THE SYNTHESIS AND MASS SPECTRAL STUDIES OF t-BUTYL(DEUTERATED)THIOPHENES

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN RADIATION CHEMISTRY IN THE GRADUATE SCHOOL OF THE TEXAS WOMAN'S UNIVERSITY

COLLEGE OF

ARTS AND SCIENCES

BY

ROSEMARY GARRETT FOWLER, B. S., M. S.

DENTON, TEXAS

JUNE, 1968

Texas Woman's University

Denton, Texas

June, 19 68

We hereby recommend that the dissertation prepared under our supervision by Rosemary Garrett Fowler entitled "The Synthesis and Mass Spectral Studies of t-Butyl(deuterated)thiophenes"

be accepted as fulfilling this part of the requirements for the Degree of Doctor of Philosophy.

Committee:

Rosemary R. Fowler
Chairman
Norman G. Foster
Helen A. Lindeman
William T. McCoy
Nancy A. Sanders

Accepted:

T. L. Morrison
Dean of Graduate Studies

ACKNOWLEDGMENTS

The author wishes to dedicate this manuscript to her research advisor, Dr. Robert W. Higgins, who represented high ideals and desire for excellence in teaching and research catalyzed by contagious enthusiasm. Without the help and encouragement given to me personally by Dr. Higgins this research problem and manuscript could not have been completed.

A debt of gratitude is expressed to the Robert A. Welch Foundation who made this project possible and gave financial support to the researcher. The author is indebted and gives special thanks to the Texas Woman's University Foundation and to the Willis H. Clark Fellowship Fund for additional financial support during the course of her graduate studies at the Texas Woman's University.

Appreciation for help and suggestions in preparation of this dissertation is expressed by the author to the members of her committee, namely Drs. Helen A. Ludeman, L. R. Caswell, N. G. Foster, W. L. Mecay and M. G. Sturrock.

TABLE OF CONTENTS

		Page
ACKNOWLEDGMENTS		iii
LIST OF TABLES		vi
LIST OF FIGURES		vii
Chapter		
I.	INTRODUCTION	1
II.	HISTORICAL	3
	A. The Mass Spectra Behavior of the Alkylthiophenes	3
	B. The Synthesis of t-Butylthiophenes	22
	C. Deuterated Thiophenes	25
III.	DISCUSSION	28
	A. Synthesis of 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)thiophene	28
	B. Synthesis of 2,5-di(t-Butyl-5-$^2H_9$)thiophene and 2,4-di(t-Butyl-4-$^2H_9$)thiophene	31
	C. Friedel-Crafts Alkylation of Mono-t-Butylthiophenes Using Labeled t-Butyl Chloride-$^2H_9$	37
	D. Interpretation of Mass Spectral Data for Mono-t-Butylthiophene	41
	E. Interpretation of Mass Spectral Data for Di-t-Butylthiophenes	60
IV.	EXPERIMENTAL	76
	A. Preparation of 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)thiophene	76

Chapter Page

B. Preparation of Unlabeled 2,5-di-t-Butyl-thiophene 77

C. Preparation of 2,5-di(t-Butyl-5-$^2H_9$)-thiophene and 2,4-di(t-Butyl-4-$^2H_9$)-thiophene 89

D. Friedel-Crafts Alkylation of Mono-t-Butyl-thiophenes using t-Butyl chloride-$^2H_9$ . . 91

E. Mass Spectral Operating Conditions 93

F. Gas Chromatographic Operating Conditions . . 94

V. SUMMARY. 96

REFERENCES. 99

APPENDIX A: POLYISOTOPIC MASS SPECTRAL DATA--LABELED t-BUTYLTHIOPHENES. 103

APPENDIX B: GAS CHROMATOGRAPHIC DATA 117

LIST OF TABLES

Table		Page
1.	Deuterated Thiophenes	26
2.	Infrared Overtone Region Data on Purified Fractions and Some Disubstituted Alkylthiophenes	36
3.	Partial Mass Spectra of Mono-t-Butylthiophenes	42
4.	Doubly Charged Ions of Labeled Mono-t-Butylthiophenes	54
5.	Calculated Metastable Peaks in the Mass Spectra of the Labeled Mono-t-Butylthiophenes	57
6.	Metastables Observed in the Spectra of 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)-thiophene	58
7.	Partial Mass Spectral Data of the Di-t-Butylthiophenes	61
8.	Doubly Charged Ions of Labeled Di-t-Butylthiophenes	72
9.	Observed Metastables in the Fragmentation of Labeled Di-t-Butylthiophenes	75

LIST OF FIGURES

Figure		Page
1.	Base Peak Formation for the Mono-t-Butyl-thiophenes	12
2.	Low Ionization Voltage Data for 2-t- and 3-t-Butylthiophene	15
3.	Low Ionization Voltage Data for 2,4-di-t-Butylthiophene and 2,4-di-t-Butylthiophene	18
4.	Possible Structures of the m/e 166 Ion	19
5.	Some Fragmentation Paths of the di-t-Butyl-thiophenes	21
6.	Base Peak Formation for the Labeled Mono-t-Butylthiophenes	43
7.	Resonance Structures for the Allyl System.	44
8.	a. Molecular Models of 2-(t-Butyl-$^2H_9$) thiophene.	45
	b. Molecular Models of 3-(t-Butyl-$^2H_9$) thiophene.	46
9.	Some Fragmentation Paths of the Labeled Mono-t-Butylthiophenes	48
10.	Low Ionization Voltage Data for 2-(t-Butyl-$^2H_9$)-thiophene and 3-(t-Butyl-$^2H_9$)thiophene	50
11.	a. Molecular Models of 2,5-di(t-Butyl-5-$^2H_9$)-thiophene.	64
	b. Molecular Models of 2,4-di(t-Butyl-4-$^2H_9$)-thiophene.	65
12.	Some Fragmentation Paths of the Labeled di-t-Butylthiophenes	68
13.	Low Ionization Voltage Data for 2,5-di(t-Butyl-5-$^2H_9$)thiophene and 2,4-di(t-Butyl-4-$^2H_9$)-thiophene	70

ABSTRACT

Fowler, Rosemary Garrett

The Synthesis and Mass Spectral Studies of t-Butyl(deuterated)thiophenes

Directed by Dr. Robert W. Higgins

Submitted for the Doctor of Philosophy Degree, May, 1968

The synthesis and mass spectral studies of t-butyl(deuterated)thiophenes were undertaken to aid in elucidation of the mass spectral fragmentation routes of the unlabeled t-butylthiophenes. The desired 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene were synthesized by the interaction of 2-thienylmagnesium bromide and t-butyl chloride-$^2H_9$ forming both the 2- and 3-isomers. The isomers were separated by preparative gas chromatography. The isotopic purity of the 2-(t-butyl-$^2H_9$)thiophene was 96.3% and for the 3-(t-butyl-$^2H_9$)thiophene was 96.7%. The 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)-thiophene were synthesized by the interaction of 5-t-butyl-2-thienylmagnesium bromide and t-butyl chloride-$^2H_9$ forming both the 2,4-isomer and the 2,5-isomer. The isomers were separated by preparative gas chromatography. The isotopic purity of the 2,5-di(t-butyl-5-$^2H_9$) was 98.72% and the 2,4-di(t-butyl-4-$^2H_9$)thiophene was 95.22%.

Mass spectral studies of 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene confirmed the direct losses of methyl-$^2H_9$ groups from the t-butyl group. Preferred successive losses of methyl-$^2H_3$ groups occurred in the fragmentation of the 2-isomer, whereas loss of the t-butyl group is the preferred fragmentation route in the 3-isomer. Positional substitution is an important influence on the mode of fragmentation of the various isomers. The steric relationships of the t-butyl group to the rest of the molecule differs depending upon the location (2 or 3) of the t-butyl group. The favored interaction between the deuterium of the t-butyl group and the sulfur atom are related to the location of the t-butyl group. Mass spectral studies of the 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)thiophene confirmed that two successive losses, one of methyl and one of methyl-$^2H_3$ occurred. Preferential losses of methyl and methyl-$^2H_3$ are favored in the 2,5-isomer, whereas loss of a t-butyl group is favored in the 2,4-isomer to a considerable extent and apparently occurs with almost equal probability from either position. The fragmentation of the 2,5-isomer differs from the 2,4-isomer in ion production and in the intensity of the ions formed at high voltage. These differences may be related to steric effects and the interaction of the deuteriums of the t-butyl group with the sulfur atom. Additional study of the existing mass spectral data presented is expected to yield considerable information on the fragmentation pathways.

The Friedel-Crafts alkylation of 2-t-butylthiophene with t-butyl chloride-$^2H_9$ yielded 2,5-di-t-butylthiophene, 2,5-di(t-butyl-5-$^2H_9$)thiophene, 2,5-di(t-butyl-2,5-$^2H_{18}$)-thiophene, 2,4-di-t-butylthiophene, 2,4-di(t-butyl-4-$^2H_9$)-thiophene and 2,4-di(t-butyl-2,4-$^2H_{18}$)thiophene. The Friedel-Crafts alkylation of 3-t-butylthiophene with t-butyl chloride-$^2H_9$ yielded a product containing equal amounts of 2,4-di(t-butyl-2-$^2H_9$)thiophene and 2,4-di(t-butyl-2-$^2H_9$)-thiophene-5-$^2H_1$. Studies to elucidate the mechanism of these reactions are in progress.

I. INTRODUCTION

Mass spectrometry has been used extensively in the characterization and identification of compounds. Fragmentation studies are usually undertaken to improve the understanding of the processes occurring during electron impact, and to allow the analyst to correlate the structure with the mass spectra. The alkylthiophenes have received detailed attention and it has been noted that the t-butylthiophenes were exceptions to the correlations developed and to the mechanisms proposed for the n-alkylthiophenes. The 2-t-butylthiophene, 3-t-butylthiophene, 2,5-di-t-butylthiophene, and 2,4-di-t-butylthiophene fragmentation processes have been thoroughly investigated by Foster, whose work laid the foundation for the present study by suggesting the use of isotopically labeled molecules.

The purpose of this research was to prepare and to study the mass spectral fragmentation patterns of the following labeled molecules: 2-(t-butyl-$^2H_9$)thiophene, 3-(t-butyl-$^2H_9$)thiophene, 2,5-di(t-butyl-5-$^2H_9$)thiophene, and 2,4-di(t-butyl-4-$^2H_9$)thiophene. The spectra of these molecules were expected to answer the following general questions:

1. In the t-butylthiophenes were the observed hydrogen migrations dependent upon the isomeric structures and, therefore, specific; or were the migrations random?

2. In the 2,5-di-t-butylthiophene did successive methyl cleavages arise from the same t-butyl group or from the opposite t-butyl group or was this cleavage random?

3. In the 2,4-di-t-butylthiophene was the ion formed by loss of a t-butyl group a preferential loss at the 4 (or 3) position or was this random?

Additional information from the mass spectral studies would result from studying metastable peaks and doubly charged ions which will be shifted due to isotopic labeling.

The initial approach to synthesis of these molecules involved alkylation employing the Friedel-Crafts method.

If mixed isotopic labeling occurred, a priori thinking was that the desired molecules could be obtained by way of the Grignard synthesis.

II. HISTORICAL

A. The Mass Spectra Behavior of the Alkylthiophenes

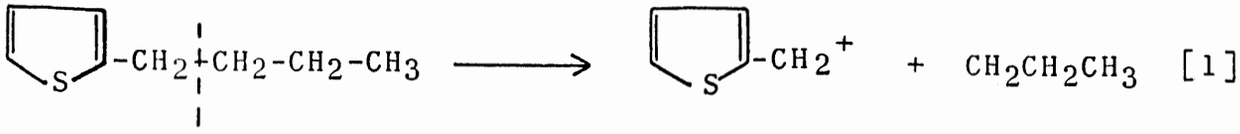
In 1956, Dr. Robert W. Higgins of this institution began contributing various thiophene derivatives to the U.S. Bureau of Mines (USBM) at Bartlesville, Oklahoma. In the past 11 years Higgins has provided over 150 compounds to be used as reference standards. When the American Petroleum Institute Research Project 48 (API-RP 48), "Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum," was established a part of the project was conducted at the Bartlesville Petroleum Research Center of the U.S.B.M. These sections were concerned with the separation and identification of the sulfur compounds in petroleum. The identification of these compounds usually is accomplished by preliminary separations using conventional techniques such as distillation, extraction, chromatography and thermal diffusion followed by instrumental confirmation of identification. Prominent among the instruments used are infrared and ultraviolet spectrophotometers and the mass spectrometer.

