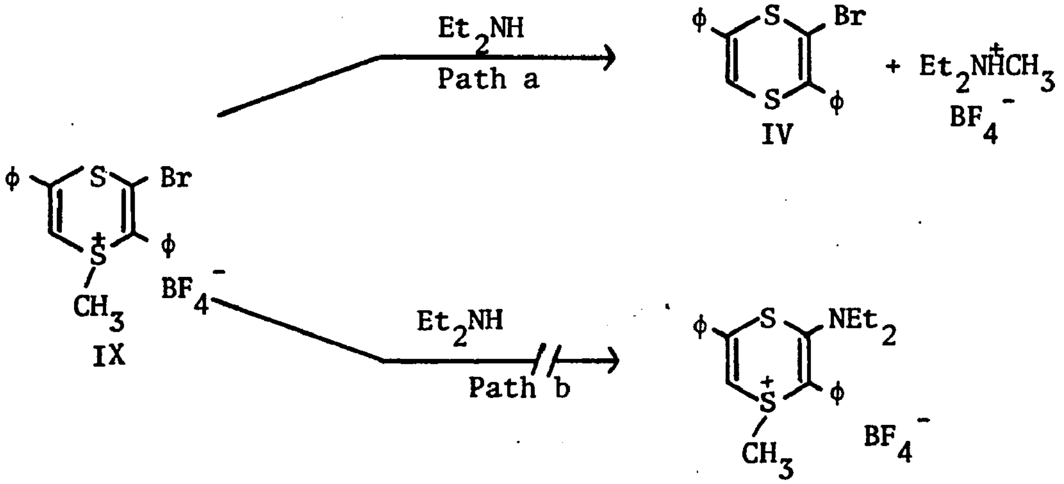


IV

IX

Since the 3-position of these dithiinium compounds is known to carry a partial positive charge (see Ia), attack by nucleophiles on IX might involve attack at the methyl group and/or C-3 as shown in Scheme I.

Scheme I

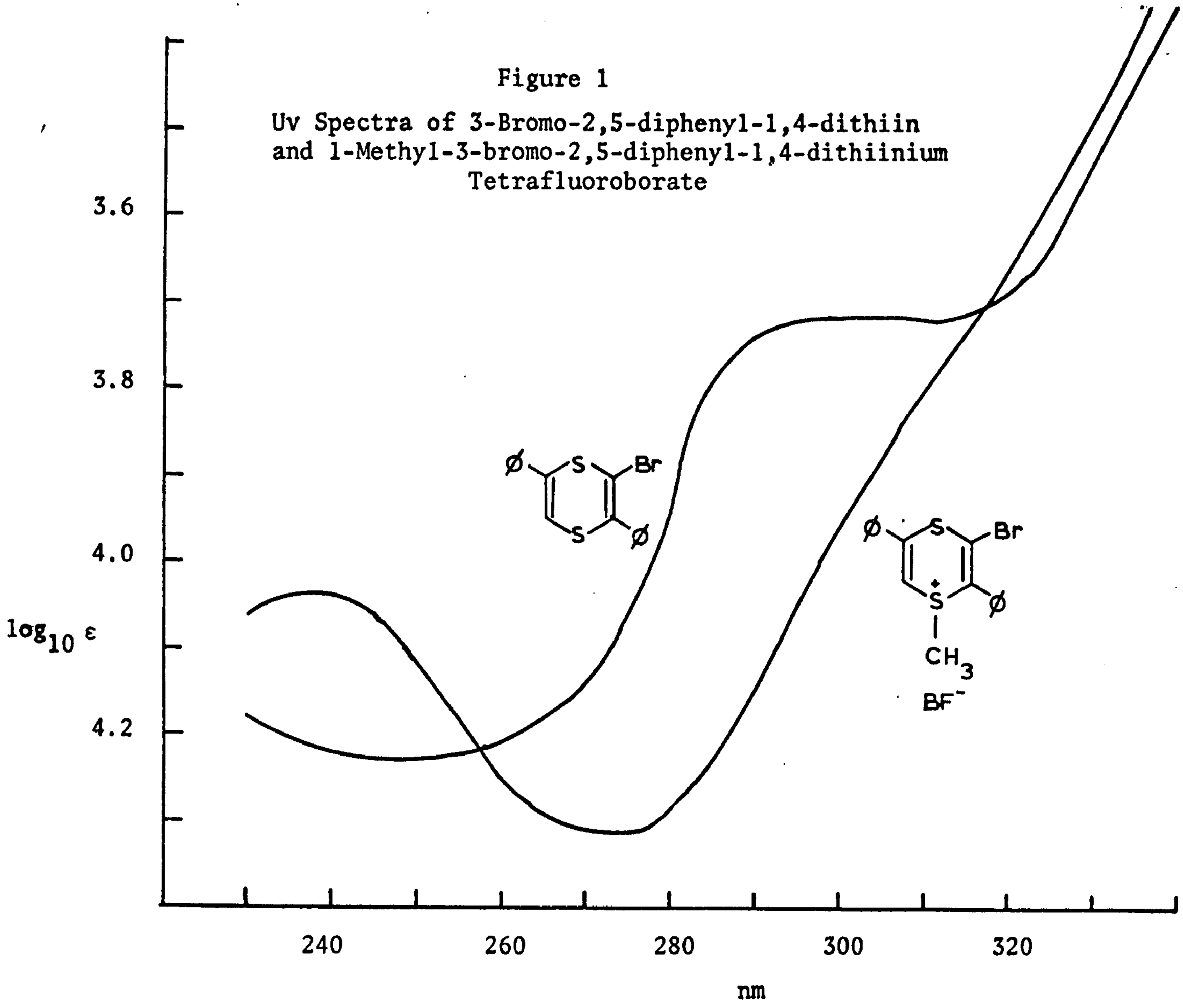


Reaction of the dithiinium salt IX with diethylamine was found to follow "path a" to yield 72% of the parent dithiin IV which was the only dithiin compound isolated. A comparison of the ultraviolet spectra (Figure 1) of 3-bromo-2,5-diphenyl-1,4-dithiin (IV) and 1-methyl-3-bromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (IX) shows that the ratio $\varepsilon_{IX}/\varepsilon_{IV}$ reaches a maximum value of only 2.6 at 290 nm, which is not sufficient for reliable kinetic studies using the procedure described in Part A of this thesis.

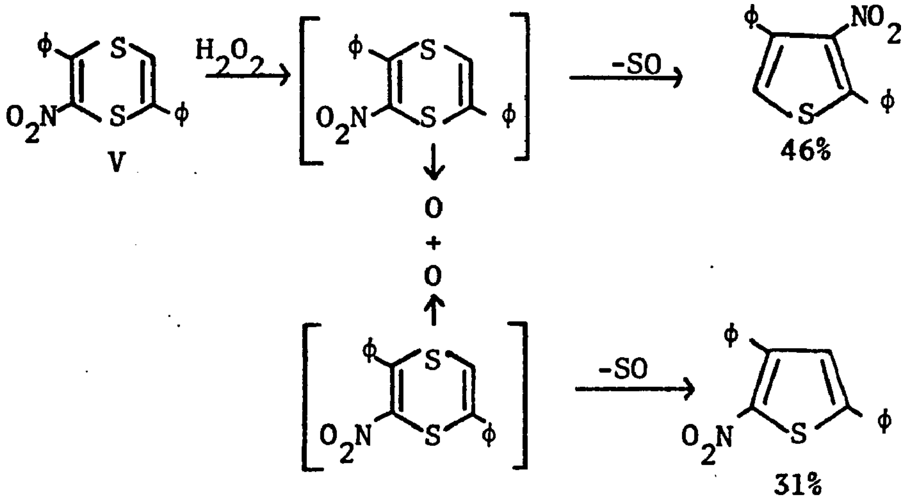
Parham and co-workers[3,5] found that oxidation of 3-nitro-2,5-diphenyl-1,4-dithiin (V) gave a mixture of two isomeric thiophenes (in a ratio of 1.5/1) which were formed by loss of sulfur monoxide from the two possible intermediate sulfoxides. (Scheme II).

Figure 1

Uv Spectra of 3-Bromo-2,5-diphenyl-1,4-dithiin and 1-Methyl-3-bromo-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate



Scheme II[3,5]

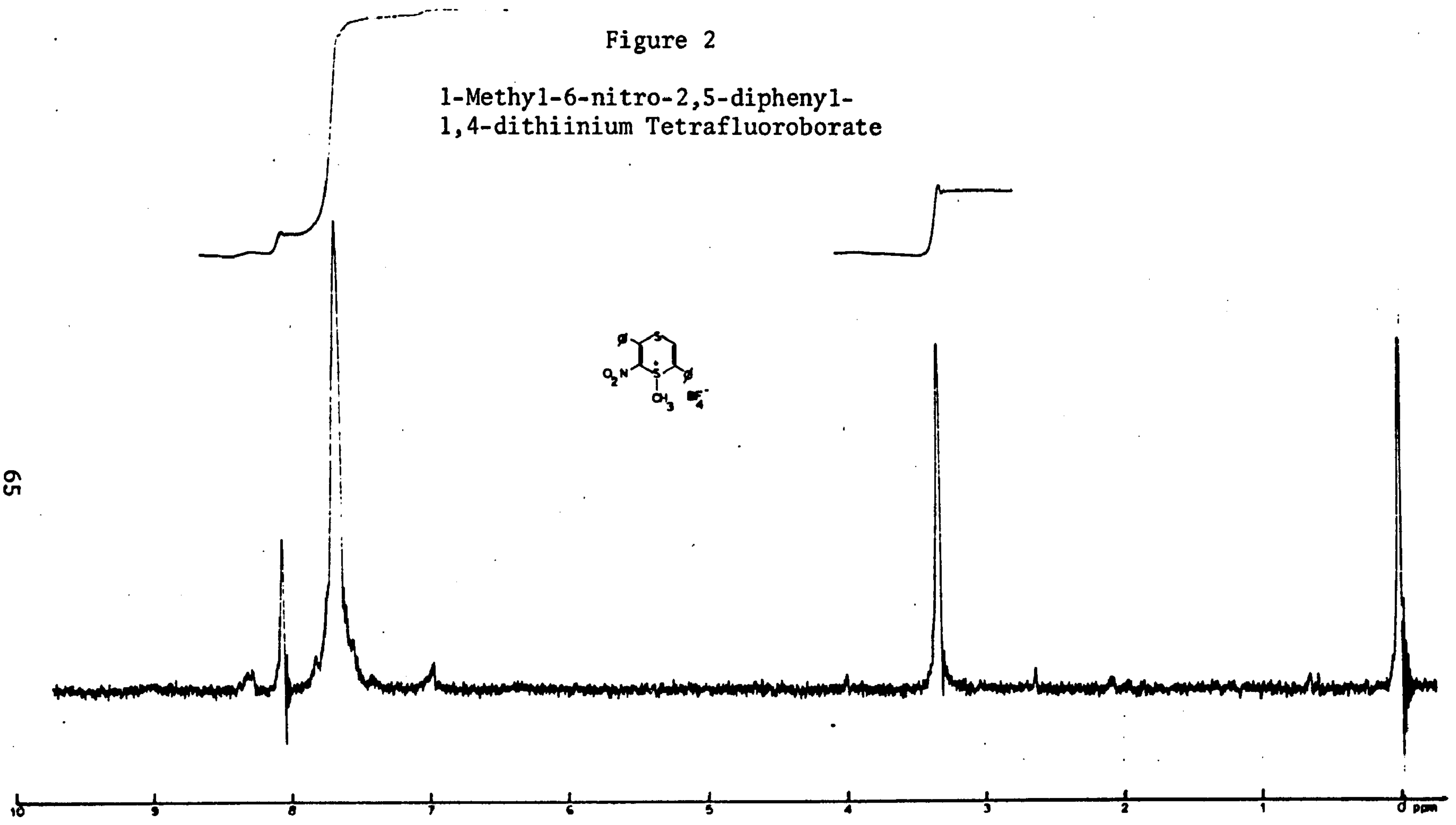


It was not unexpected, therefore, to find that methylation of V also yielded a mixture of two products in a ratio of 3:1 (see experimental section). The major product, isolated in pure form by recrystallization of the mixture using Norit A, gave an nmr spectrum (Figure 2) with a singlet at δ 8.05 ppm, an aromatic multiplet centered at 7.7, and a methyl singlet at 3.33 ppm which integrated to the ratio 1:10:3, respectively. Since the vinyl proton of this compound appears in the same region of the spectrum as that of the deshielded H-3 proton (δ8.15) of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I),[1b] the structure was assigned as 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X).

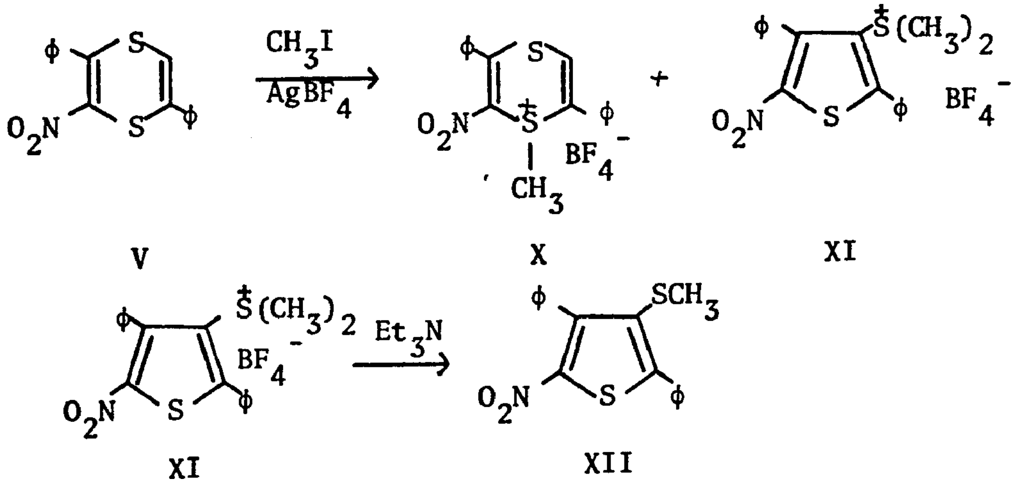
The minor product of the methylation of 3-nitro-2,5-diphenyl-1,4-dithiin (V), which was isolated in pure form by chromatography of the 3:1 mixture on a column of alumina, showed an nmr

Figure 2

1-Methyl-6-nitro-2,5-diphenyl-
1,4-dithiinium Tetrafluoroborate



spectrum (Figure 3) with a methyl singlet at δ3.02 and an aromatic multiplet at 7.7 ppm which integrated to the ratio 6:10. Demethylation of this minor product with triethylamine yielded a compound which showed a parent peak of m/e 327 in the mass spectrum and a methyl singlet at δ1.78 and an aromatic multiplet centered at 7.45 in the nmr spectrum (Figure 4) which integrated to the ratio 3:10. 3-Dimethylsulfonium-2,4-diphenyl-5-nitrothiophene tetrafluoroborate(XI) is quite consistent with the data for the minor product isolated from the methylation of V, while 2,4-diphenyl-3-methylthio-5-nitrothiophene (XII) fits the data for the product obtained when XI was demethylated.