In its work on the separation and identification sections of the API-RP 48, the U.S.B.M. became concerned with the mass spectra of sulfur compounds. Fragmentation studies

were undertaken as a natural course of events both to improve the understanding of processes occurring during electron impact, and to allow the analyst to correlate structure with the mass spectra. The need for reference spectra on all isomeric species of a series is thus obviated.

An important class of sulfur compounds in petroleum is the thiophenes. In Hartough's Thiophene and Its Derivatives (1), Hochgesang contributes a chapter on "Molecular Structure and Spectroscopy of Thiophene and Its Derivatives." In this chapter mass spectral data for thiophene and the five methyl and dimethyl derivatives of thiophene were included. These data were given in detail along with the major fragmentation patterns.

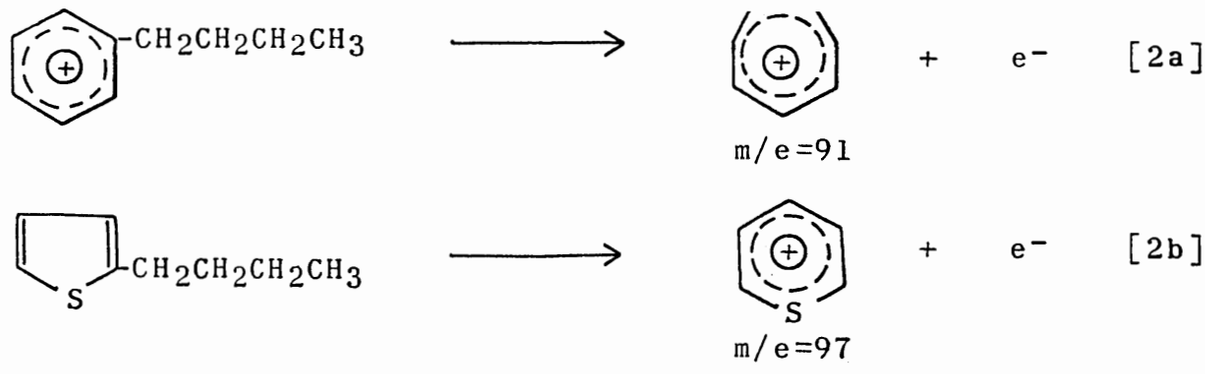
The spectra and correlations of the alkylthiophenes received early attention in the 1952 report of Kinney and Cook (2). They showed that the lower molecular weight alkylthiophenes resembled the alkylbenzenes in a number of respects. The prime similarity was that the normal alkylthiophenes formed the base peak by cleavage of the beta carbon bond from the ring on the alkyl chain. This is illustrated in equation 1.



[1]

The alkylthiophenes studied were of the 126-154 molecular weight range. The fragment ion peaks used in their correlations were: base (the peak due to the ion of largest intensity); parent (molecule ion peak); parent less 1; parent less 31; and the peaks at m/e 85 and 84. Comparison of the spectra of the alkylthiophenes with those of the alkylbenzenes indicated a parallelism in the two fragmentation mechanisms. For all mono-n-alkylthiophenes the base peak was the m/e 97 ion peak.

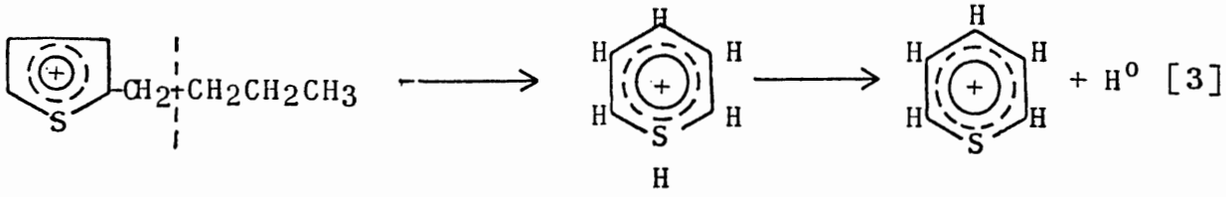
Foster and his coworkers (3,4,5), using spectra from 35 previously unreported alkylthiophenes provided by Dr. Higgins, expanded these correlations. It was shown (5) that the base peak mechanism resembled that proposed by Rylander, Meyerson, and Grubb (6) for the formation of the tropylium ion in the mass spectra of the alkylbenzenes. This is illustrated in equation 2a.



Hanuš and Čermák (7) independently claimed expansion to the ring structure shown in equation 2b on the basis of compounds of butyl substitution or less. Koutecký (8) calculated the

delocalization energy of the six-membered ring species (thiapyrilium ion) and showed that it should be even more stable than the tropylium ion.

In developing ideas about all of the fragmentation processes involved for the alkylthiophenes, low ionizing voltage data were used. Using low voltage techniques with the thirty-five compounds, Foster et al. (3,4,5) showed that the m/e 98 ion appeared at lower voltages than the m/e 97 ion. They also noted a large increase in the m/e 98 peak as the alkyl chain length increased. This suggested that the mechanism is more likely a case of the parent ion producing the m/e 98 ion, and this in turn losing a hydrogen atom to form the m/e 97 ion. This is illustrated in equation 3.



molecule ion m/e 98 m/e 97

A metastable peak in the spectrum of 2-n-hexylthiophene has been reported (9) in the support of this process. The actual location of the hydrogen atom in the resulting m/e 98 ion moiety was not known, although it might be on the sulfur atom as shown if one accepted the 10 electron sulfur atom as proposed by Cilento (10). About this same time, Meyerson and McCollum (11) reported the presence of a large m/e 92

peak (the corresponding rearrangement peak for the alkylbenzenes) from n-butylbenzene. They also demonstrated by means of deuterated compounds that the bulk of this rearrangement ion was formed by hydrogen transfer from the gamma position on the chain. It was presumed that the alkylthiophenes would do likewise.

Besides showing that beta cleavage dominated all other forms of molecule ion fragmentation in the 2-n-alkylthiophenes Foster and coworkers indicated that:

1. Alpha cleavage with one or two hydrogen atom rearrangements to form the m/e 85 and 84 ions was the next most prominent process, but was never more than 10% of the beta processes.

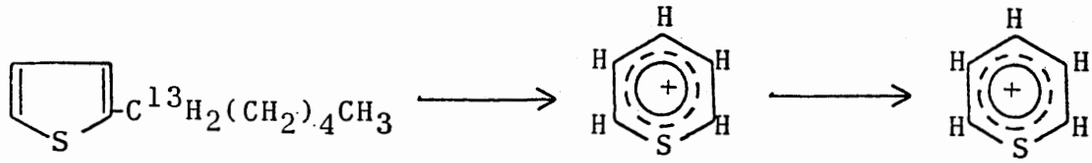
2. Gamma cleavage was usually small but did increase somewhat as the chain was lengthened.

3. Further studies of the mass spectral fragmentation patterns were fruitless at this point because the m/e 97 and 84 species apparently gave the same ions upon subsequent fragmentation.

To study the fragmentation paths further, 2-(1-hexyl-1-^{13}C)thiophene was prepared by Higgins and Wu (12). The mass spectrum reported by Foster and Higgins (13) indicated that little carbon skeletal rearrangement of the alkyl group occurred and that beta cleavage after a hydrogen transfer occurred to form the tagged complex at m/e 99. The loss of a hydrogen atom to form the 98 peak verified the process:

$$\text{Molecule Ion} \longrightarrow C_5H_6S^+ \longrightarrow C_5H_5S^+ + H^o$$

For the tagged species this is illustrated in equation 4.



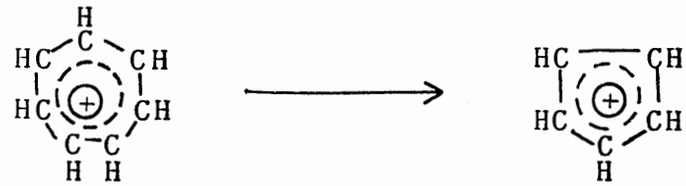
m/e 169
molecule ion

m/e 99

m/e 98

[4]

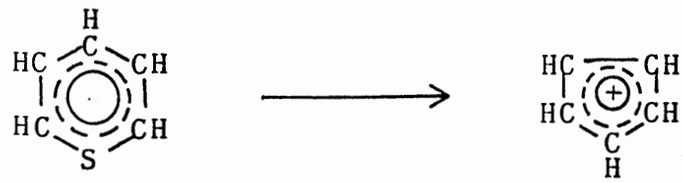
The formation of the six-membered ring at m/e 98 was supported by the subsequent fragmentation of this type of species to yield the tagged $C_5H_5^+$ ion that was also found in the fragmentation paths of the tropylium ion. This is illustrated in equation 5a, and reported by Meyerson et al. (14).



tropylium ion

m/e 65

[5a]



thiapyrilium ion

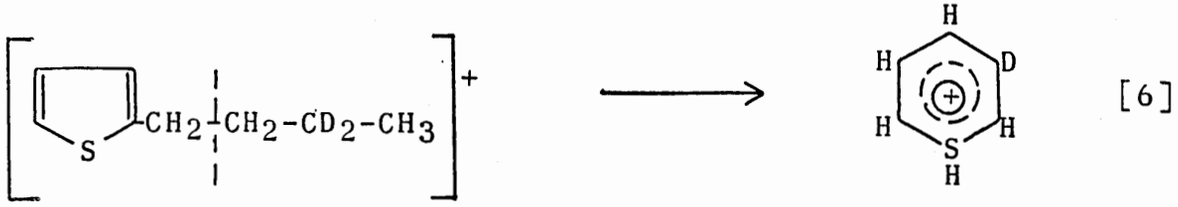
m/e 65

[5b]

Equation 5b shows the thiapyrilium parallel. The tagged species appeared at m/e 66 indicating that the tagged carbon is still with the ion. To this point, however, the exact ring structure has not been proven. Formation of the alpha cleavage ion cannot lead to the inclusion of the tagged carbon atom with the sulfur pi bonded complex unless a prior skeletal rearrangement of the carbon atoms occurs. The data indicated that this does not happen. In addition, if alpha cleavage produced the m/e 84 and 85 peaks, two hydrogen atoms must be shifted instead of one. This does not parallel the beta mechanism of the alkylbenzenes. Other ions noted as present included $C_3H_3^+$, $C_4H_3^+$, $C_2H_2S^+$ and $C_3H_3S^+$. The exact compositions of these ions have been verified by the high resolution mass spectrometer investigation provided by the Shell Oil Co. Laboratories in Houston, Texas (15). It must be emphasized that the structures are unknown, just as the structure of the m/e 85 species is unknown.

To eliminate some of the uncertainties and to better define the paths of fragmentation, studies of isotopically labeled molecules were proposed and considered. Higgins and coworkers provided 2-(n-butyl-1,1-$^2H_2$)thiophene, 2-(n-butyl-2,2-$^2H_2$)thiophene, 2-(n-butyl-3,3-$^2H_2$)thiophene and 2-n-butylthiophene-5-$^2H_1$. The mass spectra of these compounds have been obtained and partially reported (16). Confirmation that the gamma hydrogen atom was quite active

in forming the rearrangement ion at m/e 99 (17) was obtained. This is illustrated in equation 6. (Note: Location of the deuterium atom is not specifically known.) It was also apparent that the gamma hydrogen atom predominately participated in forming the m/e 84 ion when alpha cleavage occurs (16).



[6]

m/e 142 m/e 99

The formation of a five-membered cyclic ring intermediate (including two atoms of the thiophene ring) in which a hydrogen atom was shifted, at least temporarily, to the thiophene sulfur atom or some other active ring site was indicated. The beta hydrogen atom apparently participated to the extent of about 50% in the formation of the m/e 85 ion which required two hydrogen atom shifts. It is as yet uncertain whether this last process involves a ring intermediate or a hydrogen shift along a chain, or both. When beta cleavage occurs to form the most intense ions, conformation may be important in determining the extent of rearrangement observed. An examination of the contributions of the deuterated species to the amounts of m/e 84 ion

formed from the various labeled thiophenes indicated that some statistical processes were apparently involved, but superimposed upon these were the very specific processes that must be associated with the favored shifting of gamma hydrogens. The appearance of the deuterium atom in the lower m/e fragment ions subsequently formed gives promise that a complete study of these dideuterothiophenes will improve delineation of the mechanism of formation of these ions in the mass spectrometer.

Throughout four of the cited publications of Foster and coworkers (2,3,4,5) the compounds containing isopropyl or t-butyl groups have been noted as exceptions to the rule, to the correlations developed, and to the mechanisms propose Base peak formation for the t-butylthiophene is illustrated in figure 1 (18).

Rylander and Meyerson (19) in 1956 proposed the cationated cyclopropane ring as a probable ionic intermediat to account for certain rearrangements shown by t-butyl-benzene and other alpha disubstituted alkylbenzenes under electron impact.

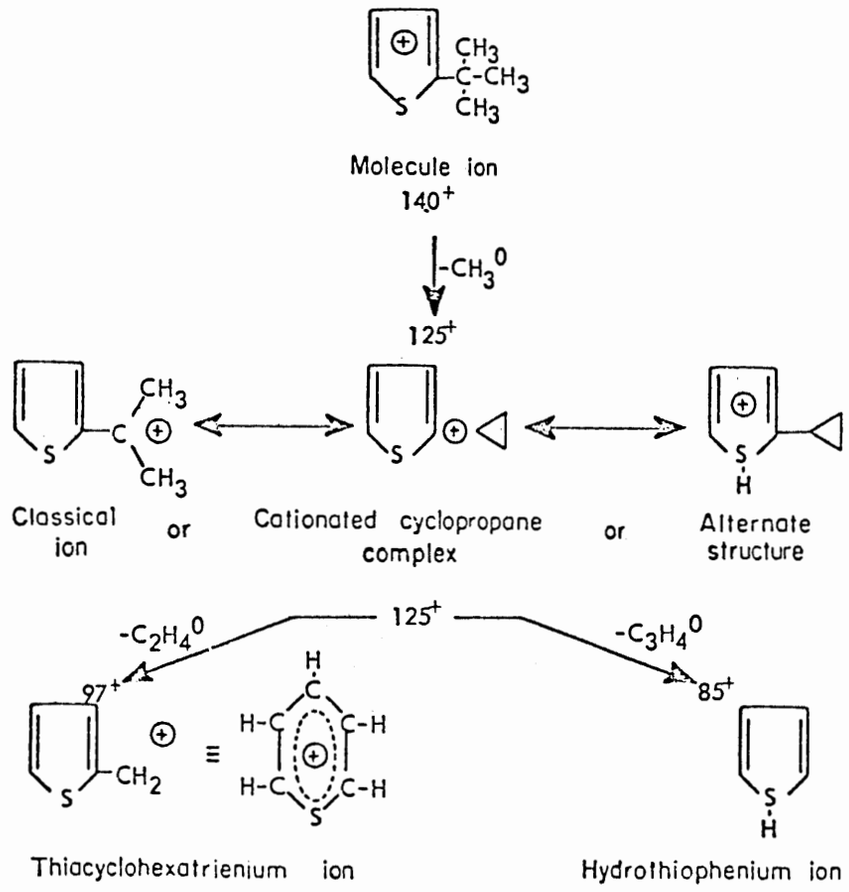


Figure 1

Base Peak Formation for the Mono-t-Butylthiophenes

If the alkylthiophenes are presumed to parallel the alkylbenzenes when the t-butyl group is present, then by analogy the m/e 125 ion could be that shown in the center of figure 1 or alternatively the classical ion shown at the left. Since these are not the only possibilities, it appears well to include the type of structure shown at the right-hand side of figure 1 in which the formal bond is made and a hydrogen atom appears to be attached to the sulfur atom. This type of structure was first proposed by Foster and his coworkers in 1959 (5) and requires the use of the concept of the 10 electron sulfur atom.

Studies of the t-butylthiophenes (18) indicated that the base peak was formed by beta cleavage (parent-15 rather than 97), but that the resulting ion was such that it did not interfere with the correlations developed throughout the alkylthiophene studies. A 2-n-butylthiophene was still directly differentiated from a 2-t-butylthiophene.

The major difference in the high voltage mass spectra of 2-t-butylthiophene and 3-t-butylthiophene was the intensity of the ions formed. The 3-t-butylthiophene appeared to have stronger peaks at m/e 97, 85, 84, 57, and 45. By contrast, the 2-t-butylthiophene had slightly more intense ions due to aromatic ions free of sulfur, such as the m/e 91, 65, 53, and 51. It appeared that the 2- and 3-compounds undergo the same general fragmentation processes but to somewhat different extents.

Low ionization voltage data illustrated in figure 2 (18) indicated that the production of the m/e 140 ion (parent) and the m/e 125 ion (base peak) proceeded with equal probability for either isomer. This suggested that the initial ionization and first fragmentation processes were essentially identical. The 85 ion for each of the isomers has the same appearance potential. Whatever process or processes form the m/e 85 ion, the low voltage data suggested it was the same for either the 2-t-butylthiophene or the 3-t-butylthiophene. The appearance potential of the 85 and 57 ions was approximately the same for the 2-t-butylthiophene and the 3-t-butylthiophene. However, the low voltage appearance of the m/e 84 and m/e 56 ions for the 2-t-butylthiophene was 5-6 ev below the corresponding m/e for the 3-t-butylthiophene.

The release of the t-butyl ion as shown by the ion production of m/e 57 appeared to be essentially the same process for both types of substitution. The m/e 57 ion (t-butyl ion) production was greater for the 3-t-butylthiophene based on low voltage data.

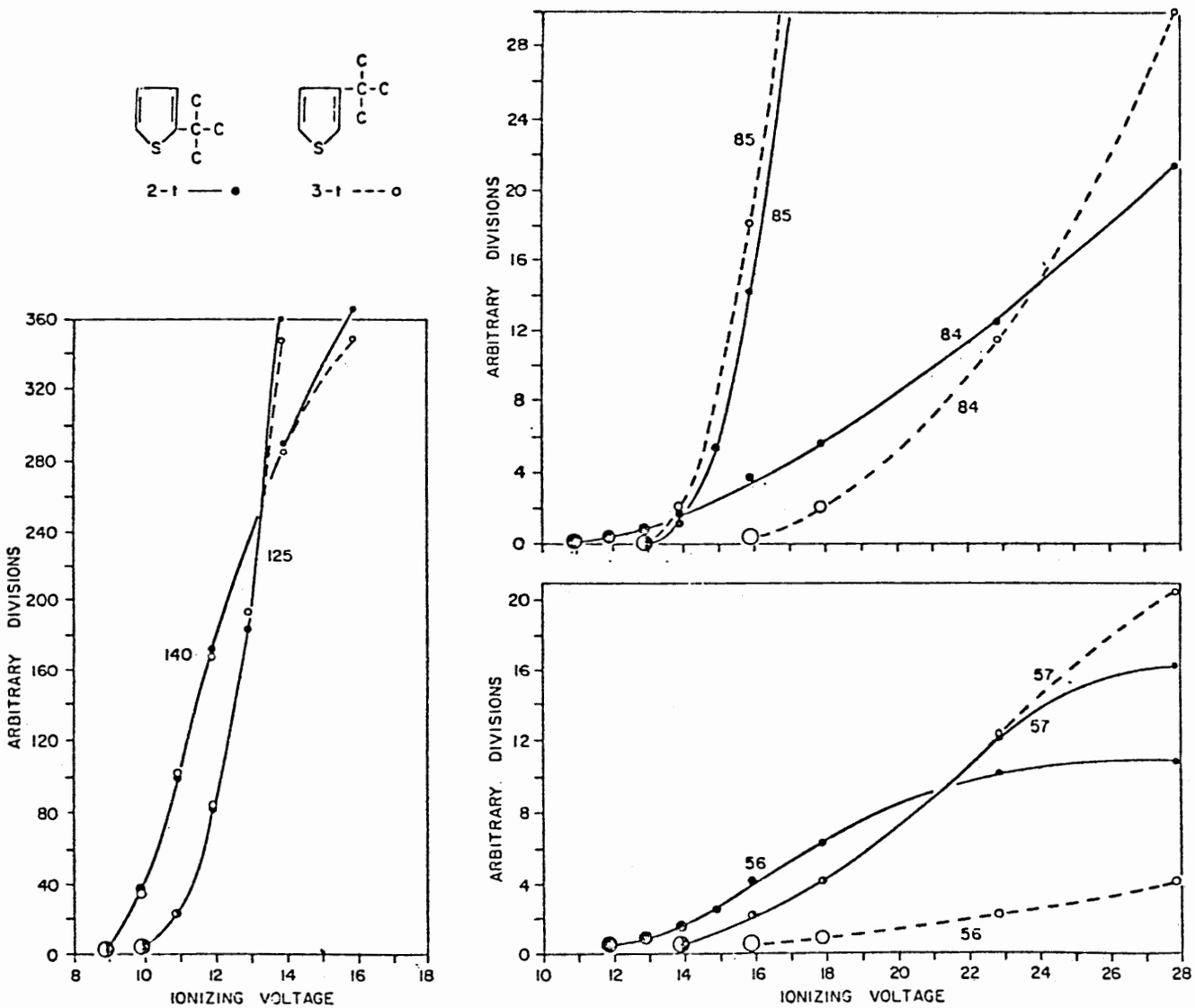


Figure 2

Low Ionization Voltage Data for 2-t- and 3-t-Butylthiophene

A number of metastable peaks have been observed in the mass spectra of 2-t-butylthiophene and 3-t-butylthiophene These metastable peaks indicate possible fragmentation routes

To eliminate some of the uncertainties and to better define the paths of fragmentation, studies of isotopically labeled molecules should be considered. For example, if a t-butyl group in which all the t-butyl group hydrogens were replaced by deuterium was available, it should show doubly charged ions at m/e 65.5, 63.5, and 61.5 due to the ion moieties of 125, 123, and 121 in the unlabeled molecules which would now appear at 131, 127, 123, respectively. In addition to this type of shifting, the metastable ions would also shift. For example, in the unlabeled molecule the processes probably occurring for the indicated metastables are:

$$(76.7),\quad 123^{+} \longrightarrow 97^{+} + C_2H_2{}^{o}$$

$$(76.9),\quad 125^{+} \longrightarrow 98^{+} + C_2H_3$$

These would be compared with the following for the labeled molecule:

$$(77.2),\quad 127^{+} \longrightarrow 99^{+} + C_2D_2{}^{o}$$

$$(77.9),\quad 131^{+} \longrightarrow 101^{+} + C_2D_3$$

Further benefits in shifting other metastable peaks can also be expected from labeled compounds.

The 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene gave high voltage mass spectra in which several striking differences were apparent. First, the parent ion and parent less 15 ion intensities were almost identical, the ions at parent less mass 30 (m/e 166) were different in intensity by a factor of 10, the 2,5-compound being the larger. Similarly, the m/e 165 peak for the 2,5-compound was twice as large as the 2,4-compound. A second feature was the large 57 ion intensity of 13.6% for the 2,4-compound and 3.24% for the 2,5-compound. This ion is presumed to be the t-butyl carbonium ion. Doubly charged ions were more prevalent in the two di-t-butylthiophenes than in the mono-t-butylthiophenes.