The probable mode of formation of the dimethylthienyl sulfonium salt (XI) in the methylation reaction of V is proposed in Scheme III. Presumably the initially formed 1-methyl-3-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate XIII loses the elements of HBF_4 to form 2,4-diphenyl-3-methylthio-5-nitrothiophene

Figure 3

3-Dimethylsulfonium-2,4-diphenyl-5-
nitrothiophene Tetrafluoroborate

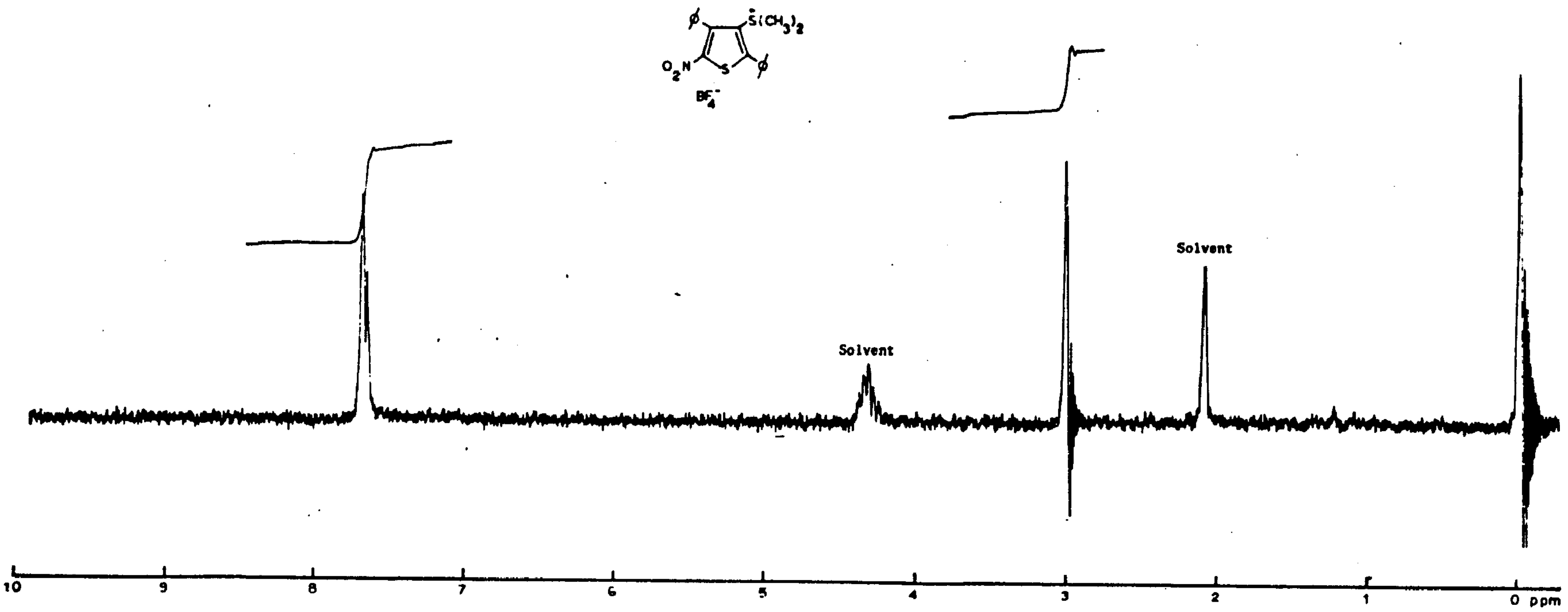
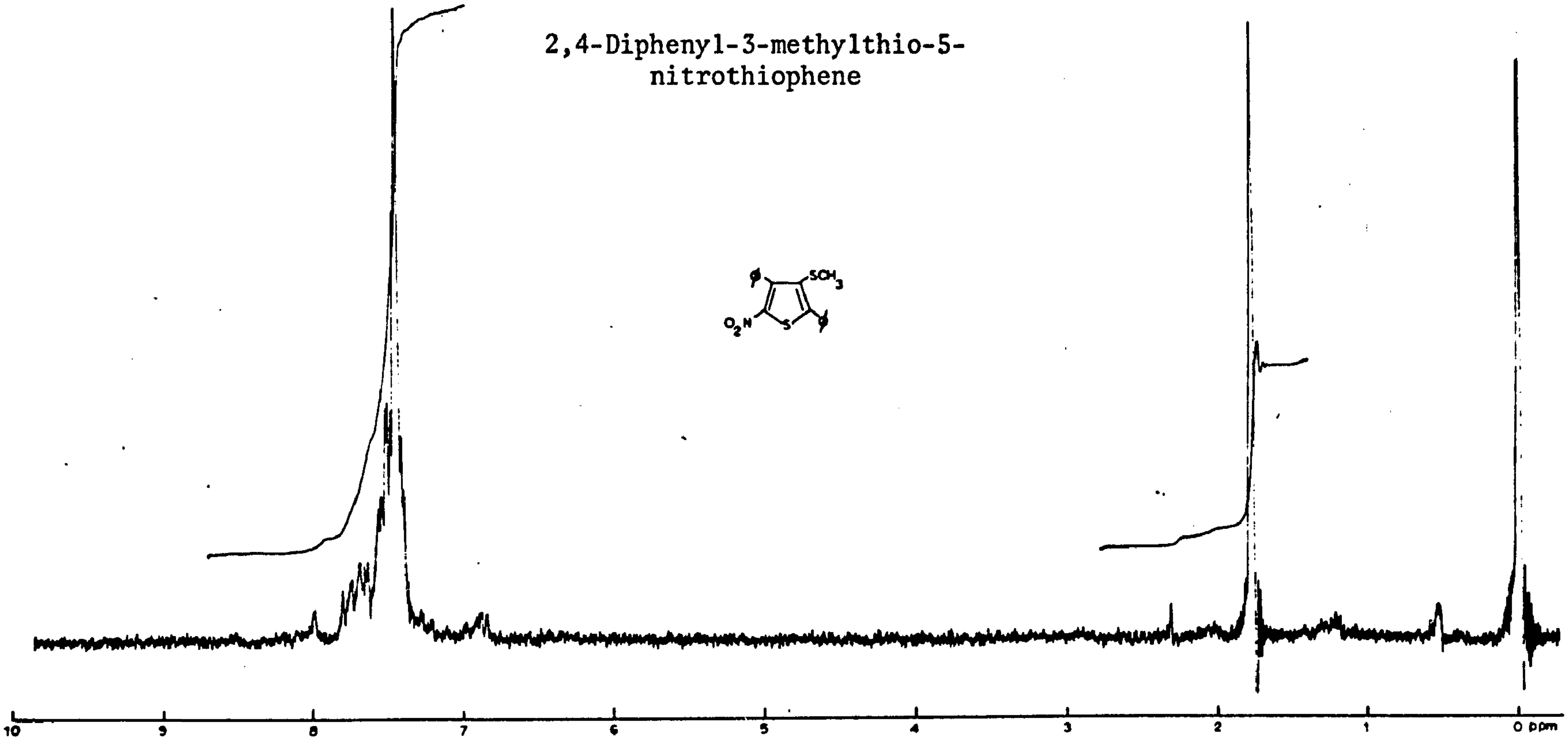
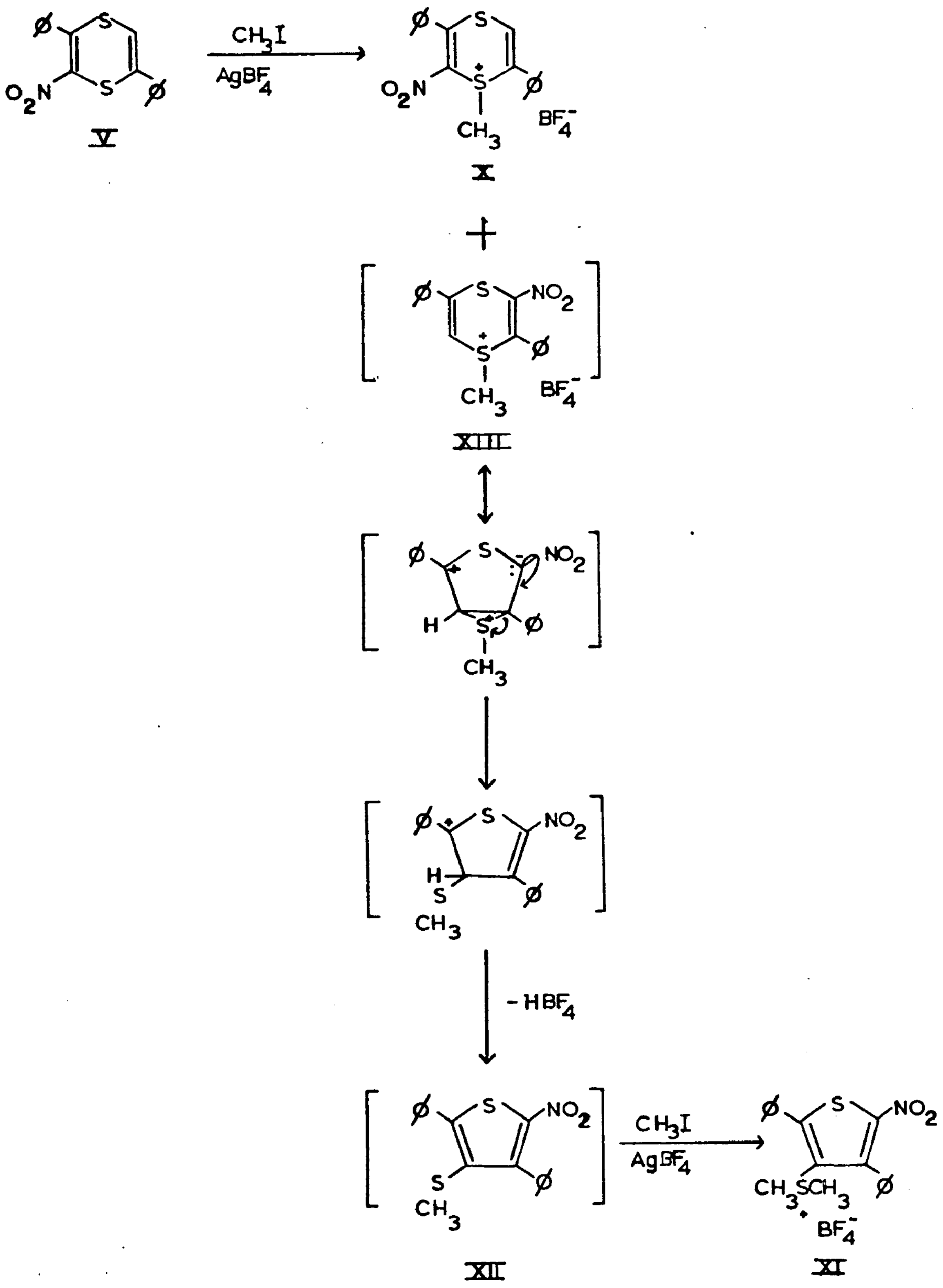


Figure 4

2,4-Diphenyl-3-methylthio-5-nitrothiophene

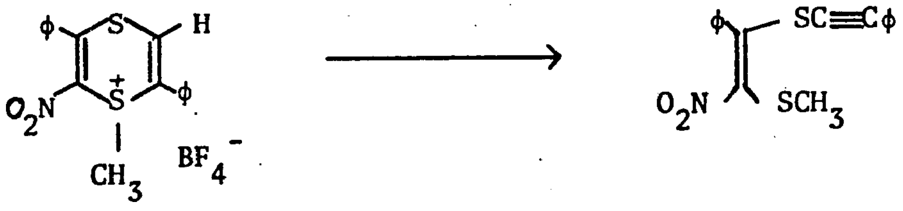


Scheme III



(XII) in a manner somewhat analogous to the known rearrangements of 2,5-diphenyl-1,4-dithiin derivatives to the more stable thiophenes by expulsion of sulfur monoxide or sulfur.[3,5,6,7] The thiophene XII is then methylated in the reaction media to the sulfonium salt XI which is the product ultimately isolated from the 3:1 mixture.

The 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X) was not eluted from the alumina column mentioned above, but rather a compound which has been assigned the structure 1-phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV) was eluted. XIV was also isolated as the sole product from the reaction of X with triethylamine and from the decomposition of X in a pH 6.8 phosphate buffer. The structural assignment of XIV was made on the basis of a triple bond stretch in the ir spectrum (Figure 5) and the nmr spectrum which showed a methyl singlet and a phenyl multiplet which integrated to the ratio 3:10 (Figure 6). The mode of formation indicates that XIV is of the *cis* configuration. A similar ring opening, which was mentioned previously, occurs when 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) is treated with sodium hydride,[1a,b] or stirred in pH 6.8 phosphate buffer.



X

XIV

Figure 5

1-Phenylethynylthio-2-methylthio-
2-nitro-1-phenylethylene

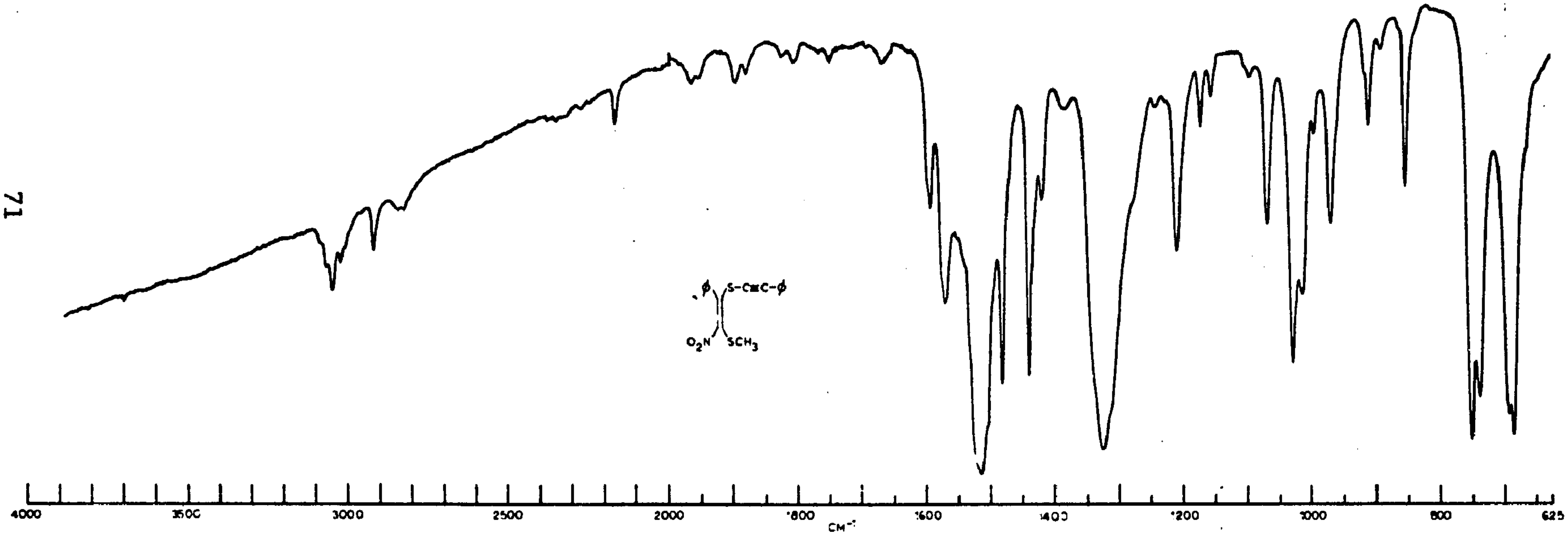
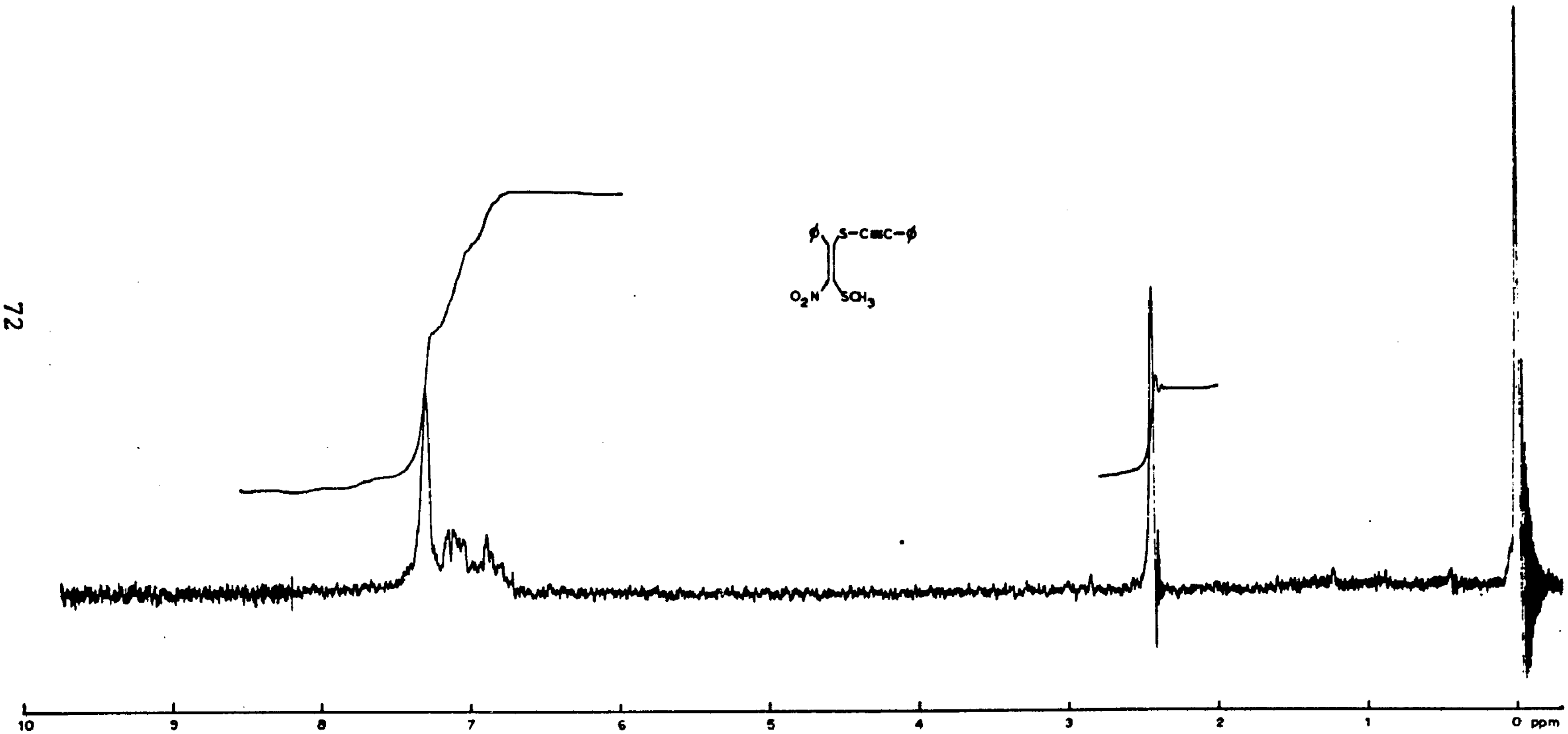
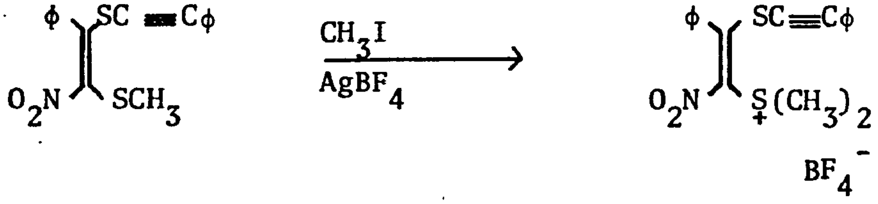