In general, the presence of di-t-butylthiophenes in a mixture of alkylthiophenes would be easily detected in the mass spectrometer. The fragment peaks from these compounds do not seriously interfere with the general correlations developed for the dialkylthiophenes. However, the presence of a strong peak at the parent less 30 mass does introduce interference with other compounds that might be present and are in the -2, -16 series.

Low ionization data for selected ions from the disubstituted compounds are shown in figure 3 (18). Once again the production of the parent ion (m/e 196) and base ion (m/e 181) were in excellent agreement for the two compounds.

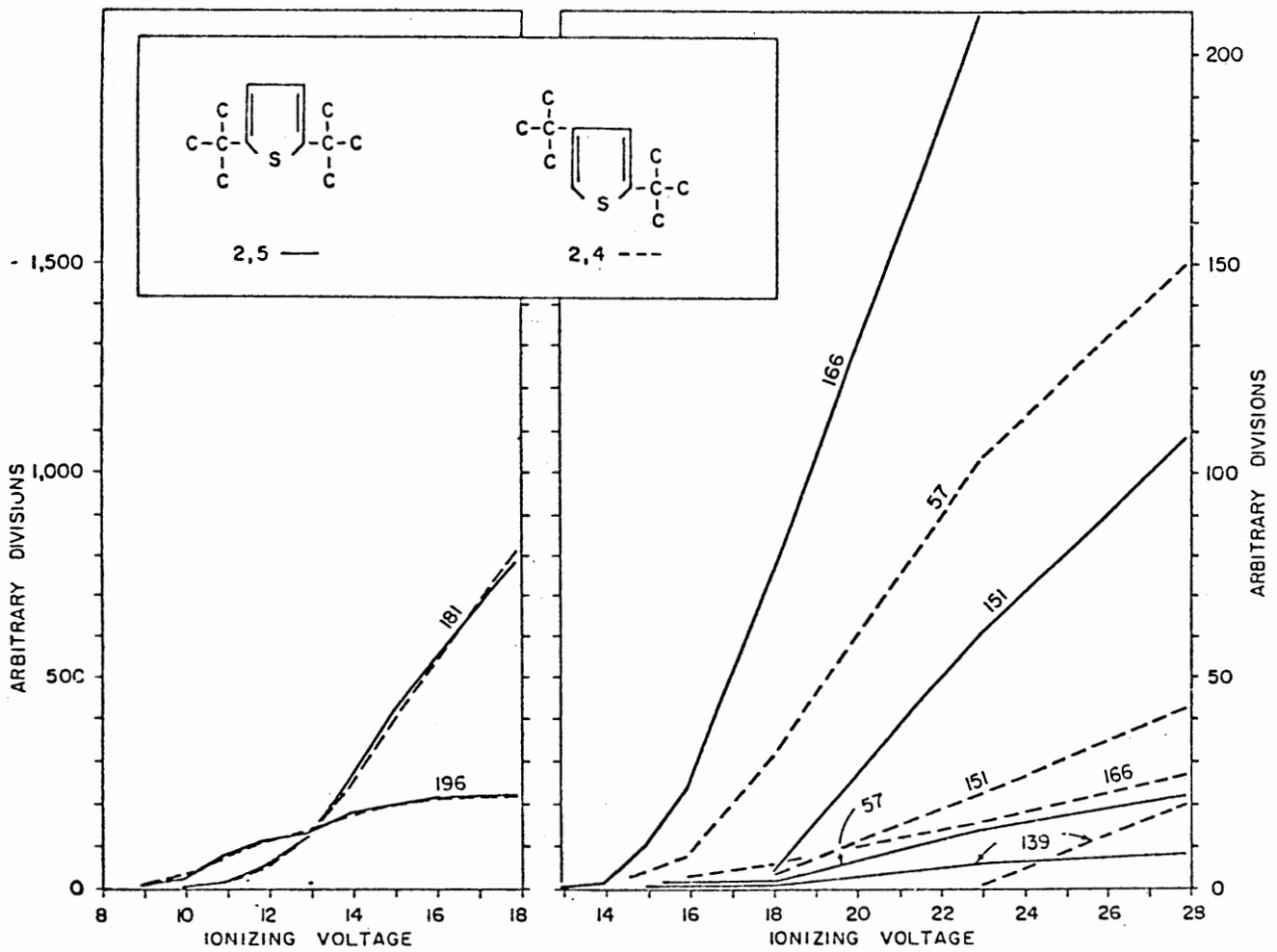


Figure 3

Low Ionization Voltage Data for 2,4-di-t- and 2,5-di-t-Butylthiophene

However, a large change occurred in the production of the m/e 166 ions. This is probably due to the influence of an interaction term that stabilizes the ion structure in the case of the 2,5-ion that is not possible for the same m/e derived from the 2,4-compound. The fact that the m/e 166 ion formed for the 2,5-compound suggested a much easier loss of a second methyl group from it, and probably from the t-butyl group on the opposite side of the molecule from that first cleaved. The 166 ion production was low for the 2,4-compound. Some possible structures of the m/e 166 ion are shown in figure 4.

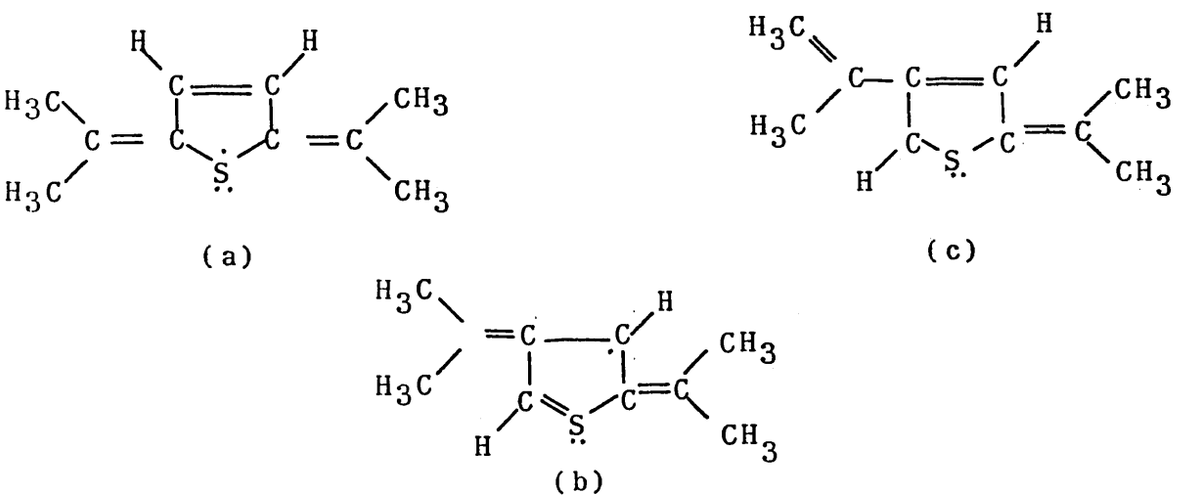


Figure 4.--Possible Structures of the m/e 166 Ion

The loss of a third methyl group from the molecule ion leads to the formation of the m/e 151 ion from either compound. This process was favored for the 2,5-di-t-butyl-thiophene; however the loss was significant in the

2,4-di-t-butylthiophene. The loss of a t-butyl group was favored for the 2,4-compound producing the m/e ion 139.

Metastable peaks appear in considerable strength in the mass spectra of both di-substituted compounds studied. These metastable peaks lead to some definite indications about the fragmentation paths of the 2,4- and 2,5-di-t-butylthiophenes. Some possible modes of fragmentation which may be derived from information obtained for the 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene are given in figure 5 (18). Final proof that these reactions occur can be determined only through the use of labeled molecules.

Isotopically labeled molecules containing a completely deuterated t-butyl group in the 2- and 5- positions, while being unlabeled in the 4- position for the 2,4- and in the 2- position for the 2,5-di-t-butylthiophene, will allow considerable progress to be made in delineating these processes for di-substituted molecules. Much of what is learned can be applied to similar molecules containing a pi-aromatic ring system with t-butyl substituents.

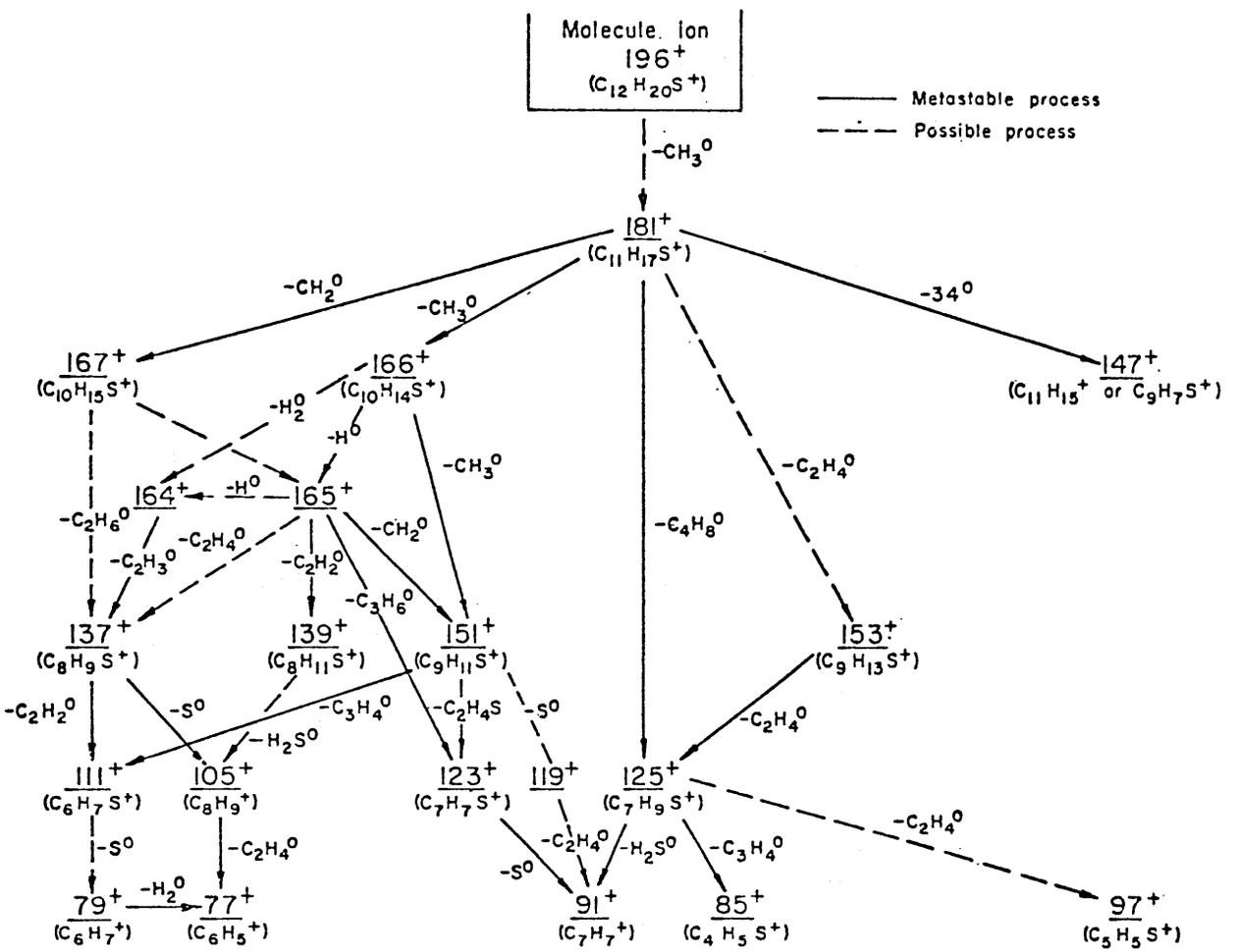


Figure 5

Some Fragmentation Paths of the di-t-Butylthiophenes

B. The Synthesis of t-Butylthiophenes

Successful syntheses of t-butylthiophenes have been reported frequently in the literature. The procedure often used is the alkylation of thiophene with isobutylene, t-butyl alcohol or t-butyl halide in the presence of various alkylating carriers. The yields reported are less than 50%.