Figure 6

1-Phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene



Since methylation of the alkyne XIV would be expected to yield a product with the same empirical formula as the minor product isolated from the methylation of 3-nitro-2,5-diphenyl-1,4-dithiin (V), a reaction of XIV with methyl iodide-silver tetrafluoroborate was carried out. The product obtained showed an infrared spectrum (Figure 7) with a triple bond stretch at 2160 cm^{-1} and an nmr spectrum (Figure 8) with a methyl singlet at δ3.38 and an aromatic multiplet at 6.8-7.8 ppm which integrated to the ratio 6:10. On the basis of these data the structure was assigned as 1-phenylethynylthio-2-dimethylsulfonium-2-nitro-1-phenylethylene tetrafluoroborate (XV), which is definitely not the same compound as the minor product obtained from the methylation of V. This result would seem to provide further evidence that the structure assignment of the minor product of the methylation reaction of V as the dimethylthienylsulfonium compound (XI) is correct.



XIV

XV

Attempts to methylate 3,6-dinitro-2,5-diphenyl-1,4-dithiin (VI) and 3-bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII) with CH_3I-$AgBF_4$ were unsuccessful. Only the starting dithiin and/or products which were later found to result from thermal decomposition of the starting dithiin could be obtained from the reaction mixture,

Figure 7

1-Phenylethynylthio-2-dimethylsulfonium-
2-nitro-1-phenylethylene Tetrafluoroborate

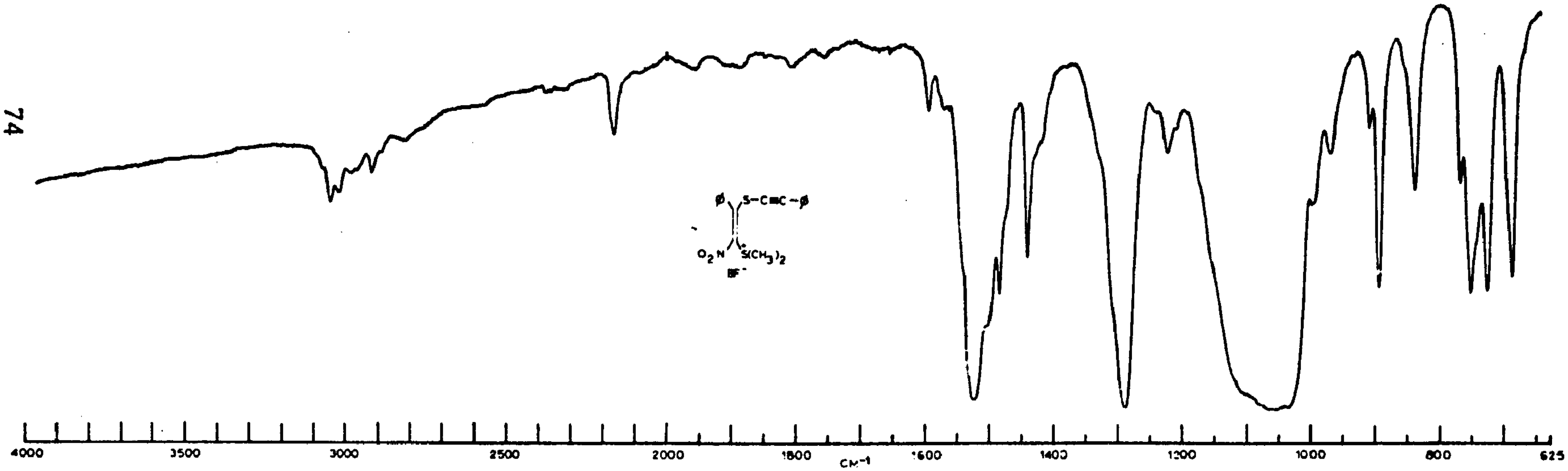
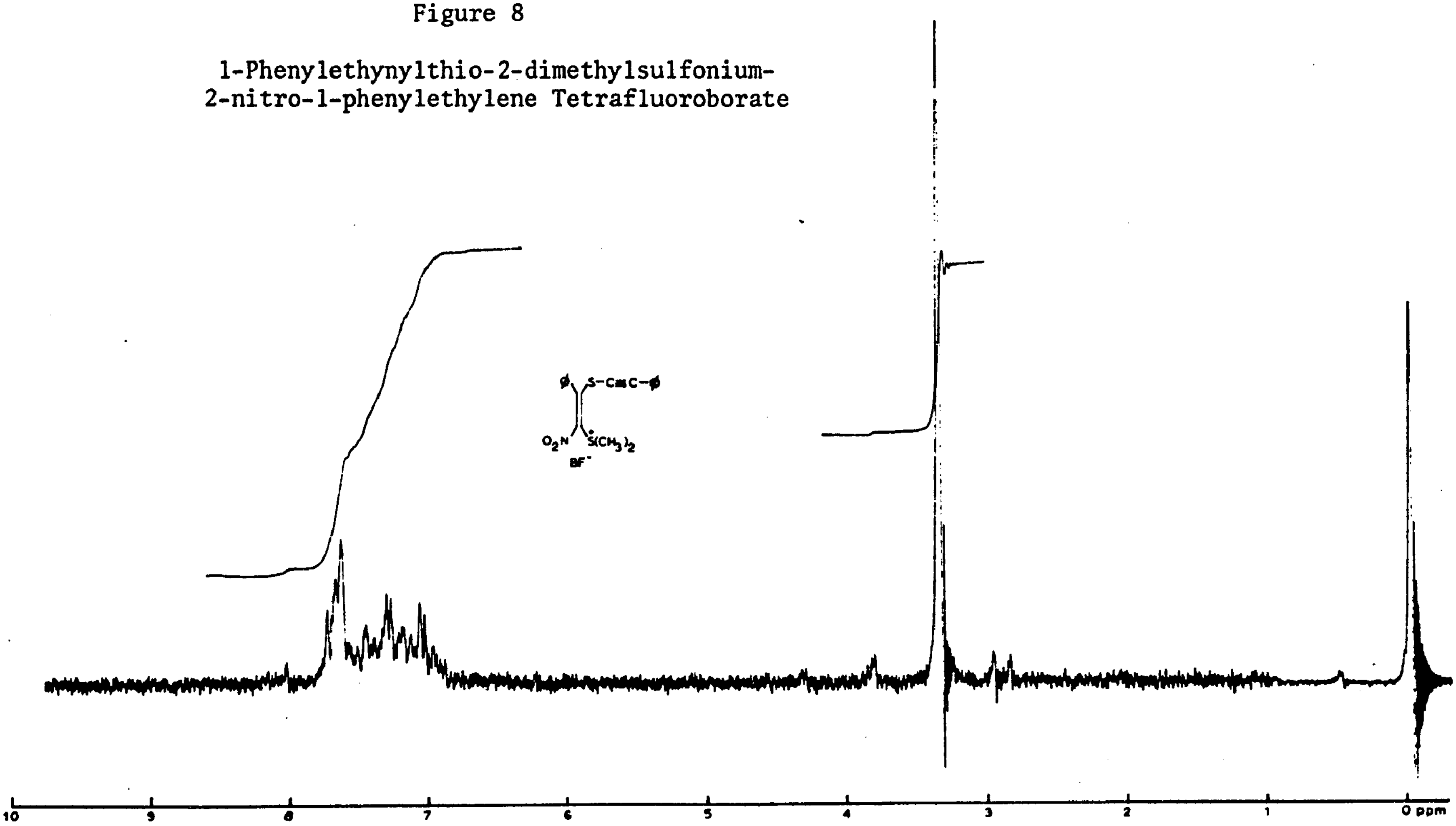
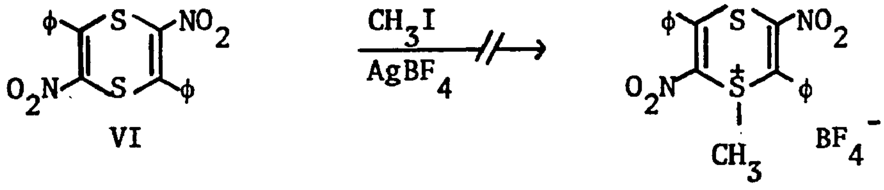


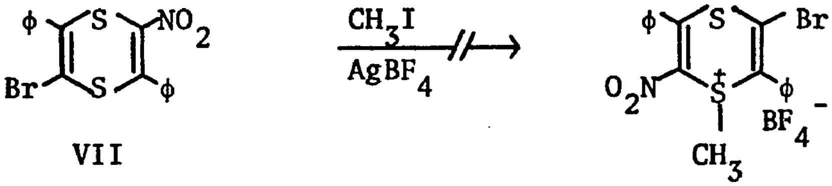
Figure 8

1-Phenylethynylthio-2-dimethylsulfonium-2-nitro-1-phenylethylene Tetrafluoroborate

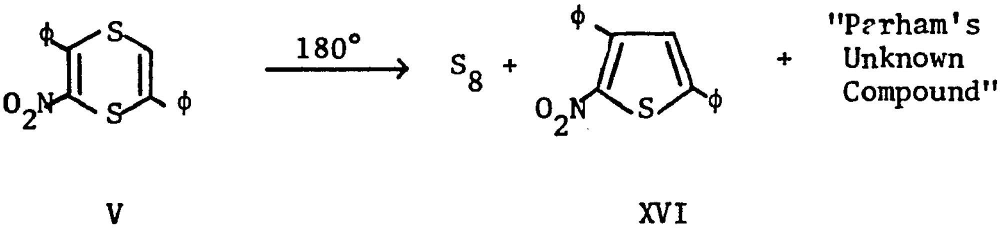


although high yields of AgI were found. However, it was found that mixing only CH_3I and $AgBF_4 \cdot 4CH_3CN$ in the same solvent system as the attempted methylation reactions (CH_2Cl_2-CH_3NO_2) also gave high yields of AgI, presumably due to methylation of the coordinated acetonitrile.

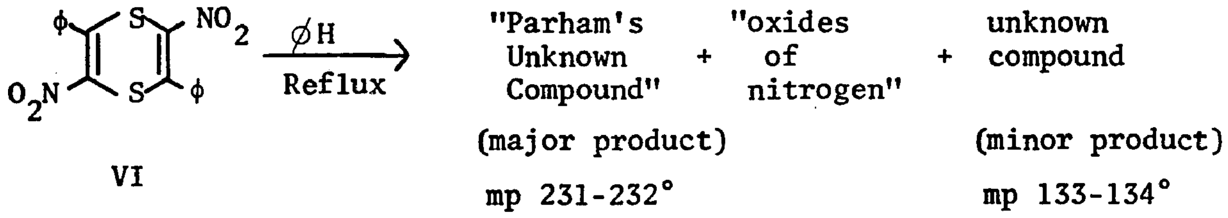




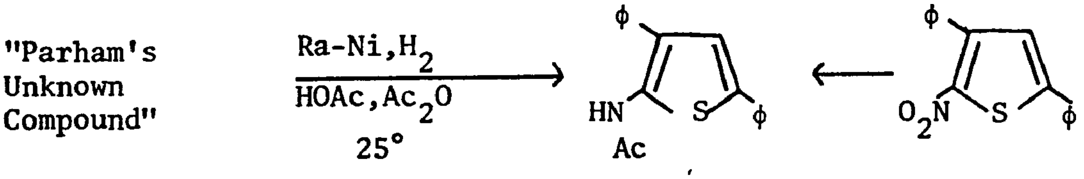
Parham and co-workers[3] found that 3-nitro-2,5-diphenyl-1,4-dithiin (V) thermally decomposed to give monoclinic sulfur, 2,4-diphenyl-5-nitrothiophene (XVI), and a compound of unknown structure which will henceforth be referred to as "Parham's Unknown Compound." In a later report,[4] these workers stated that 3,6-



dinitro-2,5-diphenyl-1,4-dithiin (VI) was found to decompose in refluxing benzene to give "Parham's Unknown Compound" and "oxides of nitrogen," as well as a small amount of another unknown compound of mp 133-134°which was not further characterized. Parham's group[4] reported that "Parham's Unknown Compound" on reductive acetylation with Raney nickel, hydrogen, and acetic anhydride gave a compound that was identical to that obtained from reductive acetylation (no details given) of 2,4-diphenyl-5-nitrothiophene (XVI). This reduced



VI

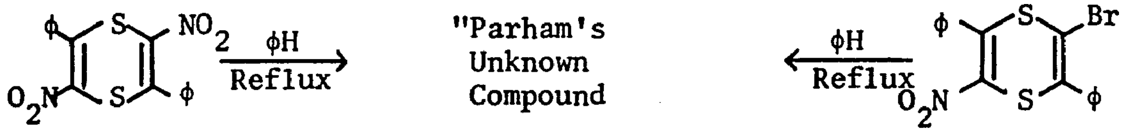


XVII XVI

compound was assigned the structure of 2,4-diphenyl-5-acetylaminothiophene (XVII) although no physical properties other than melting point were reported. These workers also reported that "Parham's Unknown Compound" was resistant to the action of hot alkaline permanganate in water but, again, no details of the experiment were given. On the basis of these data Parham's group[4] was unable to assign a structure to the compound.