Hartough, Caesar and coworkers (20) carried out fundamental studies on the alkylation of thiophene more than fifteen years ago and more recently Russian chemists (21) have made notable contributions.

In 1946 the alkylation of thiophene with isobutylene, using sulfuric acid as the acid carrier, was performed by Kutz and Corson (22). Caesar (23) in 1948 alkylated thiophene with isobutylene, using not only sulfuric acid but also aluminum chloride and a boron trifluoride-diethyl ether complex. In the same year Appleby and coworkers (24) alkylated thiophene with isobutylene in the presence of phosphoric acid. Using a Stedman column, they separated the 2-t-butylthiophene from the 3-t-butylthiophene and indicated the presence of a high boiling fraction composed of the di-t-butylthiophenes. Infrared spectra were obtained for the first time for each of the mono-t-butylthiophenes.

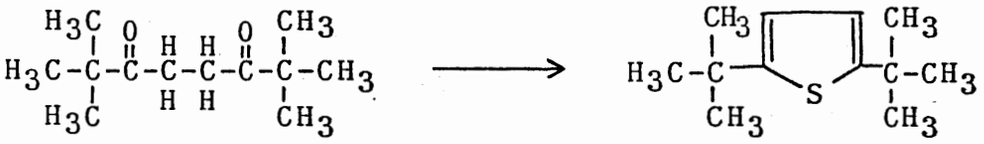
Pines and coworkers (25) in 1950 reported the alkylation of thiophene and 2-bromothiophene with various olefines, using different alkylating carriers. The

alkylation of thiophene with isobutylene proceeded with ease when stannic chloride, stannic chloride-nitromethane or boron trifluoride-diethyl ether complex was used. Alkylation of 2-bromothiophene with isobutylene was more difficult than alkylation of thiophene, but when boron trifluoride-diethyl ether complex was used as the alkylating carrier, 2-bromo-5-t-butylthiophene was obtained. Sy and coworkers (26) in 1954 alkylated thiophene with t-butyl chloride in carbon disulfide, using stannic chloride as the alkylating carrier. This large scale synthesis provided the mono-t-butylthiophenes in good yield.

The synthesis of pure 2-t-butylthiophene in 40% yield was reported by the Cagniants (27) in 1956. Goldfarb and Konstantinov (28) in 1957 reported reactions involving the structure of the acetylation and formylation products of 2-t-butyl-5-methylthiophene and 2,5-di-t-butylthiophene. The method for the preparation and purification of the 2,5-di-t-butylthiophene was not included. These workers also reported the use of 3-bromo-2,5-di-t-butylthiophene but physical constants and method of preparation were not included.

The most recent and pertinent publication by Wynberg and Wiersum (29) in 1965 investigated the rearrangements and transalkylation of t-butylthiophenes. These workers obtained small amounts of pure samples of 2-t-butylthiophene and 3-t-butylthiophene by fractional distillation and gas

chromatography, respectively. The dialkylated products were obtained in a 43% yield by using excess t-butyl chloride. The di-t-butylthiophenes were separated by chloromercuration yielding each isomer in a high degree of purity. Also these workers prepared 2,5-di-t-butylthiophene from 2,2,7,7-tetramethyl-octane-3,6-dione. This synthesis is indicated in equation 7.



[7]

The 2,4-di-t-butylthiophene was obtained by alkylation of 3-t-butylthiophene with t-butyl chloride in carbon disulfide in the presence of stannic chloride. Rearrangement of 2,5-di-t-butylthiophene in the presence of aluminum chloride yielded 2,4-di-t-butylthiophene. These workers indicated that no isomerization of the t-butyl groups occurred under the influence of stannic chloride, the carrier used in the alkylation. However, transalkylation did occur when 2,5-di-t-butylthiophene and 2,5-dimethylthiophene were treated with aluminum chloride in carbon disulfide; 3-t-butyl-2,5-dimethylthiophene was the major product.

Weinmayr in 1950 (30) indicated the synthesis of 2,3,4,5-tetra-t-butylthiophene. Wynberg and Wiersum failed to prepare 3,4-di-t-butylthiophene by use of 2,3-di-t-butylbutadiene. These workers could not substantiate the

synthesis of the 2,3,4,5-tetra-t-butylthiophene by Weinmayr nor have other workers been successful in this synthesis.

C. Deuterated Thiophenes

A number of references are reported for the preparation of deuterated thiophenes in which the deuterium is located on the thiophene nucleus.

Bak and coworkers (31) for microwave studies prepared thiophene-2-$^2H_1$, thiophene-3-$^2H_1$, thiophene-3,4-$^2H_2$ and thiophene-$^2H_4$. The technique employed involved the reduction of a specific halogenated thiophene in the presence of zinc dust, acetic acid-$^2H_1$, and deuterium oxide. The microwave spectra of these deuterated thiophenes compared with that of ordinary thiophene were utilized by Bak in the determination of bond lengths and angles in thiophene.

Several deuterated thiophene derivatives have been reported by Gronowitz and coworkers (32). These deuterated molecules were used in connection with work on the relation between substituent effects and chemical shifts in the nuclear magnetic resonance spectra of mono-substituted thiophenes. Infrared spectra were used extensively for analysis of isomeric purity. The deuterated thiophene derivatives prepared by Gronowitz and coworkers with the method used for preparation is given in Table I.

TABLE 1

DEUTERATED THIOPHENES

Substituent	Method	Yield
3-deutero	c	68
3-deutero-2-methyl	c	63
5-deutero-2-methyl	a	60
2-deutero-3-methyl	a	68
4-deutero-3-methyl	c	50
3-deutero-2-methylthio	b	70
4-deutero-2-methylthio	b	46
5-deutero-2-methylthio	a	63
4-deutero-3-methylthio	b	69
5-deutero-2-bromo	d	25
2-deutero-3-bromo	d	73
4-deutero-3-bromo	b	62
5-deutero-3-bromo	d	74

Method: (a) The reaction of Grignard reagents with D_2O.
(b) The hydrolysis of organolithium compounds, obtained through metal-halogen interconversion between bromothiophene and n-butyllithium at -70°C, with a solution of acetic acid-^2H and deuterium oxide in absolute ether at low temperature.
(c) The hydrolysis of organolithium compounds, obtained through interconversion with ethyllithium when the deuterated compounds had boiling points close to n-butyl bromide and octane.
(d) The selected removal of alpha halogens in 2,3- and 2,4-dibromothiophenes with zinc dust and acetic acid-^2H in deuterium oxide.

Orza and Sarompas (33) have studied the infrared spectra of thiophene-2-$^2H_1$, thiophene-2,5-$^2H_2$, thiophene-3,4-$^2H_2$, and thiophene-$^2H_4$.

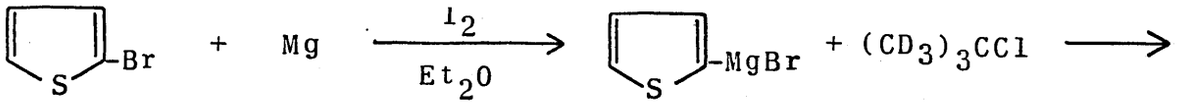
A search of the literature provided no references to the preparation of deuterated alkylthiophenes in which the deuterium was located in the side chain. However, as early as 1962, work directed toward the synthesis of deuterated alkylthiophenes was initiated in this laboratory under the direction of Higgins. At that time Pak (34) began work on the synthesis of 2-(n-butyl-1,1-$^2H_2$)thiophene, 2-(n-butyl-2,2-$^2H_2$)thiophene, and 2-(n-butyl-3,3-$^2H_2$)thiophene. This worker succeeded in obtaining the last of the three isomeric dideuterated n-butylthiophenes listed above.

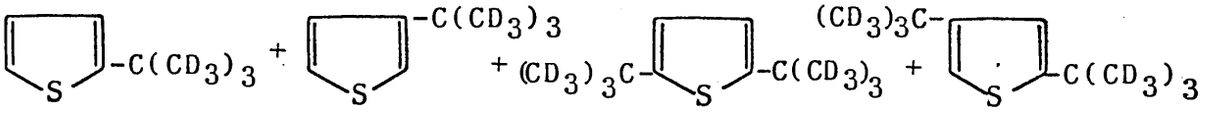
The investigation was continued, and in 1964, Lee (35) prepared 2-(n-butyl-1,1-$^2H_2$)thiophene. Chen (36) in 1966 prepared 2-(n-butyl-2,2-$^2H_2$)thiophene and 2-n-butylthiophene-5-$^2H_1$. This series of deuterated alkylthiophenes has been used to study and define fragmentation patterns of alkylthiophenes which have previously been discussed.

III. DISCUSSION

A. Synthesis of 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)-thiophene

The synthesis of 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene involved a Grignard reaction.





47.62% 24.7% 15.48% 12.20%

Before the above approach was selected the initial efforts were focused upon the synthesis of 2-(t-butyl-$^2H_9$)-thiophene. From the literature survey the synthesis of pure 2-t-butylthiophene had been reported by the Cagniants (27). The method involved the interaction of 2-thienylmagnesium bromide with t-butyl bromide. This synthesis was appealing and seemed applicable to the preparation of the labeled 2-t-butylthiophene. This method would eliminate the tedious separation of the desired 2-(t-butyl-$^2H_9$)thiophene from the

3-(t-butyl-$^2H_9$)thiophene which was present in all the other syntheses considered.

Initially, the interaction of 2-thienylmagnesium bromide with t-butyl bromide was repeated, with duplication of all the experimental details of the synthesis as given by the Cagniants (27). The reaction product was analyzed for purity by use of the gas chromatograph. Five peaks were obtained with retention time data characterizing the peaks as 2-bromothiophene, 2-t-butylthiophene, 3-t-butylthiophene, 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene. The synthesis was repeated a number of times and the product checked for purity. Each time the same components were present and in the same proportion. No difficulties were encountered with the synthesis and adequate quantities of the material were obtained for separation of the mono-t-butylthiophenes by use of a preparative gas chromatograph.

Previously, separation of the four isomers had been obtained by preparative gas chromatography using a 30% QF-1 column at 138°C. However, the 2-bromothiophene interfered with the separation and purification of the sample obtained from the Grignard synthesis. Polymerization of the 2-bromothiophene occurred in the injection port and on the column. The mono-t-butylthiophenes separated were contaminated by this red polymer after several hours of operation.

The Cagniants' procedure (27) was modified for the preparation of 2-t-butylthiophene and 3-t-butylthiophene.

The Grignard reaction was performed using excess magnesium and an extended reflux time in order to convert all of the 2-bromothiophene to 2-thienylmagnesium bromide. Excess magnesium was removed before the addition of t-butyl chloride was started. The products obtained were the isomeric t-butylthiophenes which were separated successively on the gas chromatograph.

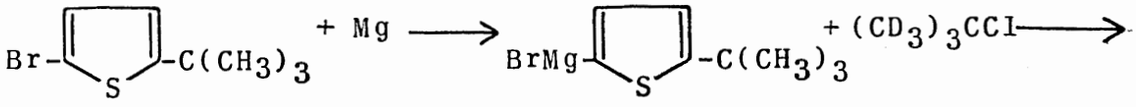
The two fractions separated were identified by use of the infrared and mass spectrometer. The major difference in the infrared spectrum of 2- and 3-positional isomers of thiophene is the extremely strong band present in the latter at 13 microns. Fraction 1 was characterized as 2-t-butylthiophene due to minimum absorption at 10.9 and 12.8 microns. Fraction 2 was characterized as 3-t-butylthiophene due to maximum absorption at 10.9 and 12.8 microns. The spectra of 2-t-butylthiophene (fraction 1) and 3-t-butylthiophene (fraction 2) were identical with the spectra reported (37). The mass spectra obtained indicated fraction 1 was 2-t-butylthiophene and fraction 2 was 3-t-butylthiophene. The first fraction (2-t-butylthiophene) had more intense peaks at m/e 91, 65, 53, and 51. The second fraction (3-t-butylthiophene) had more intense peaks at m/e 97, 85, 84, and 57. This correlated with the data reported (18) for these two isomers.