The Parham thermal decomposition experiment of 3,6-dinitro-

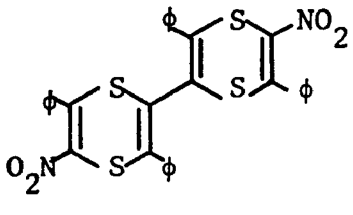
2,5-diphenyl-1,4-dithiin (VI) was repeated in an effort to gain more data on "Parham's Unknown Compound." The initial mixture obtained was recrystallized to give a single pure compound of melting point 237-238°. This compound, which was assumed to be "Parham's Unknown Compound," was found to be identical to the only product formed when 3-bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII) was thermally decomposed. The mass spectrum (see experimental section) of "Parham's Unknown Compound," in contrast to the nmr spectrum (Figure 9) which is not very illuminating, showed a parent peak at



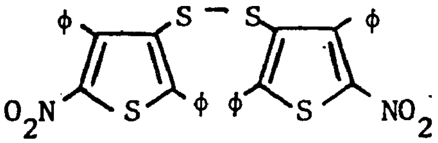
VI VII

m/e 624 and another major peak at m/e 312 with no peaks appearing between these values. This spectrum would therefore seem to suggest a symmetrical dimeric structure.

It appears that structures XVIII and XIX are the only two possible structures for "Parham's Unknown Compound" which are



XVIII



XIX

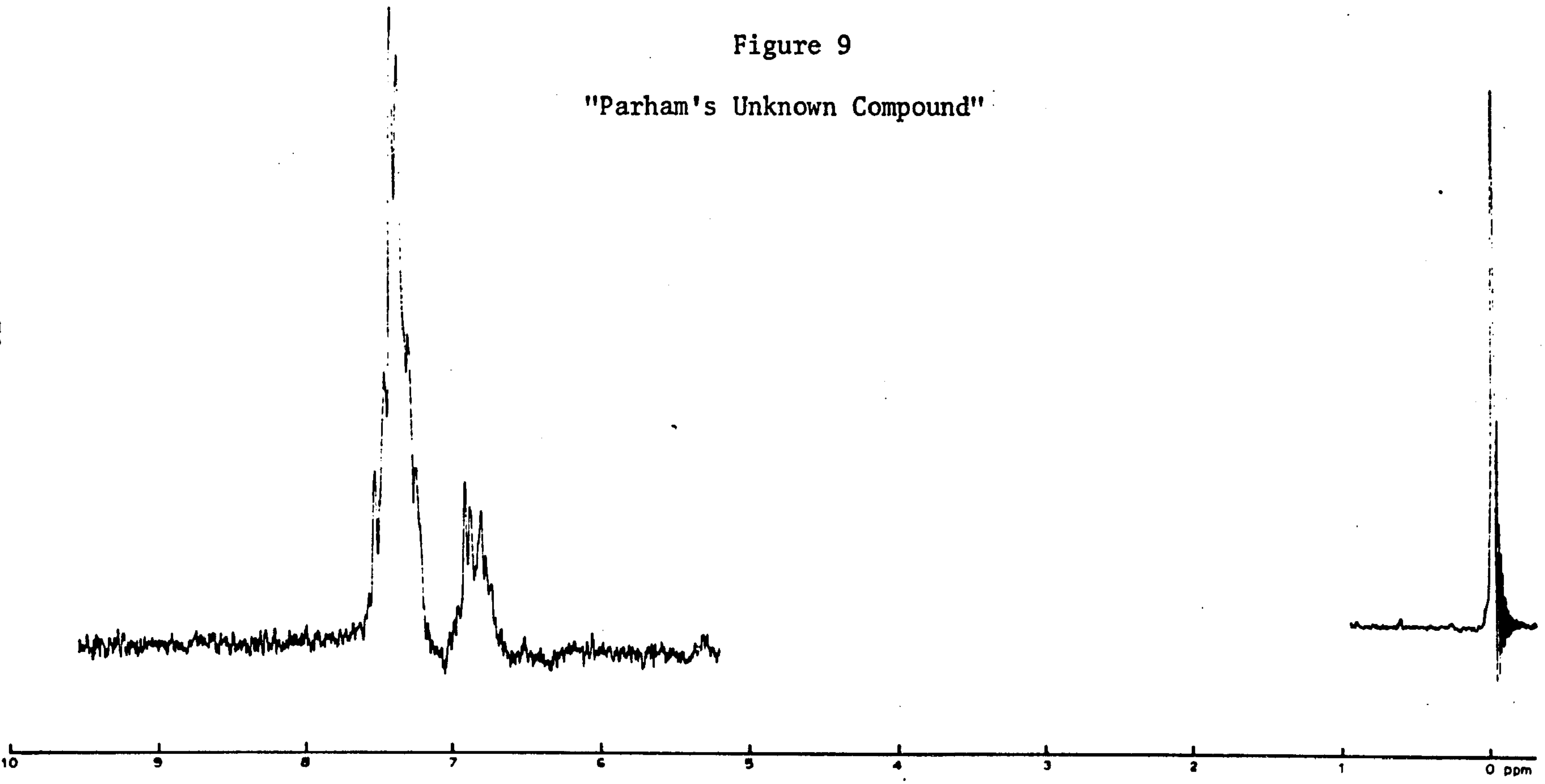
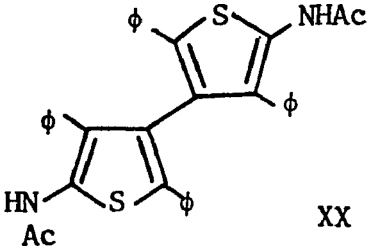


Figure 9

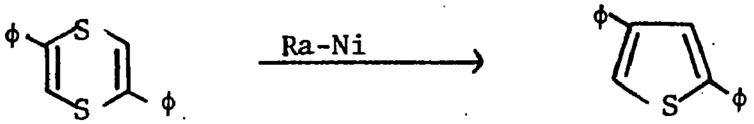
"Parham's Unknown Compound"

consistent with the mass spectral data and the elemental analysis. Although both XVIII and XIX would be expected to be oxidized in Parham's permanganate experiment,[4] it may be rationalized that lack of reaction was due to the insolubility of "Parham's Unknown Compound" in the aqueous media. If it is assumed that Parham[4] correctly identified the product of reductive acetylation of "Parham's Unknown Compound" as 2,4-diphenyl-5-acetylaminothiophene (XVII), then structure XVIII may be eliminated since the conditions of the experiment would not lead to cleavage of a carbon-carbon bond to produce the thiophene XVII.[8] However, it must be pointed out that Raney nickel may lead to formation of dimeric aromatic compounds from monomers,[9] and, therefore, the dimer XX may perhaps have been the compound to which Parham[4] assigned the structure of the monomer



XX

XVII. This dimeric compound XX would be a possible product of reductive acetylation of the dithiin dimer structure XVIII by analogy to a report of Badger et al.[10] that treatment of 2,5-diphenyl-1,4-dithiin (III) with Raney nickel led to 2,4-diphenylthiophene (XXI).



III

XXI

The dithienyl disulfide structure XIX, in contrast to the dithiin dimer XVIII, would be expected to give 2,4-diphenyl-5-acetylaminothiophene (XVII) on reductive acetylation.[11] Furthermore the dithienyl disulfide XIX would definitely be expected to undergo cleavage in the mass spectrometer between the two disulfide sulfurs by analogy to diphenyl disulfide.[12]

Taking all of these considerations into account, the structure of "Parham's Unknown Compound" cannot be assigned with absolute certainty; however, the evidence does seem to favor the bis(2,4-diphenyl-5-nitro-3-thienyl)disulfide (XIX).

Methylation of 3,6-dibromo-2,5-diphenyl-1,4-dithiin (VIII) gave only a 3% yield of the expected 1-methyl-3,6-dibromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (XXII) with a 73% recovery of starting material. A comparison of the ultraviolet spectra of VIII and XXII (Figure 10) indicates that the ratio $\epsilon_{XXII}/\epsilon_{VIII}$ reaches a maximum of 3.16 at 288 nm. Although a much higher ratio is desirable, it is perhaps possible to carry out kinetic studies with XXII using an ultraviolet technique. However, the bromine in the 6-position would preclude making any conclusions from such kinetic studies on the (p-d)-π interaction mentioned previously.

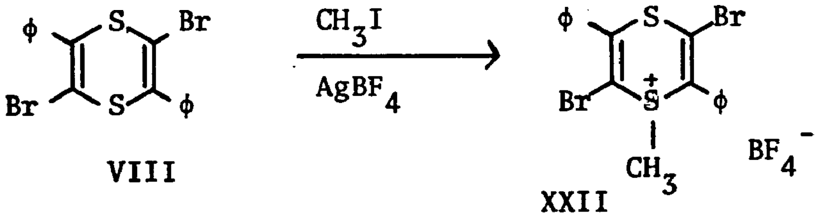
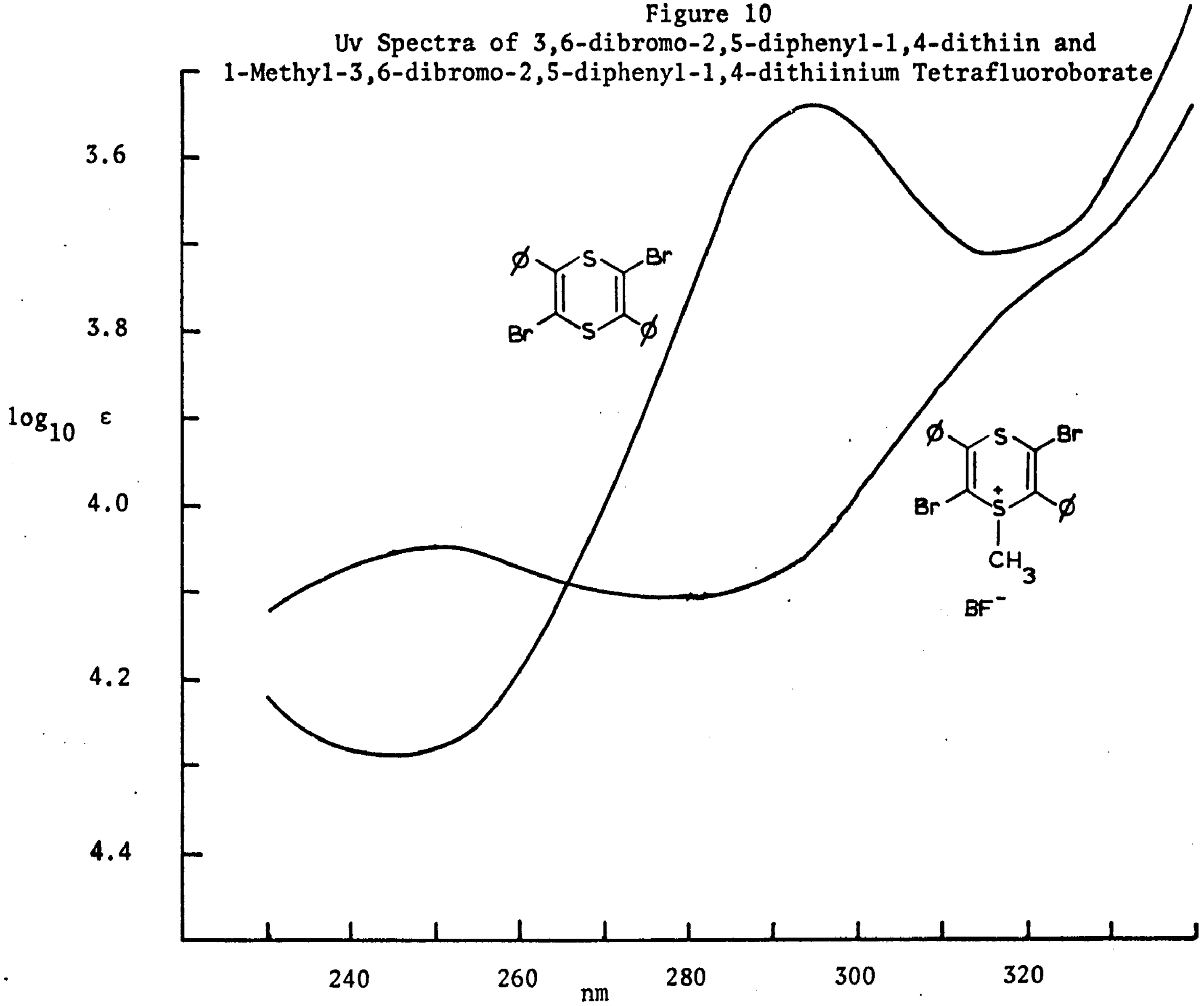


Figure 10
Uv Spectra of 3,6-dibromo-2,5-diphenyl-1,4-dithiin and
1-Methyl-3,6-dibromo-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate



No further work was carried out with this sulfonium salt (XXII).

CONCLUSIONS

It may be concluded from this work that methylation of a substituted 2,5-diphenyl-1,4-dithiin may occur on a sulfur that is sterically hindered or on a sulfur that is electronically deactivated, but methylation will only occur to a small extent if at all on a sulfur that is both sterically hindered and electronically deactivated.

EXPERIMENTAL SECTION

Melting points were determined in capillary tubes using a calibrated Mel-Temp apparatus. Ultraviolet spectra were recorded on a Perkin-Elmer 402 spectrophotometer and infrared spectra were taken on a Perkin-Elmer 257 or on a Beckman IR-33 instrument. Nuclear magnetic resonance spectra were determined on a Hitachi Perkin-Elmer R-20A high resolution spectrometer using tetramethylsilane as internal standard. Data are reported in the order δ (multiplicity, number of protons, assignment). Mass spectra were run at 70 eV by Dr. James E. Sturm on a Hitachi 6E high resolution instrument equipped with double focusing sector. Microanalyses were performed by Robertson Laboratories, Florham Park, New Jersey. 2,5-Diphenyl-1,4-dithiin was prepared using the procedure reported by Lazarus[1b], which is a modification of the method of Baker and Barkenbus.[13] $AgBF_4 \cdot 4CH_3CN$ was likewise prepared by the method of Lazarus[1a,b].

Decomposition of 1-Methyl-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate in Phosphate Buffer

Two-tenths g (0.00054 mol) of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (I) was stirred in 160 ml of pH 6.8 phosphate buffer (0.025 M in both KH_2PO_4 and Na_2HPO_4) at 37° overnight. The solid material that separated was removed by ether extraction to give 0.08 g (53%) of white crystals with mp 71-72° (Lit.[1a,b] mp 72-74°) and ir and nmr spectra identical to those reported by Lazarus[1a,b] for 1-phenylethynylthio-2-methylthio-1-phenylethylene (II).

Preparation of 3-Bromo-2,5-diphenyl-1,4-dithiin (IV)

The method of Parham[4] was used. To a stirred solution of 12.0 g (0.0445 mol) of 2,5-diphenyl-1,4-dithiin (III) in 600 ml of acetic anhydride was added dropwise a solution of 7.20 g (0.0450 mol) of bromine in 30 ml of glacial acetic acid. Ten minutes after the addition was complete, the solution was poured into ice water and stirred for 1 hr. The crude yellow solid was filtered, washed with water, and recrystallized from 95% ethanol to give 12.1 g (78.6%) of yellow needles with mp 83-84° (Lit.[4] mp 85-86°). Nmr (CCl_4) δ7.7-7.2 (m, 10, ArH), 6.62 (s, 1, vinyl H) ppm. Uv max (CH_3CN) 255 nm (log ε4.20).

Preparation of 1-Methyl-3-bromo-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (IX)

A procedure similar to that employed by Lazarus[1b] for the preparation of the corresponding perchlorate salt was followed.

To a stirred solution of 9.12 g (0.0263 mol) of 3-bromo-2,5-diphenyl-1,4-dithiin (IV) and 36.9 g (0.26 mol) of methyl iodide in 80 ml of methylene chloride and 40 ml of nitromethane was added a solution of 9.45 g (0.0263 mol) of $AgBF_4 \cdot 4CH_3CN$ in 80 ml of nitromethane. The reaction vessel was covered with aluminum foil and the mixture stirred for 18 hr. The yellow precipitate was then removed by filtration and washed with hot acetonitrile to give 6.0 g (97%) of silver iodide after drying. The filtrate and washings were combined and evaporated to yield material which was recrystallized from acetonitrile-ether to give 7.88 g (67%) of 1-methyl-3-bromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (IX) with mp 177-178° dec. Nmr (CD_3CN) δ 7.65 (m, 10, ArH), 6.69 (s, 1, H-6), 3.08 (s, 3, CH_3) ppm. Uv max (CH_3CN) 275 nm (log ε 4.32).

Anal. Calcd for $C_{17}H_{14}S_2BrBF_4$: C, 45.46; H, 3.14; S, 14.28; Br, 17.79; F, 16.92. Found: C, 45.45; H, 3.27; S, 14.43; Br, 18.00; F, 17.10.

Reaction of 1-Methyl-3-bromo-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (IX) with Diethylamine

To a stirred solution of 1.00 g (0.00222 mol) of 1-methyl-3-bromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (IX) in 40 ml of acetonitrile was added 0.324 g (0.00444 mol) of diethylamine in 2 ml of acetonitrile. After stirring overnight, 300 ml of ether was added to form a cloudy solution which was filtered and evaporated to give 0.55 g (72%) of a yellow solid which after recrystallization from 95% ethanol melted at 82-83°. The ir spectrum was identical to an authentic sample of 3-bromo-2,5-diphenyl-1,4-dithiin (IV).

Preparation of 3-Nitro-2,5-diphenyl-1,4-dithiin (V)

The procedure reported by Parham[3] was followed. A 10 M nitrating solution was prepared by mixing 31.6 ml of concentrated nitric acid (0.5 mol), 0.5 g urea and diluting the solution to 50 ml with glacial acetic acid. Four ml (0.040 mol) of the nitrating solution was added dropwise to a stirred solution of 10 g (0.0373 mol) of 2,5-diphenyl-1,4-dithiin (III) in 500 ml of acetic anhydride at room temperature. The resulting red solution was stirred for 5 min after the addition was complete and then poured into ice water. The solid which separated was recrystallized one time from ethyl acetate to yield 8.33 g (71%) of deep-red needles, mp 133-136° dec. (Lit.[3] mp 132-133° dec.). Nmr ($CDCl_3$) δ 7.8-7.0 (m, 10, ArH), 6.63 (s, 1, H-5)ppm. Uv max (CH_3CN) 226 nm (log ε 4.26).

Methylation of 3-Nitro-2,5-diphenyl-1,4-dithiin (V)

To a stirred solution of 4.57 g (0.0146 mol) of 3-nitro-2,5-diphenyl-1,4-dithiin (V) and 21 g (0.15 mol) of methyl iodide in 50 ml of methylene chloride was added 5.38 g (0.015 mol) of $AgBF_4 \cdot 4CH_3CN$ in 75 ml of nitromethane. The reaction flask was covered with aluminum foil and the mixture stirred overnight. The yellow precipitate that formed was removed by filtration and washed with nitromethane and ether to give 3.35 g (95%) of silver iodide. The combined washings and filtrate were concentrated on a rotary evaporator to the point at which a red precipitate appeared. The least amount of methylene chloride necessary to redissolve this precipitate was then added. Slow addition of ether with constant stirring precipitated 3.02 g of an olive-drab powder which was recrystallized once from acetonitrile-ether to yield 2.34 g of a yellow solid. This solid was roughly a 3:1 mixture of 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X) and 3-dimethylsulfonium-2,4-diphenyl-5-nitrothiophene tetrafluoroborate (XI) as determined by the ratio of the area of the nmr methyl peak of X to one-half the area of the nmr methyl peak of XI. The etheral filtrate was evaporated to yield a red solid which was recrystallized from ethyl acetate to give 0.92 g (20%) of unreacted V.

a. Isolation of 3-Dimethylsulfonium-2,4-diphenyl-5-nitrothiophene Tetrafluoroborate (XI)

The 2.34 g of the 3:1 mixture was stirred in 100 ml of approximately pH 7 phosphate buffer (0.025 M in both Na_2HPO_4 and KH_2PO_4) at 25° for 2 hr and at 50° for another 2 hr. The insoluble solid was removed and washed with benzene and ether to give 0.54 g of a white salt which showed only one of the two methyl groups originally present in the nmr spectrum of the mixture. An additional 0.05 g of product was obtained by evaporating the aqueous filtrate and recrystallizing the residual material from acetonitrile-ether. The total yield of 0.59 g* (9.4% based on V) was recrystallized

---

*This quantity represents the theoretical amount expected from 2.34 g of a 3:1 mixture of X and XI.

from absolute ethanol to yield material of mp 192° with nmr and ir spectra identical to those of the salt isolated in the chromatographic separation described below.

In another experiment the 3:1 mixture prepared by a methylation reaction analogous to that described above, was chromatographed on a column of alumina using acetonitrile as the eluent. Evaporation of the initial fractions yielded a yellow oil which crystallized. Recrystallization from absolute ethanol gave yellow needles of mp 60-61.5°. The ir and nmr spectra of the compound were identical to those of material subsequently prepared from pure 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X) and assigned the structure 1-phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV). Addition of ether to the later fractions precipitated a white salt which was recrystallized from absolute ethanol to yield analytical material with mp 194.5-195.5°, which is believed to be 3-dimethylsulfonium-2,4-diphenyl-5-nitrothiophene tetrafluoroborate (XI). Nmr (CD_3NO_2) δ 7.65 (m, 10, ArH), 2.85 (s, 6, CH_3's) ppm. Uv max (CH_3CN) 320 nm (log ε3.97). Ir(KBr) 3030 cm^{-1} (aromatic C-H), 2930 (aliphatic C-H). 1535, 1505, 1445, 1425, 1320 ($C-NO_2$), 1220, 1380, 1350-950 (B-F), 860, 795, 755, 700.

Anal. Calcd for $C_{18}H_{16}NS_2O_2BF_4$: C, 50.36; H, 3.76; N, 3.26; S, 14.94; F, 17.70. Found: C, 50.05; H, 3.84; N, 3.23; S, 15.42; F, 16.95.

b. Isolation of 1-Methyl-6-nitro-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (X)

The 3:1 mixture of X and XI was again prepared in a similar fashion using 11.7 g (0.0374 mol) of V, 53 g (0.374 mol) of methyl iodide, and 26.8 g (0.0748 mol) of $AgBF_4 \cdot 4CH_3CN$. Recrystallization of the mixture from acetonitrile-ether using Norit-A (neutral) gave 3.87 g (25% based on V) of a yellow solid with mp 152-152° dec. and nmr spectra containing only one of the two methyl peaks originally present in the spectrum of the mixture. Further recrystallization gave analytically pure 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X) with mp 150° dec. Nmr (CD_3NO_2) δ 8.28 (s, 1, H-3), 7.9-7.5 (m, 10, ArH), 3.38 (s, 3, CH_3) ppm; (CF_3COOD) δ 8.05 (s, 1, H-3), 7.9-7.5 (m, 10, ArH), 3.33 (s, 3, CH_3)ppm; (CD_3CN) δ 8.20 (s, 1, H-3), 7.9-7.5 (m, 10, ArH), 3.2 (s, 3, CH_3) ppm. Uv max (CH_3CN) 230 nm (log ε 4.22), 288 (4.14).

<u>Anal</u>. Calcd for $C_{17}H_{14}NS_2O_2BF_4$: C, 49.17; H, 3.40; N, 3.37; S, 15.44; F, 18.30. Found: C, 49.26; H, 3.49; N, 3.11; S, 15.20; F, 18.24.

Reaction of 3-Dimethylsulfonium-2,4-diphenyl-5-nitrothiophene Tetrafluoroborate (XI) with Triethylamine

Excess triethylamine was added to an nmr tube containing a concentrated solution of 3-dimethylsulfonium-2,4-diphenyl-5-nitrothiophene tetrafluoroborate (XI) in CD_3CN. The spectrum taken after 3 min showed only peaks corresponding to 2,4-diphenyl-3-methylthio-5-nitrothiophene (XII), triethylamine, and Et_3NMeBF_4. Addition of ether to the solution precipitated a white, hygroscopic solid with an nmr spectrum identical to that of Et_3NMeI prepared by reacting trimethylamine and methyl iodide. Evaporation of the filtrate gave a yellow solid of mp 88-91°. Recrystallization from absolute ethanol gave yellow crystals with mp 90.5-91°, believed to be 2,4-diphenyl-3-methylthio-5-nitrothiophene (XII). Nmr ($CDCl_3$) δ 7.9-7.2 (m, 10, ArH), 1.78 (s, 3, CH_3) ppm. Ir (KBr) 3030 cm^{-1} (aromatic C-H), 2920 (alkane C-H), and strong bands at 1500 (aromatic $C-NO_2$), 1310 (aromatic $C-NO_2$), 755, and 690. Uv max (CH_3CN) 248 nm (log ε 4.05), 338 (3.90). Mass spectrum m/e 327 (M^+) (relative intensity 100%), 266 (9), 234 (24), 221(14), 218 (10), 202 (15), 189 (17), 155 (8), 133 (12), 121 (34), 105 (13), 89 (15), 81 (35), 77 (10).

Anal. Calcd for $C_{17}H_3NS_2O_2$: C, 62.36; H, 4.00; N, 4.28; S, 19.59. Found: C, 62.17; H, 4.23; N, 4.08; S, 19.50.

Preparation of 1-Phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV)

Five-tenths g (0.0012 mol) of 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (X) was vigorously stirred in 100 ml of pH 7 phosphate buffer (see above) at 50° for 1.5 hr. Filtration yielded 0.34 g (87%) of a gold solid with mp 58-60°. Recrystallization from absolute ethanol gave yellow needles of mp 64-65°. Nmr (CCl_4) δ 7.5-6.7 (m, 10, ArH), 2.45 (s, 3,CH_3) ppm. Ir (KBr) 2170 cm^{-1} ($C\equiv C$).

Anal. Calcd for $C_{17}H_{13}NS_2O_2$: C, 62.36; H, 4.00; N, 4.28; S, 19.59. Found: C, 62.13; H, 4.14; N, 4.10; S, 19.44.

Reaction of 1-Methyl-6-nitro-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (X) with Triethylamine

Five-tenths g (0.0012 mol) of 1-methyl-6-nitro-2,5-diphenyl 1,4-dithiinium tetrafluoroborate (X) and 0.122 g (0.0012 mol) of triethylamine were stirred in 25 ml of acetonitrile at 25° for 1 hr. Addition of 450 ml of ether and stirring for 0.5 hr on an ice bath led to precipitation of a hygroscopic white solid (Et_3NHBF_4?) which was removed by filtration. Evaporation of the etheral filtrate yielded 0.34 g (87%) of a yellow-gold solid of mp 59-63°. One recrystallization from absolute ethanol gave yellow needles with mp 64-65° and nmr and ir spectra identical to those of 1-phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV) described above.

Methylation of 1-Phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV)

To a stirred solution of 0.50 g (0.00153 mol) of 1-phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene (XIV) and 2.2 g (0.015 mol) of methyl iodide in 10 ml of methylene chloride was added 0.55 g (0.00153 mol) of $AgBF_4 \cdot 4CH_3CN$ in 15 ml of nitromethane. The flask was covered with aluminum foil and the mixture was stirred for 24 hr. The silver iodide, removed by filtration and washed with nitromethane, weighed 0.34 g (94%). Ether was added to the combined filtrate and washings to yield 0.49 g (75%) of 1-phenylethynylthio-2-dimethylsulfonium-2-nitro-1-phenylethylene tetrafluoroborate (XV) of mp 178° dec. Recrystallization from acetonitrile-ether gave yellow crystals with mp 180-182° dec. Nmr (CD_3NO_2) δ 7.9-7.0 (m, 10, ArH), 3.39 (s, 6, CH_3's) ppm; (CF_3COOD) δ 7.8-6.8 (m, 10, ArH), 3.38 (s, 6, CH_3's) ppm. Ir (KBr) 2160 cm^{-1} (C≡C).

Anal. Calcd for $C_{18}H_{16}NS_2O_2BF_4$: C, 50.36; H, 3.76; N, 3.26; S, 14.94; F, 17.70. Found: C, 50.25; H, 3.88; N, 3.39; S, 15.03; F, 17.68.

Preparation of 3,6-Dinitro-2,5-diphenyl-1,4-dithiin (VI)

The method of Parham[4] was employed. To a stirred solution of 10.05 g (0.0375 mol) of 2,5-diphenyl-1,4-dithiin (III) in 600 ml of acetic anhydride was added dropwise 12.5 ml (0.125 mol) of the 10 M nitrating solution prepared as described above. After the addition was complete the mixture was stirred for a few minutes and filtered. The orange product obtained was washed with acetic anhydride and methanol and dried to give material with mp 138° dec. The acetic anhydride filtrate was poured into ice water to yield additional product which was recrystallized from chloroform-pet. ether (b.p. 30-60°) to give a solid with mp 136-137° dec. The combined yield amounted to 7.0 g (52%). Further recrystallization gave analytically pure material with mp 142° dec. (Lit.[4] mp 136.5° dec.). Nmr ($CDCl_3$) 7.45 (s, ArH) ppm.

Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 53.60; H, 2.81; N, 7.81; S, 17.90. Found: C, 53.38; H, 2.98; N, 7.86; S, 17.70.

Preparation of 3-Bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII)

The procedure of Parham[4] was followed. To a stirred solution of 11.0 g (0.0317 mol) of 3-bromo-2,5-diphenyl-1,4-dithiin (IV) in 275 ml of acetic anhydride was added dropwise 4.33 ml (0.0433 mol) of the 10 M nitrating solution. The orange needles that formed were collected and washed with 95% ethanol to give 7.85 g (63%) of 3-bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII) of mp 146.5-147° (Lit.[4] mp 143-144°).

Thermal Decomposition of 3,6-Dinitro-2,5-diphenyl-1,4-dithiin (VI)

Three g (0.0084 mol) of 3,6-dinitro-2,5-diphenyl-1,4-dithiin (VI) was placed in 100 ml of benzene and refluxed until the evolution of brown gas ceased (*ca.* 2 hr). Addition of petroleum ether (bp 20-40°) precipitated a yellow solid which after washing with petroleum ether (bp 20-40°) weighed 1.1 g. The filtrate was evaporated to yield a brown oil which was stirred in absolute ethanol to yield an additional 0.24 g of product. The combined yields, which were shown by ir to be a mixture, were washed with hot ethanol and recrystallized from ethyl acetate to give 0.65 g (24%) of "Parham's Unknown Compound" with mp 234-236°. Further recrystallization from methylene chloride-ether yielded analytical material of mp 236.5-238°. (Parham[4] reported mp 231-232° for the major product in an identical reaction, but made no structure assignment.) Nmr ($CDCl_3$) δ 7.6-7.2 (m, 16, ArH), 7.15-6.65 (m, 4, ArH) ppm. Ir (KBr) 3045 cm^{-1} and 3010 (aromatic C-H), and strong bands at 1495 (C-NO_2), 1440, 1410, 1310 (C-NO_2), 860, 740, 690. Mass spectrum, m/e 624 (M^+)(relative intensity 60%), 312 (57), 296 (79), 281 (19), 279 (19), 266 (100), 249 (32), 234 (43), 221 (52), 216 (65), 206 (75), 189 (42), 178 (88), 129 (85), 121 (43), 105 (91), 89 (31), 77 (98), 51 (52).

Anal. Calcd for $C_{32}H_{20}S_4N_2O_4$: C, 61.52; H, 3.23; N, 4.48; S, 20.53. Found: C, 61.20; H, 3.45; N, 4.45; S, 20.28.