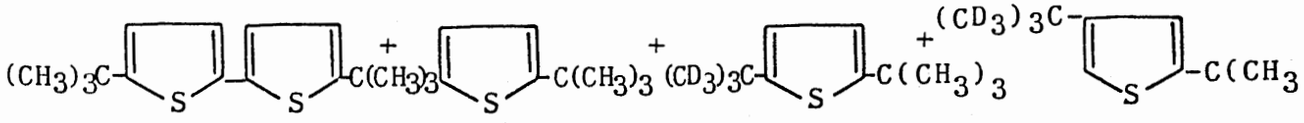
The reaction was repeated using t-butyl chloride-$^2H_9$. The 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene were separated and collected by use of the preparative scale

gas chromatograph. No difficulties were encountered with the labeled molecules, since all the problems were solved using unlabeled species. The mass spectra of the compounds indicated high isotopic purity of each. The isotopic purity was indicated by the absence of m/e 140^+ and peak intensities at m/e 148^+ and at m/e 150^+ were those calculated for loss of hydrogen and isotope contributions, respectively.

B. Synthesis of 2,5-di(t-Butyl-5-$^2H_9$)thiophene and 2,4-di(t-Butyl-4-$^2H_9$)thiophene

The synthesis of 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)thiophene involved a Grignard reaction. The reaction is depicted in equation form.

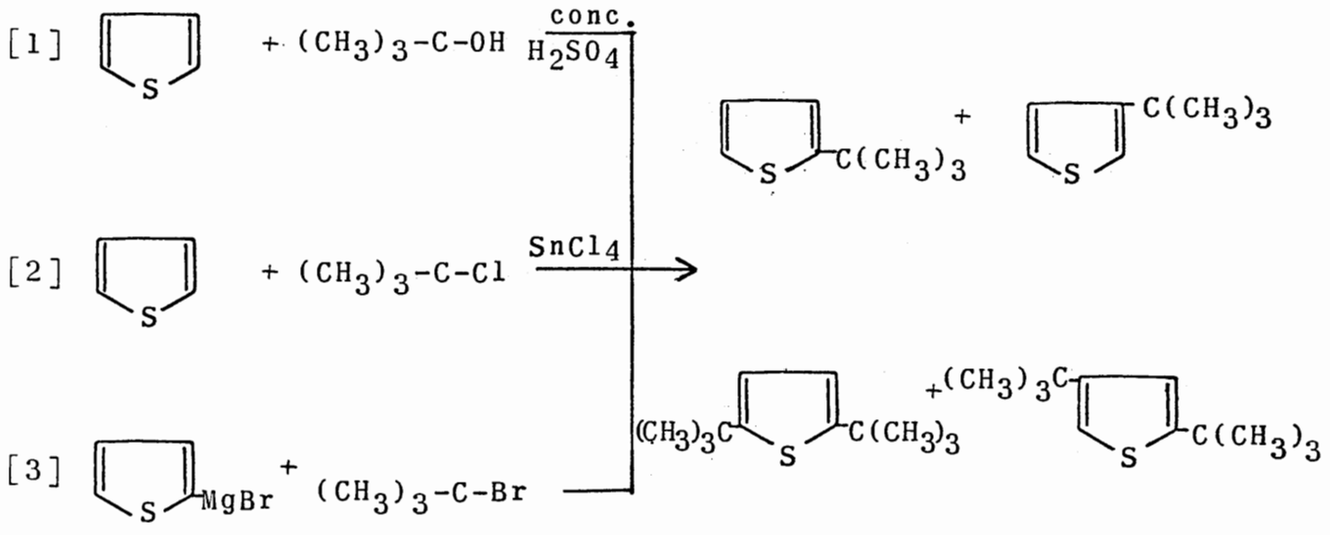




10.75% 22.94% 34.77% 31.54%

The intermediate necessary for the synthesis of 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)-

thiophene was 2-t-butylthiophene of high purity. Three syntheses were investigated for the preparation of 2-t-butylthiophene. A mixture of four products was obtained in each case as shown by the following equations.



Alkylation of thiophene with t-butyl alcohol in the presence of sulfuric acid proceeded with extensive polymerization. However, a 57% yield of the mono-t-butylthiophenes was obtained. The isomer ratio of 2-t-butylthiophene to 3-t-butylthiophene was 1:1. The proportional yield of the isomeric compounds was determined by quantitative gas chromatography. This mixture was difficult to separate by use of the spinning-band column.

The second approach involved the interaction of 2-thienylmagnesium bromide with t-butyl bromide. Little polymerization was observed and a yield of 36% of the

mono-t-butylthiophenes was obtained. The ratio of 2-t-butylthiophene to 3-t-butylthiophene was 2:1. Separation could be effected without difficulty using the spinning-band column. Several distillations were required to produce 2-t-butylthiophene of high purity.

However, a large scale synthesis reported by Sy (26) was investigated. The Friedel-Crafts alkylation of thiophene with t-butyl chloride in the presence of stannic chloride proceeded in 60% yield with minimum polymerization. By careful control of the temperature and reaction time polyalkylation was reduced to a minimum. The ratio of 2-t-butylthiophene to 3-t-butylthiophene was 3.44 to 1. The separation of this mixture (ratio 3.44 to 1) by use of the spinning-band column was achieved with greater purity of the 2-t-butylthiophene on the initial distillation. A second distillation resulted in 2-t-butylthiophene of 99.95+% purity. As the isomer ratio increases, ease of separation by use of the spinning-band column increases. The method for the synthesis of the mono-t-butylthiophenes used by Sy was preferred for the above reason.

The preparation of 2-bromo-5-t-butylthiophene was accomplished by a modification of Cagniants' procedure (38) for the preparation of 2-bromo-5-ethylthiophene. No 2-bromo-5-t-butylthiophene was obtained after a reaction time of two hours, the time required for the bromination of 2-ethylthiophene. However, after a reaction time of

forty-eight hours a good yield of 2-bromo-5-t-butylthiophene was obtained. Mass spectral analysis indicated peaks of equal intensity at m/e 218^+ and m/e 220^+. This was expected since bromine has isotopic masses of 79 (50.54%) and 81 (49.46%). These values (m/e 218^+ and m/e 220^+) corresponded to the molecular weight of 2-bromo-5-t-butylthiophene. Secondly, low voltage data showed only two parent ions at m/e 218^+ and m/e 220^+. An isomer could not be detected by mass spectral analysis.

Gas chromatographic data showed only one symmetrical peak. Three different analytical columns were used and both flow and column temperature were varied. Under the gas chromatographic conditions employed, no evidence of another isomer (2-t-butyl-4-bromothiophene) or compound was obtained. Gas chromatography indicated a purity of 99.95^+%.

Another approach to the synthesis of 2-bromo-5-t-butylthiophene involved the attempted alkylation of 2-bromothiophene with t-butyl chloride using stannic chloride. The only reaction obtained was polymerization with partial recovery of the 2-bromothiophene. Also, alkylation of 2-bromothiophene with t-butyl chloride in the presence of aluminum chloride resulted in extensive polymerization and recovery of some of the 2-bromothiophene.

Before carrying out the Grignard reaction of 2-bromo-5-t-butylthiophene using labeled t-butyl chloride

the reaction was first carried out using unlabeled t-butyl chloride. The Grignard reaction was performed using excess magnesium and an extended reflux time in order to convert all of the 2-bromo-5-t-butylthiophene to 5-t-butyl-2-thienyl-magnesium bromide. The excess magnesium was then removed before t-butyl chloride was added. Analysis of the product of the reaction by gas chromatography indicated three components. By gas chromatographic retention times the components were tentatively identified as 2-t-butylthiophene, 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene. Low voltage mass spectrometry indicated two parent ions at m/e 140 and at m/e 196. These m/e values corresponded to 2-t-butylthiophene and to the di-t-butylthiophenes. The di-t-butylthiophenes were separated by preparative gas chromatography. The infrared spectra characterized fraction 1 as 2,5-di-t-butylthiophene and fraction 2 as 2,4-di-t-butylthiophene. The assignments were made based on the data given in Table 2.

Mass spectra of fraction 1 and 2 were in general agreement with the spectra of 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene as reported by Foster (18). The two parts of the spectra compared were the m/e 165^+ peak and the m/e 57^+ peak. The m/e 165^+ ion was twice as intense in the 2,5-di-t-butylthiophene.

TABLE 2

INFRARED OVERTONE REGION DATA ON PURIFIED FRACTIONS AND SOME DISUBSTITUTED ALKYLTHIOPHENES

Fraction 1 from GLC microns	Fraction 2 from GLC microns	2,5-dialkyl-thiophenes correlation (18) microns	2,4-dimethyl-thiophene (18) microns
5.75	----	5.8	----
6.0	5.98	6.0	6.08
6.26	----	6.27	----
6.46	6.46	6.43	6.41

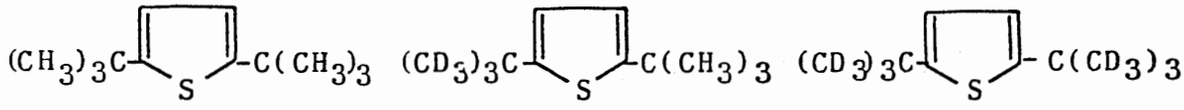
Infrared spectra characterized fraction 1 as 2,5-di-t-butylthiophene and fraction 2 as 2,4-di-t-butylthiophene. Mass spectra of fraction 1 and fraction 2 were in general agreement with the spectra of 2,5-di-t-butylthiophene and 2,4-di-t-butylthiophene, respectively.

The reaction was repeated using t-butyl chloride-$-^2H_9$. No difficulty was encountered and the 2,5-di(t-butyl-$-5-^2H_9$)thiophene and 2,4-di(t-butyl-4-$-^2H_9$)thiophene were obtained and separated as indicated above. The mass spectra of the compounds indicated each sample was of high isotopic purity.

The Grignard reaction is unusual in that both di-t-butylthiophenes were obtained. This was expected since both mono-t-butylthiophenes had been obtained in a reaction of the same type.

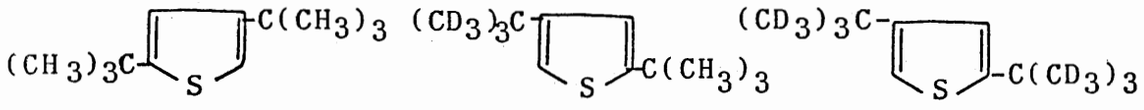
C. Friedel-Crafts Alkylation of Mono-t-Butylthiophenes Using Labeled t-Butyl Chloride-$^2H_9$

An approach investigated for the synthesis of 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)thiophene involved the alkylation of 2-t-butylthiophene by t-butyl chloride in the presence of stannic chloride. The reaction proceeded without difficulty and the 2,5-isomer was separated from the 2,4-isomer by use of the preparative gas chromatograph. Analysis of the two isomers by mass spectroscopy indicated that transalkylation had occurred during the reaction. The following indicates the 2,5-isomers obtained and the percentage obtained from mass spectral data of each in the mixture:



36.2%	61.5%	2.28%
m/e 196	m/e 205	m/e 214

The 2,4-isomers obtained and the percentage obtained from mass spectral data of each is as follows:



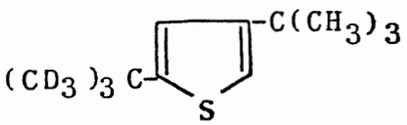
35.05% 63% 1.95%

m/e 196 m/e 205 m/e 214

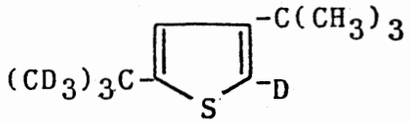
The mass spectra were obtained at low voltage for the two fractions. The parent ions at m/e 196, 205 and 214 appeared in the mass spectrum of each isomer. The percentage for each m/e value was calculated by dividing the sum of the peak heights (m/e 196, 205, 214) into each individual peak height.