Thermal Decomposition of 3-Bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII)

3-Bromo-6-nitro-2,5-diphenyl-1,4-dithiin (VII) (0.67 g, 0.00171 mol) was dissolved in 30 ml of benzene and heated at reflux for 2 hr. The solvent was evaporated and a small amount of ethyl acetate was added to the residue to form a solid which was collected on a filter. The yellow crystals, after washing with ether, weighed 0.33 g (62%) with mp 236-238°. Recrystallization from ethyl acetate gave analytically pure material with mp 238.5-239°. The ir spectrum was identical to that of "Parham's Unknown Compound" isolated from the thermal decomposition of 3,6-dinitro-2,5-dipenyl-1,4-dithiin (VI). A mixed melting point was undepressed.

Anal. Calcd for $C_{32}H_{20}S_4N_2O_4$: C, 61.52; H, 3.23; N, 4.48; Br, 0. Found: C, 61.60; H, 3.45; N, 4.42; Br, 0.

Preparation of 3,6-Dibromo-2,5-diphenyl-1,4-dithiin (VIII)

The procedure of Parham[4] was used. To a stirred solution of 8.00 g (0.0298 mol) of 2,5-diphenyl-1,4-dithiin (III) was added dropwise 9.6 g (0.060 mol) of bromine in 12 ml of acetic acid. After the addition was complete the mixture was stirred for an additional 5 min and cooled. The white precipitate was filtered off, washed with water and methanol and recrystallized from ethyl acetate to yield 5.23 g (41%) of 3,6-dibromo-2,5-diphenyl-1,4-dithiin (VIII) with mp 166-168° (Lit.[4] mp 165-166°). Uv max (CH_3CN) 245 nm (log ε 4.29), 3.18 (3.71).

Preparation of 1-Methyl-3,6-dibromo-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (XXII)

To a stirred solution of 4.50 g (0.0105 mol) of 3,6-dibromo-2,5-diphenyl-1,4-dithiin (VIII) and 14 g (0.1 mol) of methyl iodide in 310 ml of methylene chloride and 345 ml of nitromethane was added 3.78 g (0.0105 mol) of $AgBF_4 \cdot 4CH_3CN$ in 100 ml of nitromethane. The flask was covered with aluminum foil and stirred overnight. The silver iodide filtered off from the lime-green solution weighed 1.46 g (61%) after washing with methylene chloride, nitromethane, and ether. Concentration of the combined filtrate and washings to 400 ml under aspirator pressure led to precipitation of 2.95 g of starting material VIII. The filtrate was then concentrated to 100 ml on a rotary evaporator. The precipitate obtained was combined with the starting material obtained previously to give a total recovery of 3.28 g (73%). About 800 ml of ether was added to the filtrate to precipitate a brown solid which was washed with benzene and ether. One recrystallization from acetonitrile-ether gave 0.17 g (3%) of product with mp 156-157° dec. Further recrystallization gave pure 1-methyl-3,6-dibromo-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (XXII) with mp 161-163° dec. Nmr (CD_3CN) 7.62 (m, 10, ArH), 3.30 (s, 3, CH_3) ppm. Uv max (CH_3CN) 282 nm (log ϵ 4.11).

Anal. Calcd for $C_{17}H_{13}S_2Br_2BF_4$: C, 38.67; H, 2.48; S, 12.14. Found: C, 38.47; H, 2.61; S, 12.40.

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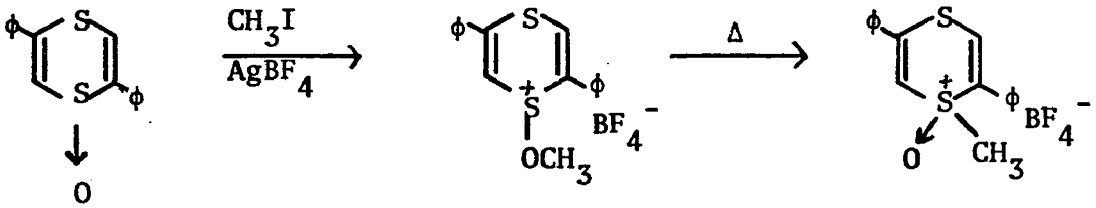
PART C

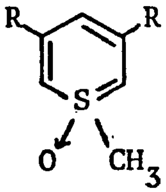
Methylation of 2,5-Diphenyl-1,4-dithiin-1-oxide

INTRODUCTION

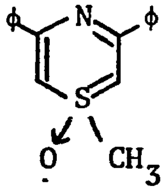
Methylation of a sulfoxide is known to yield an alkoxysulfonium salt which may rearrange to a more stable S-methyloxosulfonium salt.[1-4] Thus it would be expected that methylation of 2,5-diphenyl-1,4-dithiin-1-oxide (I) would initially yield the alkoxysulfonium salt (II) which might rearrange to the S-methyloxosulfonium salt (III), a compound somewhat similar in structure to compounds IV[5] and V[6] previously examined for aromaticity involving (p-d)-π bonds.



I II III



IV

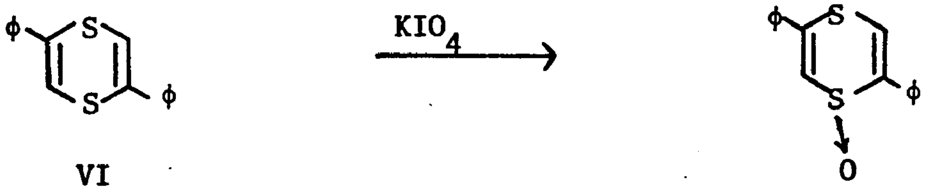


V

This section describes a study of the methylation of the sulfoxide (I) and an unexpected reaction that occurred when the initial product thermally decomposed.

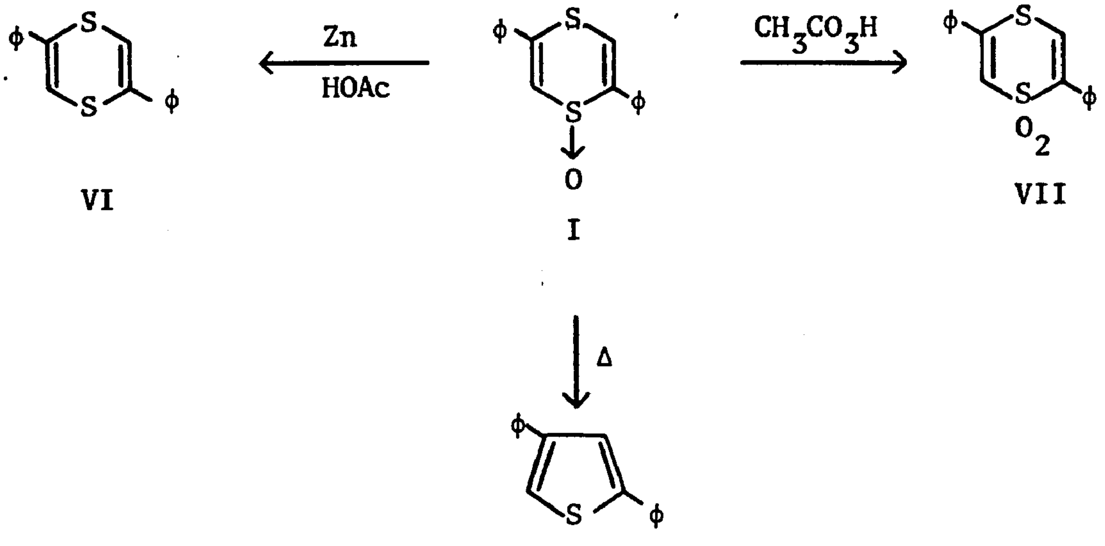
RESULTS AND DISCUSSION

2,5-Diphenyl-1,4-dithiin-1-oxide (I) was prepared for this work by treating 2,5-diphenyl-1,4-dithiin (VI) with potassium meta-periodate, although Szmant and Alfonso[7] originally used peracetic acid. These latter workers[7] found that the sulfoxide (I) could be further oxidized to 2,5-diphenyl-1,4-dithiin-1,1-dioxide (VII) with excess peracetic acid or reduced to the sulfide (VI) with zinc. Thermal decomposition of I led to 2,4-diphenylthiophene (VIII).[7]



VI

I



VI

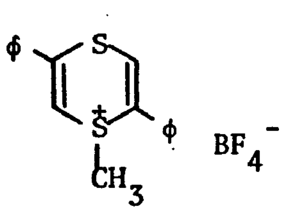
I

VII

VIII

More recently, Bandoli and co-workers[8] using x-ray methods showed that I is of the boat conformation with oxygen in an axial position. The mean C-S bond lengths were 1.71 Å and 1.75 Å for the unoxidized sulfur and the oxidized sulfur, respectively, in comparison to 1.82 Å for the normal C-S single bond.[8] The mean value of 1.335 Å for the length of the C-C bonds agrees with the length of the ethylene double bond.[8]

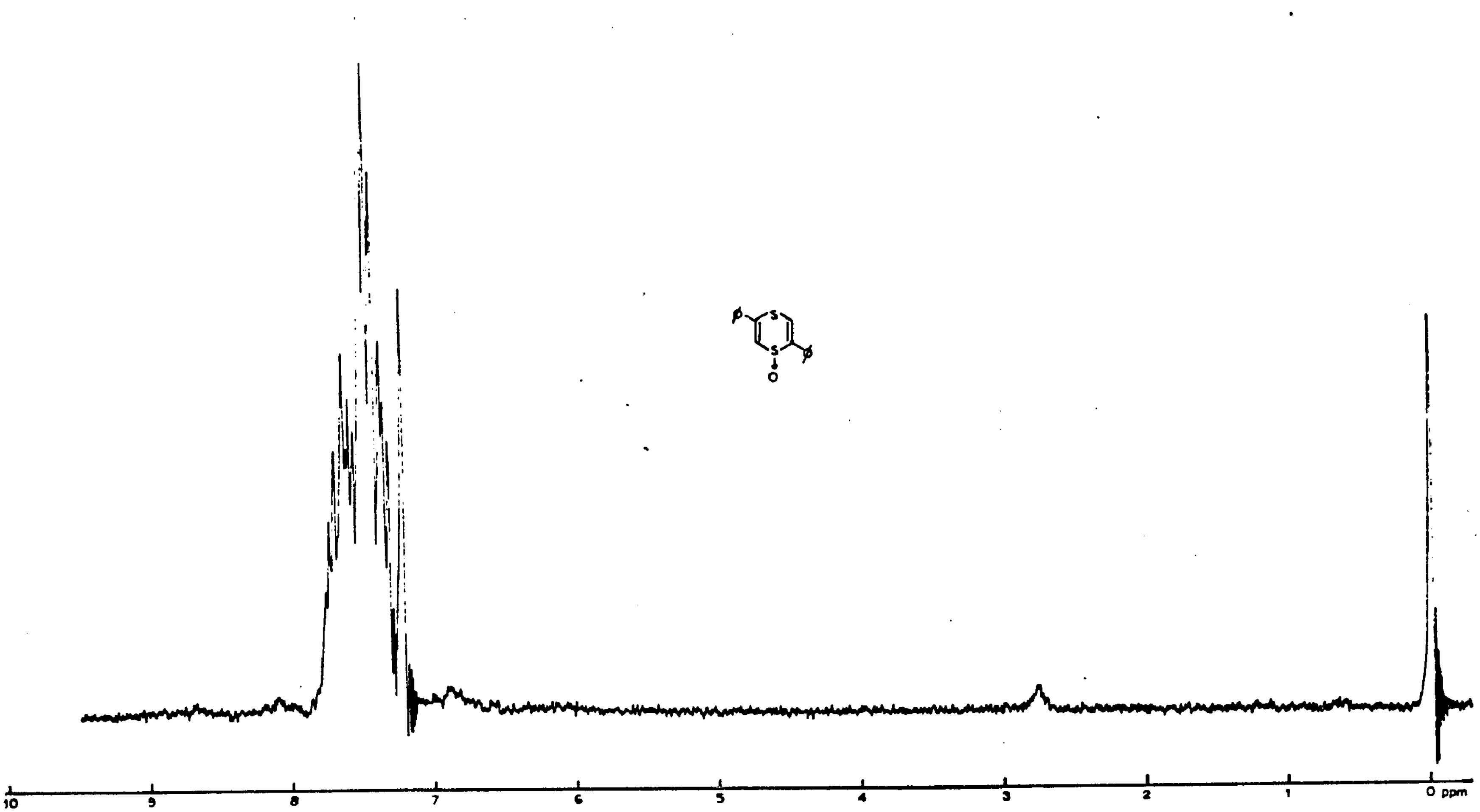
Bandoli et al.[8] also reported that the nmr spectrum ($CDCl_3$, TMS) of I showed two singlets at δ 7.32 ppm and 7.58 ppm corresponding to the vinyl protons. The lower field signal, which overlapped with the phenyl protons centered at δ 7.60 ppm, was shown by the spectrum of the corresponding sulfoxide in which the phenyl rings were deuterated.[8] The nmr spectrum ($CDCl_3$, TMS) of a sample of the sulfoxide (I) used in the present work, shown in Figure 1, shows a singlet at δ 7.23 and a multiplet centered at 7.52 ppm. The lower field singlet can probably be assigned to the H-3 proton of I by analogy to the deshielded H-3 proton of 1-methyl-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (IX)[9a,b] which was discussed in Part B of this thesis. The much smaller amount of deshielding of the H-3 proton of the sulfoxide I in comparison to the H-3 proton of the sulfonium salt IX is most likely due to the (p-d)-π bonding of the sulfoxide group,[10] which leads to a lower positive



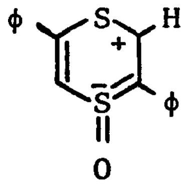
IX

Figure 1

2,5-Diphenyl-1,4-dithiin-1-oxide

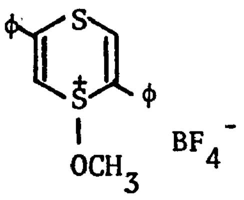


charge on the sulfoxide sulfur. However, since some deshielding of the H-3 proton of the sulfoxide occurs in respect to the vinyl proton of the dithiin VI,* a contributing resonance structure such as Ia may be postulated.[10]

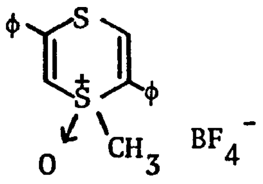


Ia

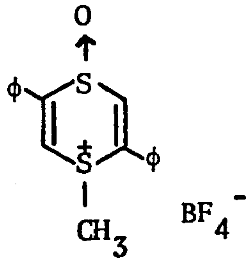
Methylation of 2,5-diphenyl-1,4-dithiin-1-oxide (I) with methyl iodide-silver tetrafluoroborate at 23°C yielded a white, unstable solid with elemental analysis and nmr spectrum (Figure 2) consistent with the alkoxysulfonium salt (II), the S-methyloxosulfonium salt (III), or the 1-methyl-4-oxide salt (X). The nmr spectrum



II



III



X

(CD_3CN, TMS) of this product (Figure 2), shows a vinyl proton singlet at δ 8.76 ppm, an aromatic multiplet centered at 7.70, a vinyl singlet at 7.48, and a methyl singlet at 3.64 ppm which integrated to the ratio 1:10:1:3, respectively. This spectrum is similar to that reported by Lazarus[9b] for 1-methyl-2,5-diphenyl-