Using unlabeled compounds, Wynberg and Wiersum (29) in 1965 indicated that no isomerization or transalkylation occurred using stannic chloride. When anhydrous aluminum chloride was used isomerization and transalkylation were observed for the t-butylthiophenes. A review of Friedel-Crafts alkylations of alkylbenzenes (39), using various Lewis acids and Bronsted acids as carriers, gave numerous examples of isomerization and transalkylation. Hence, the alkylthiophenes simply parallel the alkylbenzenes in their behavior when exposed to Friedel-Crafts carriers.

An approach investigated for the synthesis of 2,4-di(t-butyl-2-$^2H_9$)thiophene involved alkylation of 3-t-butylthiophene with t-butyl chloride-$^2H_9$ in the presence of stannic chloride. Alkylation of the 3-t-isomer proceeded at a much slower rate than alkylation of the 2-t-isomer. Gas chromatographic analysis of the product isolated indicated the presence of the 2,4-di-t-isomer. Analysis of the isomer by mass spectroscopy indicated that a replacement of hydrogen by deuterium had occurred in 50% of the 2,4-isomer. The following two compounds were indicated by mass spectroscopy.



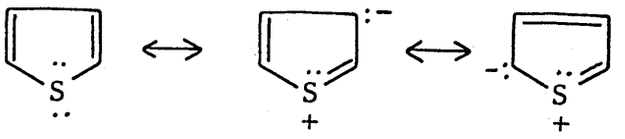
m/e 205^+



m/e 206^+

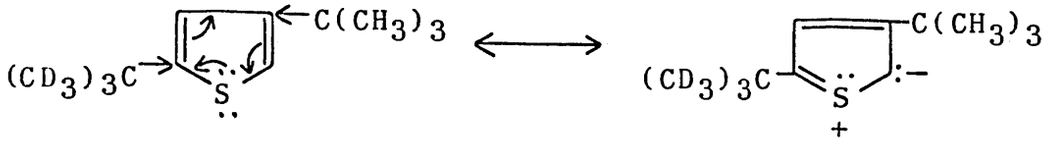
The positions of the deuterium and of the hydrogen on the ring are not known. Mass spectral analysis indicated parent ions at m/e 205 and m/e 206. The peak heights of the m/e 205 and m/e 206 ions were equal. This indicated that each was present to the extent of 50% in the mixture. The deuterium is believed to be substituted on the 5-position.

Major resonance contributors of thiophene are:



I II III

Possible resonance forms of 2,4-di(t-butyl-$^{2}H_{9}$)thiophene are:



(a) (b)

Structure (b) resembles resonance form III. Thus any entering electrophilic group would find electrons more available at the 5-position. A nuclear magnetic resonance spectrum would be useful in determining this location. An infrared spectrum was obtained but sufficient literature correlations have not been made to allow an exact interpretation of the position of the deuterium atom.

D. Interpretation of Mass Spectral Data for Mono-t-butylthiophene

Only minor differences appeared between the 70 electron volt mass spectra of 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene. The complete mass spectral data obtained for these two molecules are presented in the Appendix. A partial listing of the spectra is presented in Table 3 for the discussion. The 3-(t-butyl-$^2H_9$)-thiophene has slightly more intense peaks at m/e 100, 99, 87, 85, and 66 than the 2-(t-butyl-$^2H_9$)thiophene. The 2-(t-butyl-$^2H_9$)thiophene has more intense peaks at m/e 131, 97, 84, 83, 65, and 58 than the 3-(t-butyl-$^2H_9$)thiophene. There is also a slight increase in the parent ion intensity of the 2-(t-butyl-$^2H_9$)thiophene compared to the 3-(t-butyl-$^2H_9$)thiophene. The ion distributions of the unlabeled mono-t-butylthiophenes parallel that obtained from the labeled mono-t-butylthiophenes. The major difference between the mass spectra of the labeled mono-t-butylthiophenes and those of the unlabeled mono-t-butylthiophenes was the expected shift of the m/e's due to isotopic labeling.

1. Major fragment ions

Base peak formation as shown in Figure 6 confirms the loss of a methyl from the t-butyl group as observed by Foster and coworkers (18).

TABLE 3

PARTIAL MASS SPECTRA OF MONO-t-BUTYLTHIOPHENES

m/e	Total Ion Intensity (labeled) 2-t-	3-t-	Probable Ion	Total Ion Intensity (unlabeled) 2-t-	3-t-	Probable Ion
57	0.595	0.421	C_2SH^+	0.668	0.474	$C_4H_9^+$
58	0.595	0.516	$C_2H_2S^+$	1.176	1.082	$C_2H_2S^+$
65	0.410	0.396	$C_5HD_2^+$	2.079	1.905	$C_5H_5^+$
66	0.245	0.251	$C_4D_9^+$	0.515	0.416	$C_5H_6^+$
83	0.251	0.237	$C_4H_3S^+$	0.298	0.356	$C_4H_3S^+$
84	0.262	0.254	$C_4H_4S^+$	0.624	0.952	$C_4H_4S^+$
85	0.351	0.499	$C_4H_3DS^+$	3.701	4.371	$C_4H_5S^+$
86	0.304	0.524	$C_4H_2D_2S^+$	0.258	0.293	$C_4H_6S^+$
87	2.172	2.675	$C_4H_3D_2S^+$	0.196	0.219	$C_4H_7S^+$
91	0.024	0.017	$C_7H_3D_2^+$	1.719	1.306	$C_7H_7^+$
97	0.380	0.312	$C_7D_6H^+$	4.718	5.724	$C_5H_5S^+$
99	3.035	3.894	$C_5H_3D_2S^+$	0.290	0.384	---
100	1.400	1.813	$C_5H_2D_3S^+$	0.018	0.021	---
101	0.501	0.633	$C_5H_3D_3S^+$	0.015	0.010	---
109	0.071	0.081	---	1.415	1.270	$C_6H_5S^+$
111	0.928	0.820	$C_6H_3D_2S^+$	0.225	0.224	---
113	0.654	0.569	$C_6H_3D_3S^+$	0.022	0.031	---
114	0.162	0.154	$C_6H_2D_4S^+$	---	---	---
125	0.026	0.031	---	27.217	25.759	$C_7H_9S^+$
126	0.030	0.028	---	2.221	2.092	$C_7H_{10}S^+$
127	0.139	0.139	---	1.198	1.197	$C_7H_{11}S^+$
130	1.892	1.866	$C_7H_2D_6S^+$	---	---	---
131	29.468	27.890	$C_7H_3D_6S^+$	---	---	---
132	3.734	3.428	$C_7H_2D_7S^+$	---	---	---
133	1.435	1.328	$C_7H_3D_7S^+$	0.004	---	---
139	---	---	---	0.015	0.010	$C_8H_{11}S^+$
140	0.006	---	---	6.314P	6.713P	$C_8H_{12}S^+$
148	0.625	0.639	$C_8H_2D_9S^+$	---	---	---
149	6.769P	6.738P	$C_8H_3D_9S^+$			

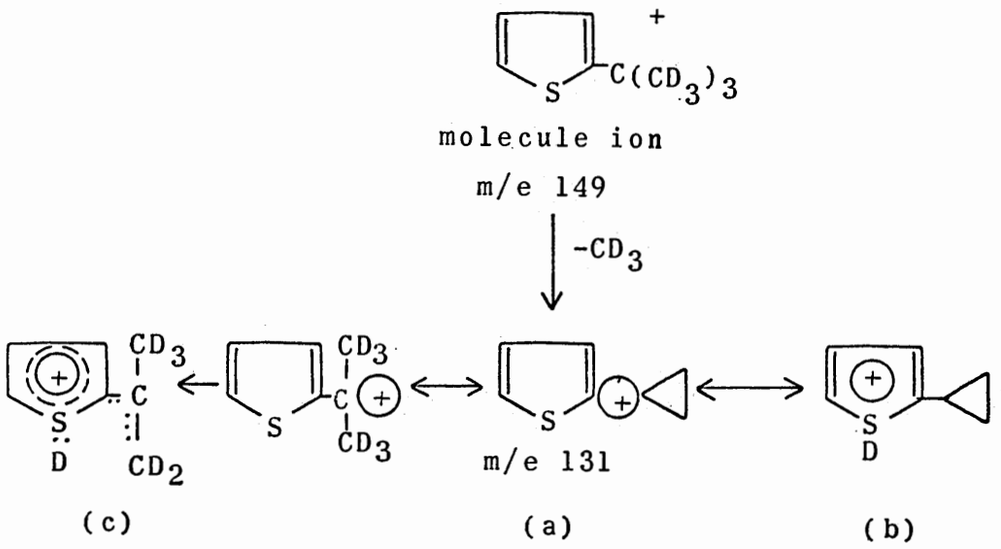
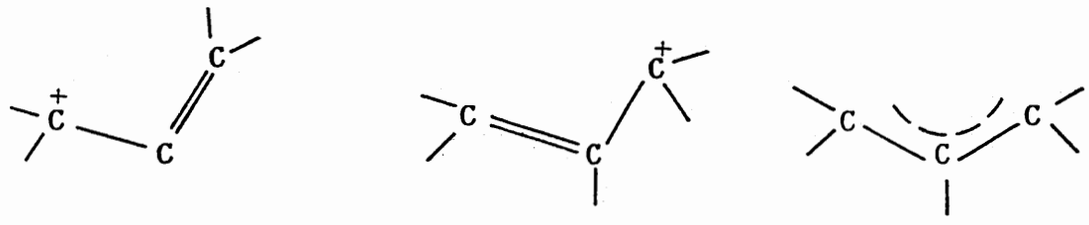


Figure 6

Base Peak Formation for the Labeled Mono-t-Butylthiophenes

Several possibilities may be considered which give additional stability to the m/e 131^+ ion. The cationated cyclopropane complex was proposed in 1956 by Rylander and Meyerson (6) as a probable ionic intermediate to account for certain rearrangements shown by t-butyl-benzenes under electron impact. If the alkylthiophenes are presumed to parallel the alkylbenzenes when the t-butyl group is present, then by analogy the m/e 131 ion could be that shown in Figure 6 (a). An alternate structure is the formation of cyclopropylthiophene as shown in Figure 6 (b). The cyclopropylthiophene structure was proposed by Foster in 1959 (18) and requires the use of the concept of the 10 electron sulfur atom. The m/e 131 structure contains an allyl system. The allyl system shown in Figure 7 is a classical one in resonance theory.



(a) (b) (c)

Figure 7

Resonance Structures for the Allyl System

The m/e 131 ion is shown as a nonclassical carbonium ion in Figure 6 (c). Winstein in 1954 reported the first nonclassical carbonium ions in an allylic system, however, this was in solution. Since that time numerous examples of nonclassical carbonium ions have appeared in the literature (40). Mass spectroscopists also like to utilize these structures.

A higher intensity of the ions of 2-(t-butyl-$^2H_9$)-thiophene as compared to that of 3-(t-butyl-$^2H_9$)thiophene for certain m/e's can be related to the formation of an ionic structure of a greater stability for the particular ion in the 2-isomer. The 2-(t-butyl-$^2H_9$)thiophene will always have one or two deuterium atoms in the vicinity of the sulfur atom (Figure 8) regardless of the modes of vibration within the molecule. The deuterium atom may interact with the sulfur atom possibly by utilizing the d orbital of the sulfur to form a S-D bond.