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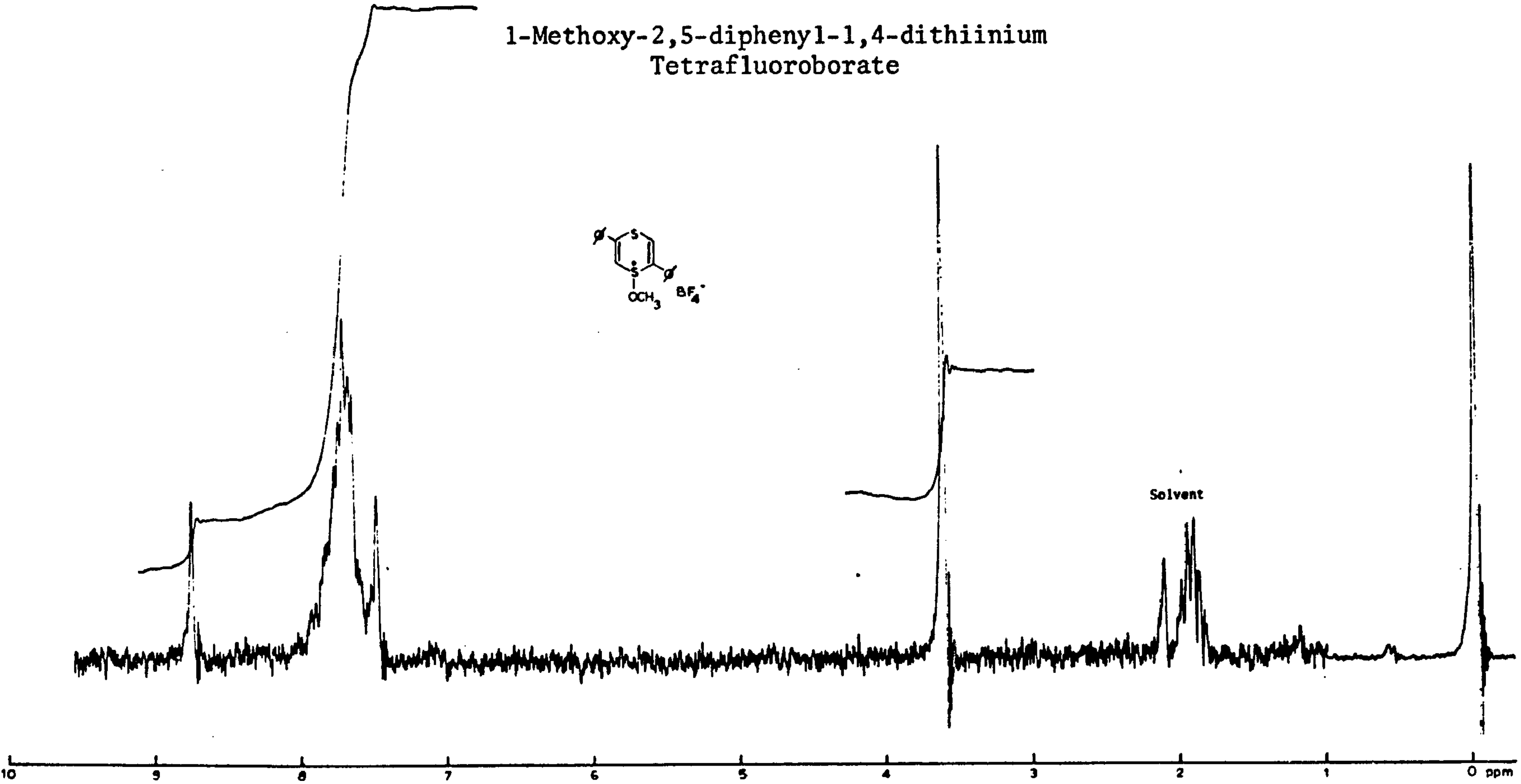
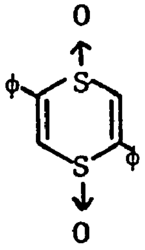
* Lazarus[9b] reported that the nmr spectrum ($CDCl_3$, TMS) of 2,5-diphenyl-1,4-dithiin (VI) showed a vinyl singlet at δ 6.58 and an aromatic multiplet at 7.5 ppm.

Figure 2

1-Methoxy-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate



1,4-dithiinium tetrafluoroborate (IX) in the same solvent: a vinyl singlet at δ 8.35 ppm, an aromatic multiplet centered at 7.72, a vinyl singlet at 6.65, and a methyl singlet at 2.98 ppm. The infrared spectrum of the unstable product (Figure 3) lacks the very strong absorbance at 1233 cm^{-1} that is characteristic of the +S=O stretch,[11] which would be present if the product were the S-methyl oxosulfonium salt III. Furthermore, it might be reasoned that the 1-methyl-4-oxide structure (XI) for the product is relatively unlikely by analogy to the oxidation of the sulfoxide I to the sulfone VII[7] rather than to the disulfoxide (XI). The extreme heat and light sensitivity of this product would suggest the alkoxysulfonium



XI

structure II by analogy to the methylation of other sulfoxides.[2,4]

In contrast to S-methyloxosulfonium compounds, alkoxysulfonium compounds are known to undergo facile hydrolysis to produce one equivalent of acid.[2,4] This reaction has been shown to involve attack on the sulfur atom as shown in Scheme I.[4,12] When

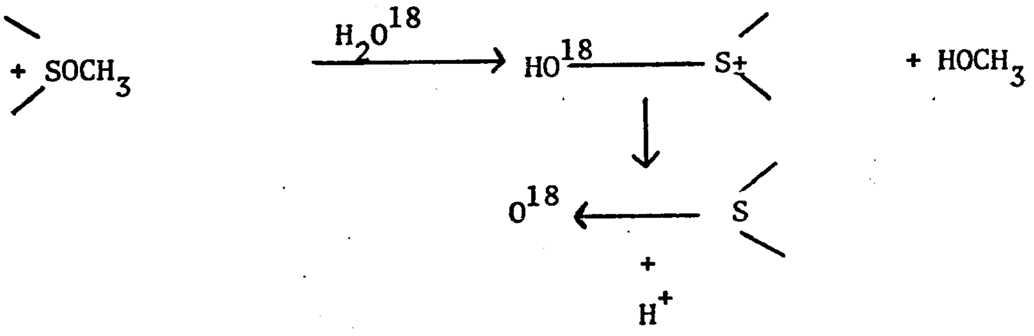
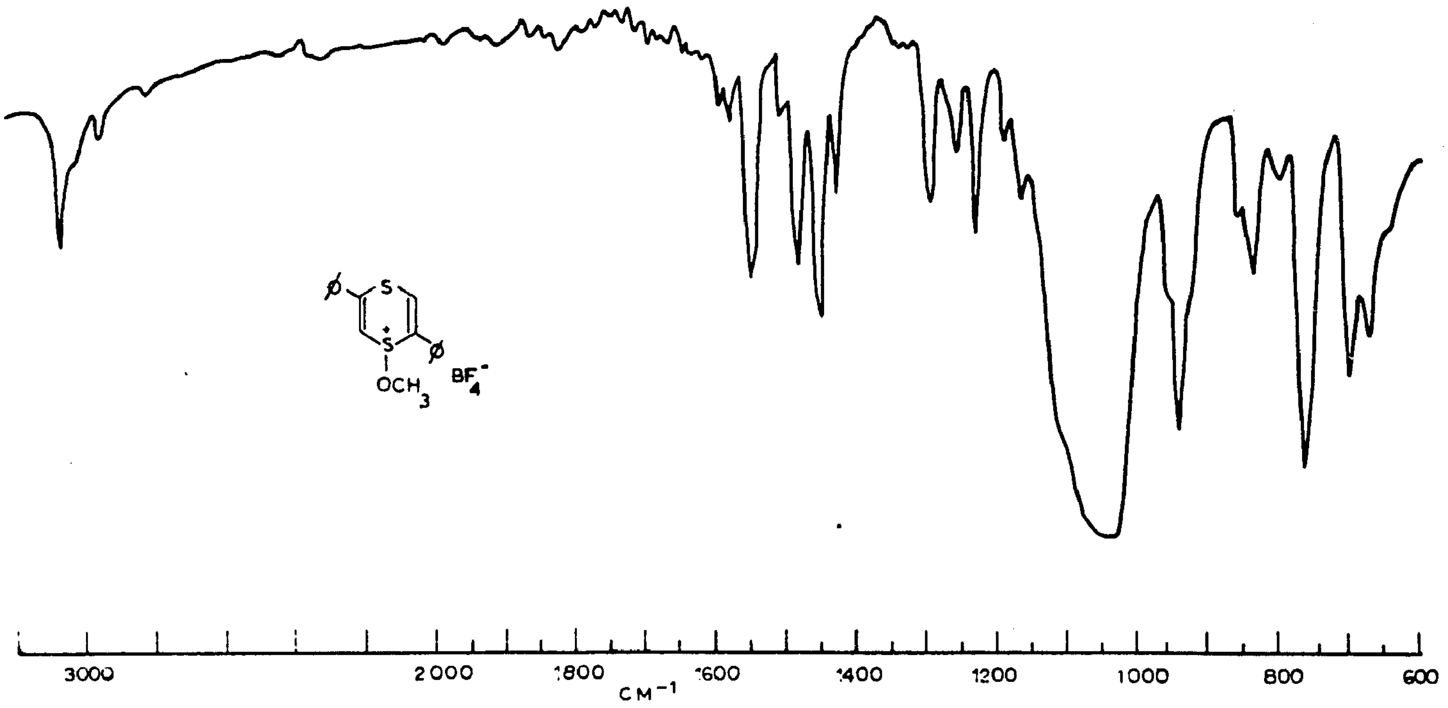
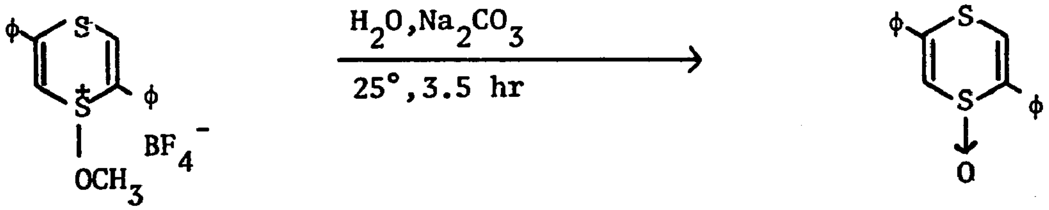


Figure 3

1-Methoxy-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate



the unstable product derived from methylation of I was slurried in water at room temperature the solution became acidic. Addition of sodium carbonate and filtration led to nearly quantitative yield of 2,5-diphenyl-1,4-dithiin-1-oxide (I).



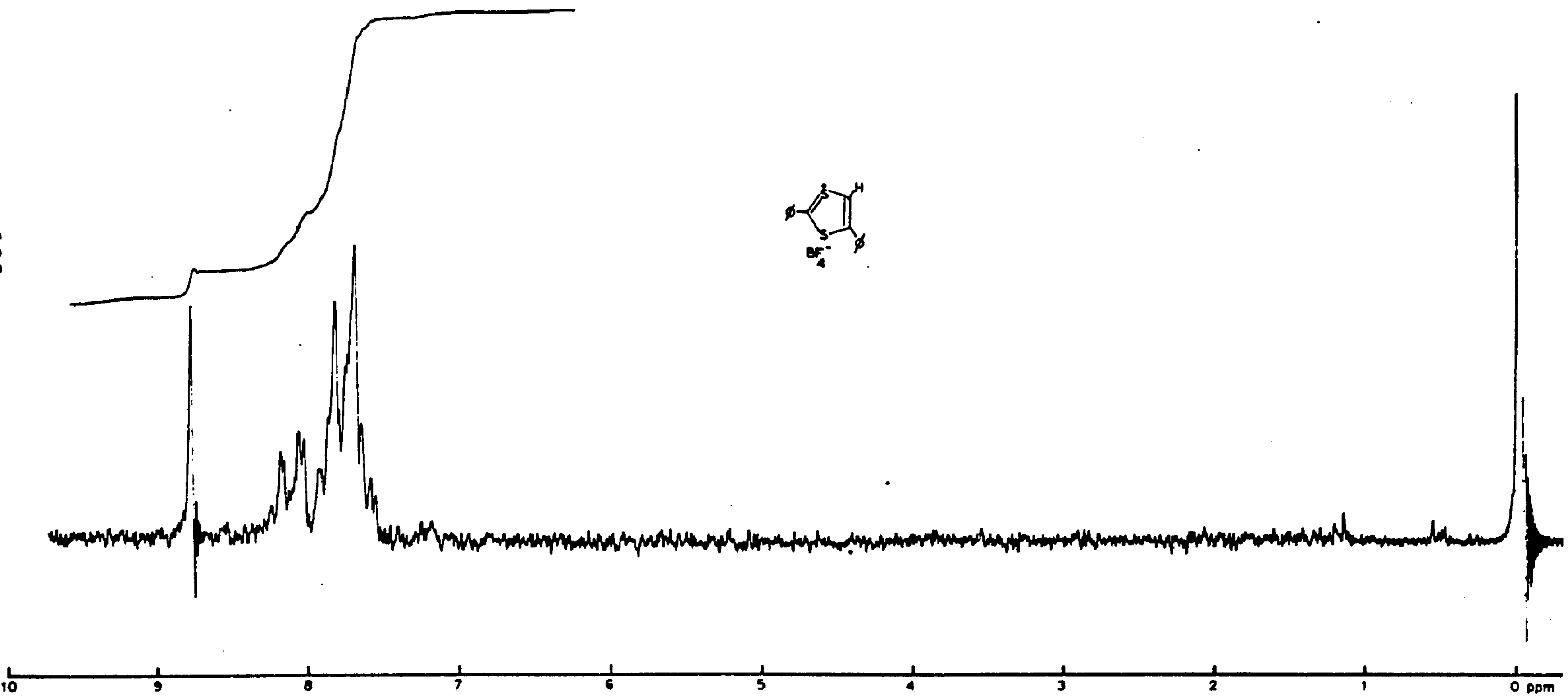
II I

On the basis of all of the above considerations, the structure of the unstable product was tentatively assigned as 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II).

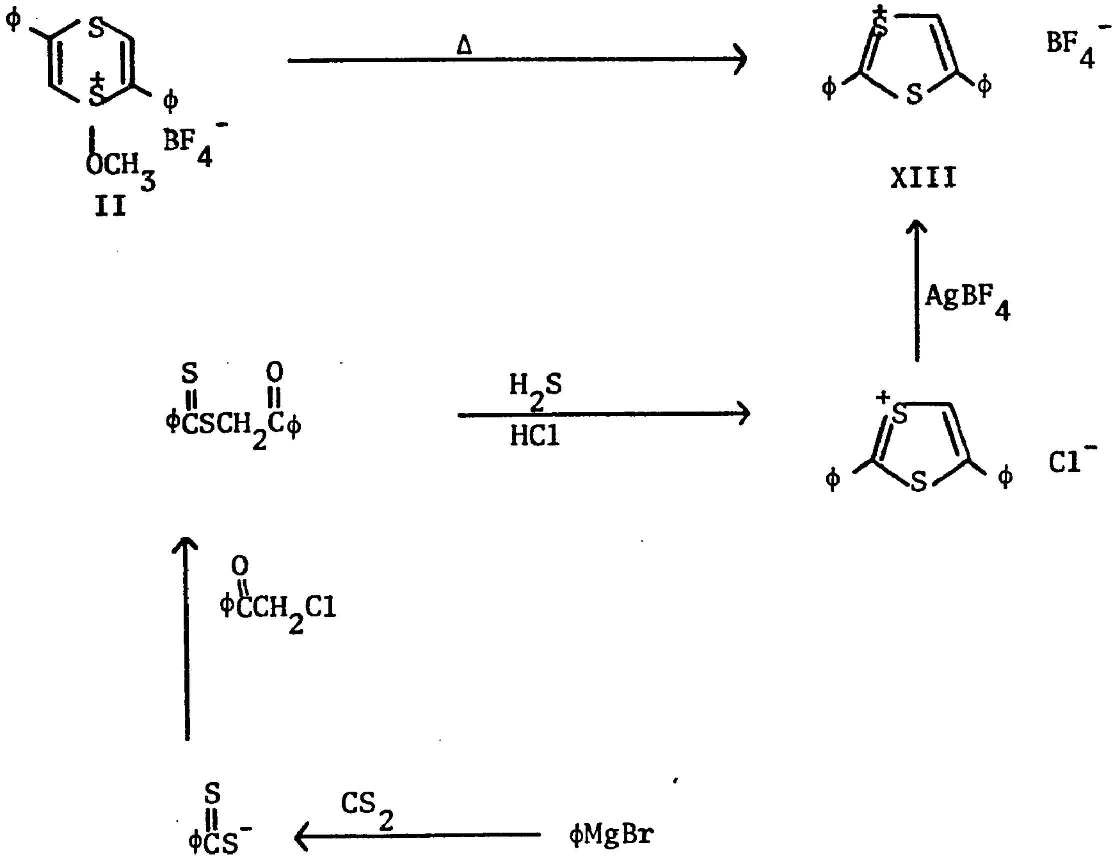
Thermal decomposition of the alkoxysulfonium salt II led to a mixture of products from which one solid compound was isolated in pure form. The nmr spectrum (CF_3COOD, TMS) of this substance (Figure 4) showed a singlet at δ 8.78 and a multiplet at 8.25-7.55 ppm which integrated to the ratio 1:11. This datum, along with the elemental analysis and a molecular weight determination by freezing point depression of sulfolane, appeared consistent with a dithiolium structure. A search of the literature revealed that the nmr spectrum of 2,4-diphenyl-1,3-dithiolium perchlorate presented by Campaigne[13] was identical to that of the unknown product. Therefore, 2,4-diphenyl-1,3-dithiolium chloride (XII) was prepared by the method of Campaigne[13] and converted to 2,4-diphenyl-1,3-dithiolium tetrafluoroborate (XIII) by treatment with silver tetrafluoroborate. Compound XIII prepared in this manner

Figure 4

2,4-Diphenyl-1,3-dithiolium
Tetrafluoroborate



was found to be identical with the solid isolated from the thermal decomposition of the alkoxysulfonium salt II.



Thermal decomposition of a solid sample of the alkoxysulfonium salt (II) in an evacuated vessel and subsequent analysis of the vapors by mass spectrometry and infrared spectroscopy (see experimental section) showed methyl formate to be another product of this reaction. Attempts to purify the benzene soluble material also produced in the reaction were unsuccessful.

CONCLUSIONS

2,5-Diphenyl-1,4-dithiin-1-oxide (I) reacts with methyl iodide-silver tetrafluoroborate to yield initially the O-alkyl derivative, 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II), which undergoes thermal decomposition via a novel ring contraction to produce 2,4-diphenyl-1,3-dithiolium tetrafluoroborate (XIII) and methyl formate as well as some additional unidentified material. A complete analysis of this unusual reaction will be forthcoming upon completion of investigations presently in progress by another worker in this laboratory.

EXPERIMENTAL SECTION*

Preparation of 2,5-Diphenyl-1,4-dithiin-1-oxide (I)

To 4.0 g (0.0149 mol) of 2,5-diphenyl-1,4-dithiin (VI) in 330 ml of acetone was added a slurry of 13.7 g (0.0596 mol) of potassium meta-periodate in 480 ml of water. The reaction flask was covered with aluminum foil and the mixture stirred for 6 days. The insoluble material was collected on a filter and washed thoroughly with acetone. The combined filtrate and washings were concentrated under aspirator pressure at 25° to precipitate a portion of white product. The filtrate was then extracted with benzene. The product previously isolated was also dissolved in the

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* See paragraph one of the experimental section of Part B of this thesis for pertinent experimental details.

benzene extract which was then dried over magnesium sulfate. Addition of petroleum ether (30-60°) to the dried benzene solution precipitated 2.45 g (58%) of 2,5-diphenyl-1,4-dithiin-1-oxide (I) with mp 108-109° dec. (Lit.[8] mp 110° dec.). Nmr ($CDCl_3$) δ 7.8-7.3 (m, ArH, H-6), 7.23 (s, H-3) ppm. Ir (KBr) 1025 cm^{-1} (S=O).

Preparation of 1-Methoxy-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (II)

To a stirred solution of 6.00 g (0.0211 mol) of 2,5-diphenyl-1,4-dithiin-1-oxide (I) and 30 g (0.211 mol) of methyl iodide in 225 ml of methylene chloride was added 7.56 g (0.0211 mol) of $AgBF_4 \cdot 4CH_3CN$[12] in 450 ml of nitromethane. The reaction vessel was covered with aluminum foil and the solution stirred for 12 hr* at 23°. The yellow precipitate (AgI) removed by filtration weighed 5.07 g (102%). The filtrate was concentrated under aspirator pressure at room temperature and diluted with ether to precipitate 4.81 g (59%) of white product with mp 96.5° dec. Recrystallization from cold acetonitrile-ether with minimum exposure to light gave pure material believed to be 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II)** with mp 95-97° dec. Nmr (CD_3CN) δ 8.76 (s, 1, H-3), 7.9-8.45 (m, 11, ArH, H-6), 3.64

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* A small scale experiment carried out later showed the reaction to be essentially complete (ca. 100% yield of AgI) after 2 hr. In view of the instability of the product, this shorter reaction time is more desirable than the 12 hr used for the particular experiment described here in detail.

** This compound is extremely light and heat sensitive. For example, one sample which was stored in a closed container in the dark at 25-27° decomposed after only 2 days to liberate a gas, although another sample at 0° was stable indefinitely.

(s, 3, CH_3) ppm. Ir(KBr) See Fig. 2. UV max (CH_3CN) 290 nm, ($\log_{10}$ ε 4.37).

Anal. Calcd for $C_{17}H_{15}S_2OBF_4$: C, 52.87; H, 3.91; S, 16.60. Found: C, 52.81; H, 4.01; S, 16.81.

Hydrolysis of 1-Methoxy-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (II)

Eight-hundredths g (0.00021 mol) of 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II) was slurried in 30 ml of water at 25° for 2.5 hr. At the end of that time the pH of the solution was about 2 although extensive hydrolysis had not occurred, probably due to lack of water solubility of II. Sodium carbonate was added to raise the pH to about 10 and the slurry was stirred for an additional 3.5 hr at 25°. The white insoluble material filtered off weighed 0.054 g (90%) with mp 110-111° dec. The infrared spectrum was identical to authentic 2,5-diphenyl-1,4-dithiin-1-oxide (I) and a mixed melting point was undepressed.

Thermal Decomposition of 1-Methoxy-2,5-diphenyl-1,4-dithiinium Tetrafluoroborate (II)

a. Isolation of 2,4-diphenyl-1,3-dithiolium tetrafluoroborate (XIII)

(1) To a stirred solution of 6.57 g (0.0231 mol) of 2,5-diphenyl-1,4-dithiin-1-oxide and 32.8 g (0.231 mol) of methyl iodide in 250 ml of methylene chloride was added 8.30 g (0.0231 mol) of $AgBF_4 \cdot 4CH_3CN$[12] in 500 ml of nitromethane. The reaction flask was covered with aluminum foil and the reaction mixture

stirred for 18 hr at 25° and then for 24 hr at 37°. The dark green solution was filtered to give 5.67 g (104%) of AgI. Concentration of the filtrate on a rotary evaporator and addition of ether precipitated a sticky black substance. The red mother liquors were poured off and the substance remaining was recrystallized from methylene chloride-ether and acetonitrile-ether (Norit A-neutral) to give 2.0 g (25%) of an orange solid of mp 166-171° dec. This material was extracted with benzene in a Soxhlet extractor for 4 hr and then recrystallized from acetonitrile-ether to give 1.24 g (15.7%) of a yellow solid with mp 175-177°. Further recrystallization from methylene chloride-ether gave analytically pure 2,4-diphenyl-1,3-dithiolium tetrafluoroborate of mp 175-176° which was found to be identical to authentic material prepared by known methods (see below). Nmr (CF_3COOD) 8.8 (s, 1, H-5); 8.25-7.55 (m, 10, ArH) ppm. Ir (KBr) 3060, 3000 and strong bands at 1480, 1440, 1290, 1060 broad (BF_4^-), 770, and 680 cm^{-1}.

Anal. Calcd for $C_{15}H_{11}S_2BF_4$: C, 52.65; H, 3.24; S, 18.74; F, 22.21. Found: C, 52.58; H, 3.43; S, 18.79; F, 21.95.

(2) Eight-tenths g (0.00207 mol) of 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II) dissolved in 10 ml of methylene chloride and 20 ml of nitromethane was maintained in a sealed container at 125° for 0.5 hr. Addition of ether precipitated a yellow solid which was recrystallized from acetonitrile-ether (Norit A-neutral) to give 0.21 g (29.5%) of yellow crystals with mp 165-170°

dec. Further recrystallization gave material with mp 174-175.5° and infrared spectrum identical to that of the analytical sample of 2,4-diphenyl-1,3-dithiolium tetrafluoroborate (XIII) discussed above.

b. Identification of methyl formate

A vessel containing a sample of 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate (II) was cooled on an ice bath and evacuated. Upon heating the vessel with a hot air gun, the sample decomposed to give a gas which was analyzed in a mass spectrometer and in a 10 cm infrared cell. The mass spectrum of the gas is compared with that of the known spectrum of methyl formate[14] in Table I. No other compound which shows a parent peak at m/e 60 was found which has a mass spectrum that is as similar to that of the unknown gas as that of methyl formate. The infrared spectrum of the gas (Figure 5) is identical to the spectrum reported for methyl formate at _ca_. 10 mm Hg in a 10 cm cell.[15,16]

Synthesis of 2,4-Diphenyl-1,3-dithiolium Tetrafluoroborate by Literature Methods

a. Preparation of Dithiobenzoic Acid

A modification of the procedure of Bloch[17] was used. A Grignard reagent was prepared in a nitrogen atmosphere by adding dropwise 60 g (0.38 mol) of bromobenzene to a stirred mixture of 9.0 g (0.37 mol) of magnesium turnings and a few crystals of iodine in 150 ml of dry ether cooled on an ice bath. Carbon disulfide (29 g, 0.38 mol) was then added drop by drop to the ice cold

Figure 5

Gas Produced by Thermal
Decomposition of 1-Methoxy-
2,5-diphenyl-1,4-dithiinium
Tetrafluoroborate

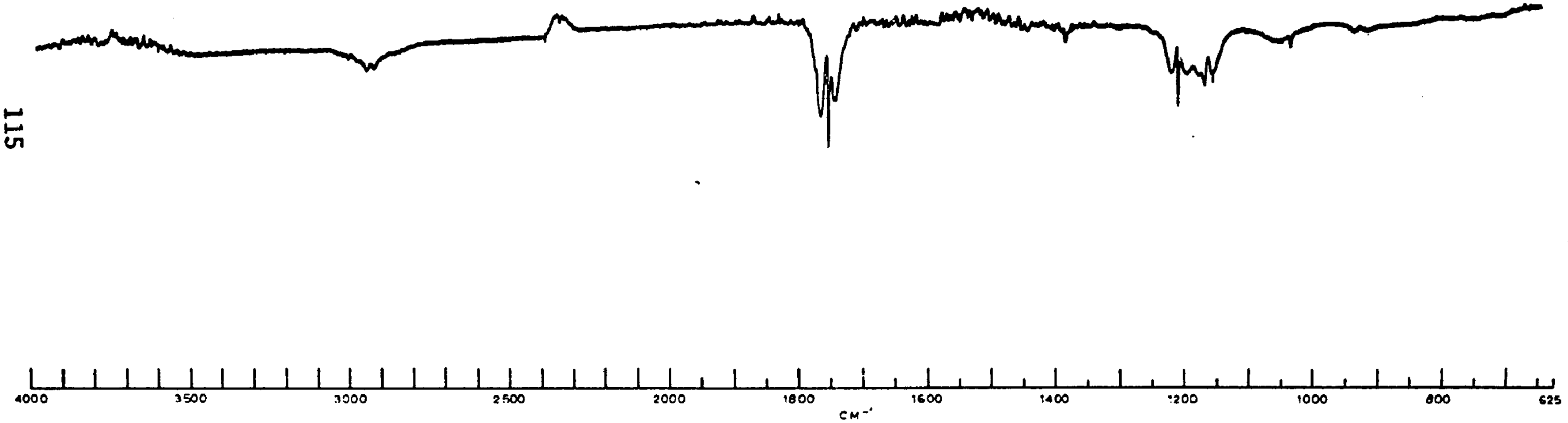

TABLE I

Comparison of Mass Spectra of Unknown Gas and Methyl Formate

m/e	Relative Intensity	
	Unknown Gas	Methyl Formate[14]
60	58	28
45	9	
32	43	42
31	100	100
30	6	6
29	35	46
28	0.3	
15	19	14

solution which was maintained on ice overnight. Care must be taken in the reaction to prevent the ether from boiling since polymerization occurs readily. Careful hydrolysis with ice and 1.5 N hydrochloric acid yielded the free acid which was removed by ether extraction. The ether extract was washed with cold water and extracted with 200 ml of cold 1.2N sodium hydroxide solution. The sodium hydroxide extract was washed several times with ether and then covered with a layer of ether. Addition of 200 ml of 1.5 N hydrochloric acid liberated the purified free dithiobenzoic acid into the ether layer which was evaporated to yield 7.7 g (13.5%) of a bluish-red oil.

b. Preparation of Phenacyl Dithiobenzoate

The method of Campaigne et al.[13] was followed. To a stirred solution of 7.7 g (0.05 mol) of dithiobenzoic acid in 135 ml of ether was added a solution of sodium ethoxide prepared by mixing 1.15 g (0.05 mol) of sodium and 30 ml of absolute ethanol. Phenacyl chloride (7.7 g, 0.05 mol) was added dropwise and the reaction mixture was refluxed for 0.5 hr. After cooling, the solution was filtered to remove the sodium chloride and evaporated to yield a red oil which was extracted into hot ethanol. The deep-orange precipitate that formed on cooling was removed to give 1.75 g (13%) of crude product of mp 55-60°. Recrystallization from absolute ethanol gave red-orange phenacyl dithiobenzoate with mp 75-76.5° (Lit.[13] mp 79-80°). Nmr (CCl_4) 8.1-7.8 (m, 4, ArH), 7.6-7.2 (m, 6, ArH), 4.78 (s, 2, CH_2) ppm.

c. Preparation of 2,4-Diphenyl-1,3-dithiolium Chloride (XII)

The method of Campaigne et al.[11] was employed. Dry hydrogen chloride and hydrogen sulfide were bubbled simultaneously for 3 hr into an ice-cold solution of 0.75 g (0.00275 mol) of phenacyl dithiobenzoate in 50 ml of ether. The reaction mixture was then allowed to stand for 3 days at room temperature. The yellow insoluble material was collected and recrystallized from acetonitrile-ether to give 0.64 g (80%) of product with mp 137-139° dec (Lit.[13] mp 134-136°).

d. Preparation of 2,4-Diphenyl-1,3-dithiolium Tetrafluoroborate

To a stirred solution of 0.56 g (0.00192 mol) of 2,4-diphenyl-1,3-dithiolium chloride in 60 ml of nitromethane and 50 ml of methylene chloride was added 0.69 g (0.00192 mol) of $AgBF_4 \cdot 4CH_3CN$[12] in 40 ml of nitromethane. After stirring for 1.75 hr at room temperature the white precipitate was removed by filtration, washed with methylene chloride, and dried to give 0.27 g (100%) of silver chloride. The combined filtrate and washings were concentrated on a rotary evaporator. Addition of ether precipitated 0.61 g (93%) of yellow product with mp 174-176°. Recrystallization from methylene chloride-ether gave material of mp 175-176°. The infrared spectrum of this product was identical to that of the material obtained previously from the decomposition of 1-methoxy-2,5-diphenyl-1,4-dithiinium tetrafluoroborate. A mixed melting point was undepressed.

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VITA

Alan Richard Oyler, the son of Melvin W. and Mildred M. Oyler, was born on October 13, 1947 in Key West, Florida.

He was graduated from Fleetwood Area High School in Fleetwood, Pennsylvania, in 1965.

Mr. Oyler received the Bachelor of Science Degree in Chemistry from Albright College, Reading, Pennsylvania, in 1969.

Mr. Oyler entered Lehigh University as a graduate teaching assistant in September, 1969. From 1970-1973 he was a National Science Foundation Trainee.

During the summers of 1967, 1968, and 1969, Mr. Oyler was employed as a laboratory technician by Glidden Paint Company in Reading, Pennsylvania.

Mr. Oyler is a member of the American Chemical Society, the American Institute of Chemists, and the American Association for the Advancement of Science.