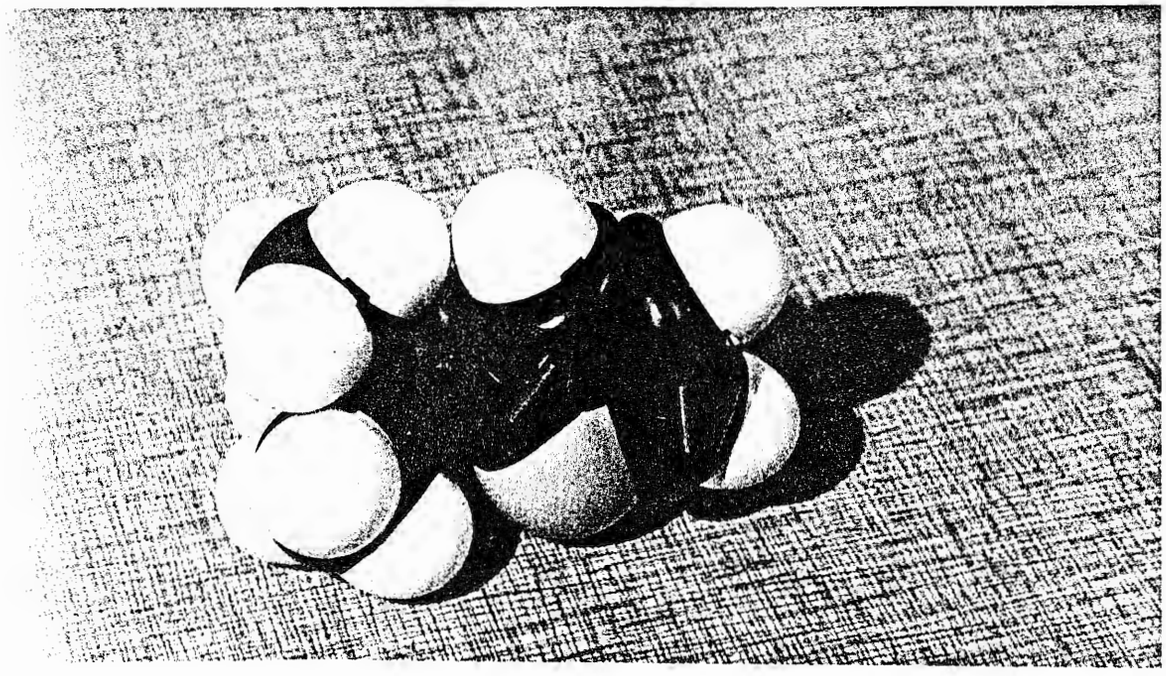
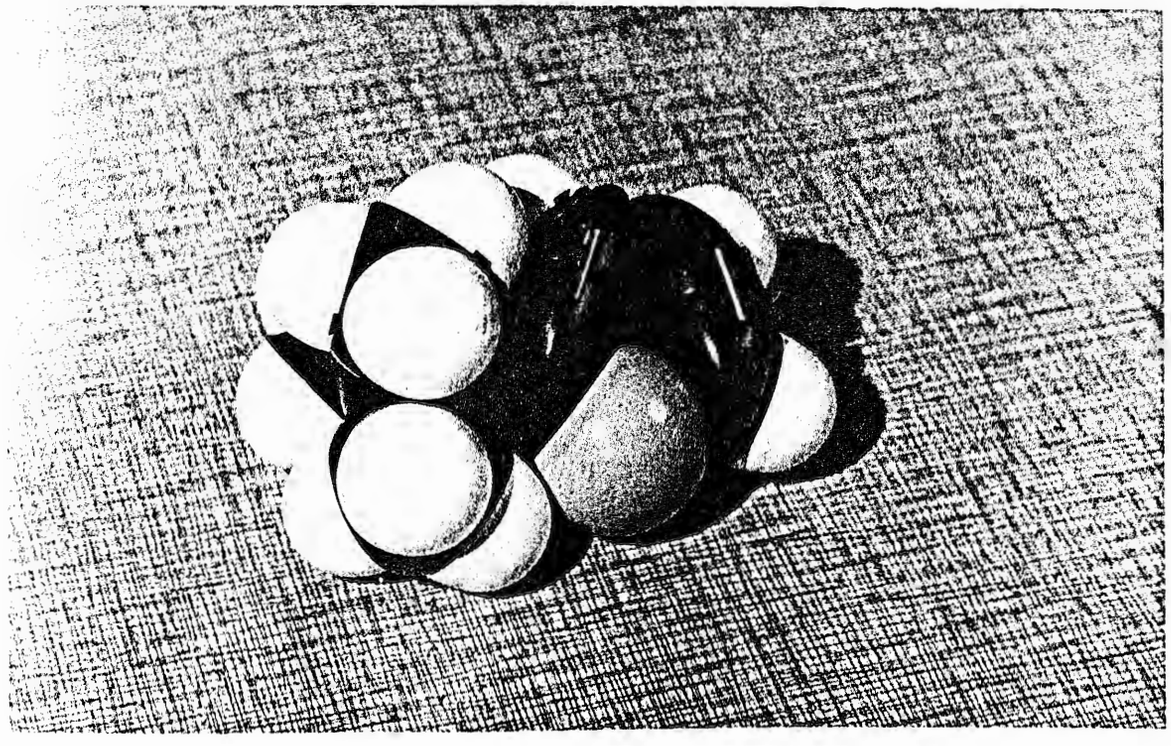


Figure 8a

Molecular Models of 2-(t-Butyl-$^{2}H_{9}$)thiophene



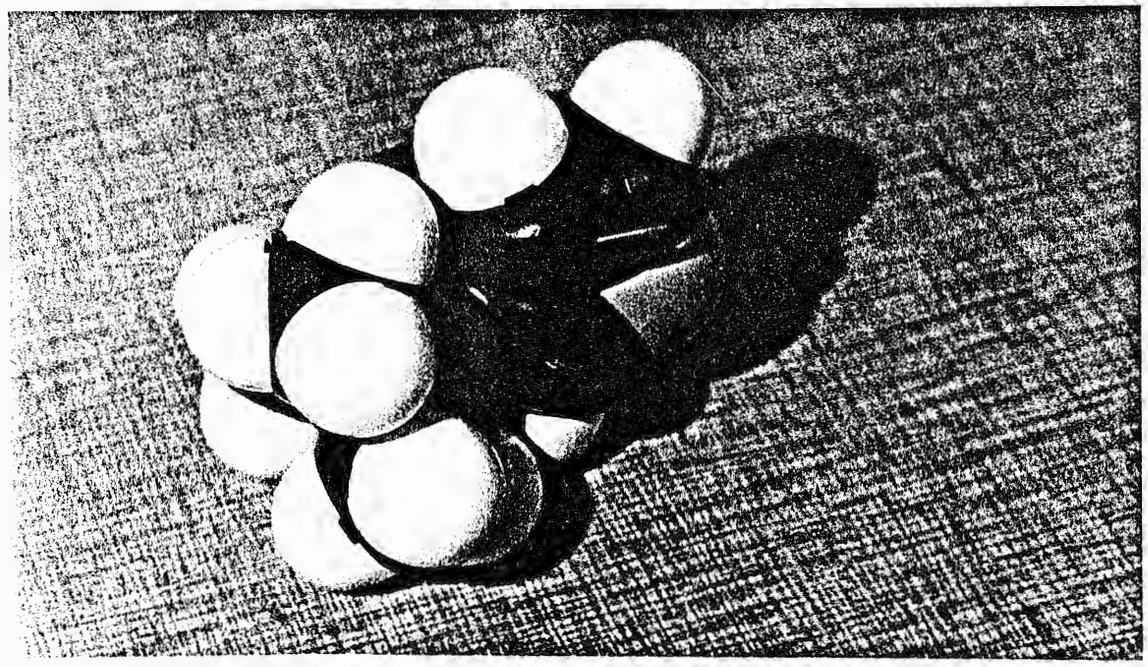
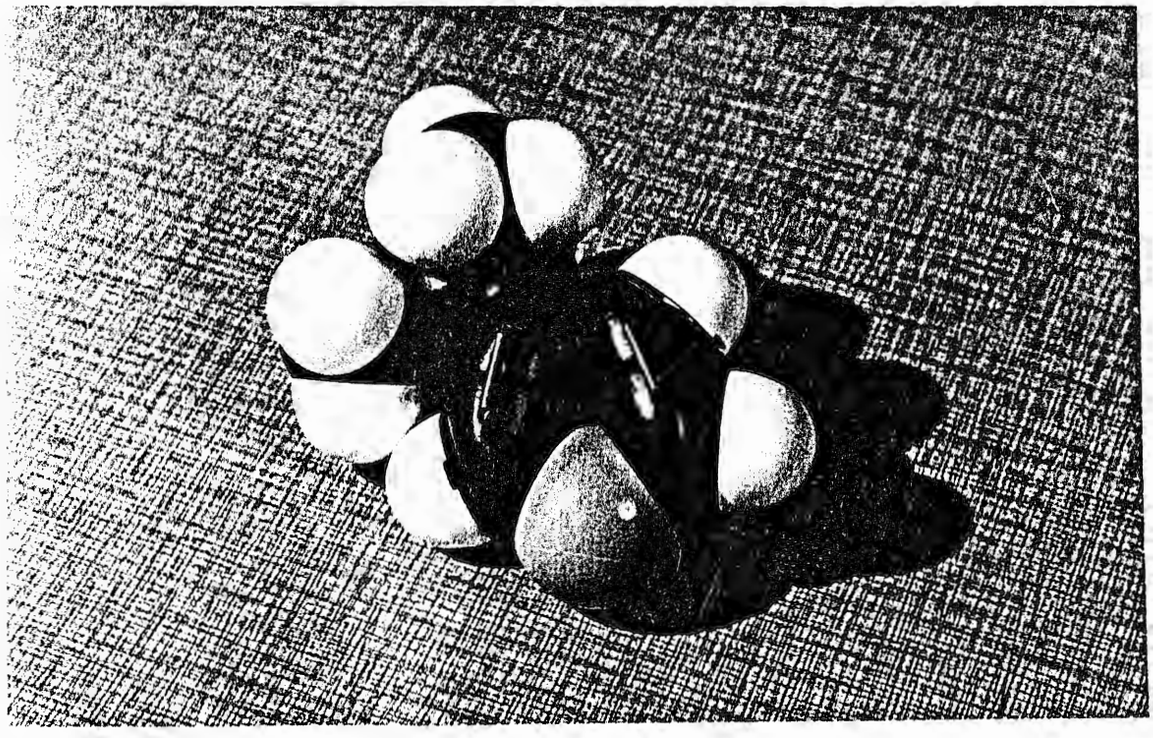


Figure 8b

Molecular Models of 3-(t-Butyl-$^{2}H_{9}$)thiophene



The major fragment ions of high intensity in addition to the parent ion and the first fragment ion (m/e 131) are m/e's 130, 113, 101, 100, 99 and 87. A suggested fragmentation pattern for the formation of these ions is shown in Figure 9. The pathways indicated for the formation of the various ions should be regarded as possible pathways and not as defined pathways. Delocalization of the electrons occurs to give an alkylaromatic system of greater stability. Nonclassical ion formation to give structures of greater stability can be written for most of the fragment ions. In the fragmentation scheme shown in Figure 9 many other processes could occur to give the charged ions by other routes. Emphasis must also be placed on the fact that observation of the presence of a given m/e does not allow us to assign a structure. Speculation is permitted and a pathway is tentatively established. A similar fragmentation scheme may be written in the same general manner for 3-(t-butyl-$^2H_9$)-thiophene. The m/e 87 and m/e 99 corresponds to the m/e 85 and m/e 97 ions proposed for the unlabeled mono-t-butylthiophenes. The loss of a neutral ring hydrogen to form m/e 130 from m/e 131 is not an unexpected occurrence since this is a high energy process. High energy processes are shown in Figure 9 by dashed arrows.

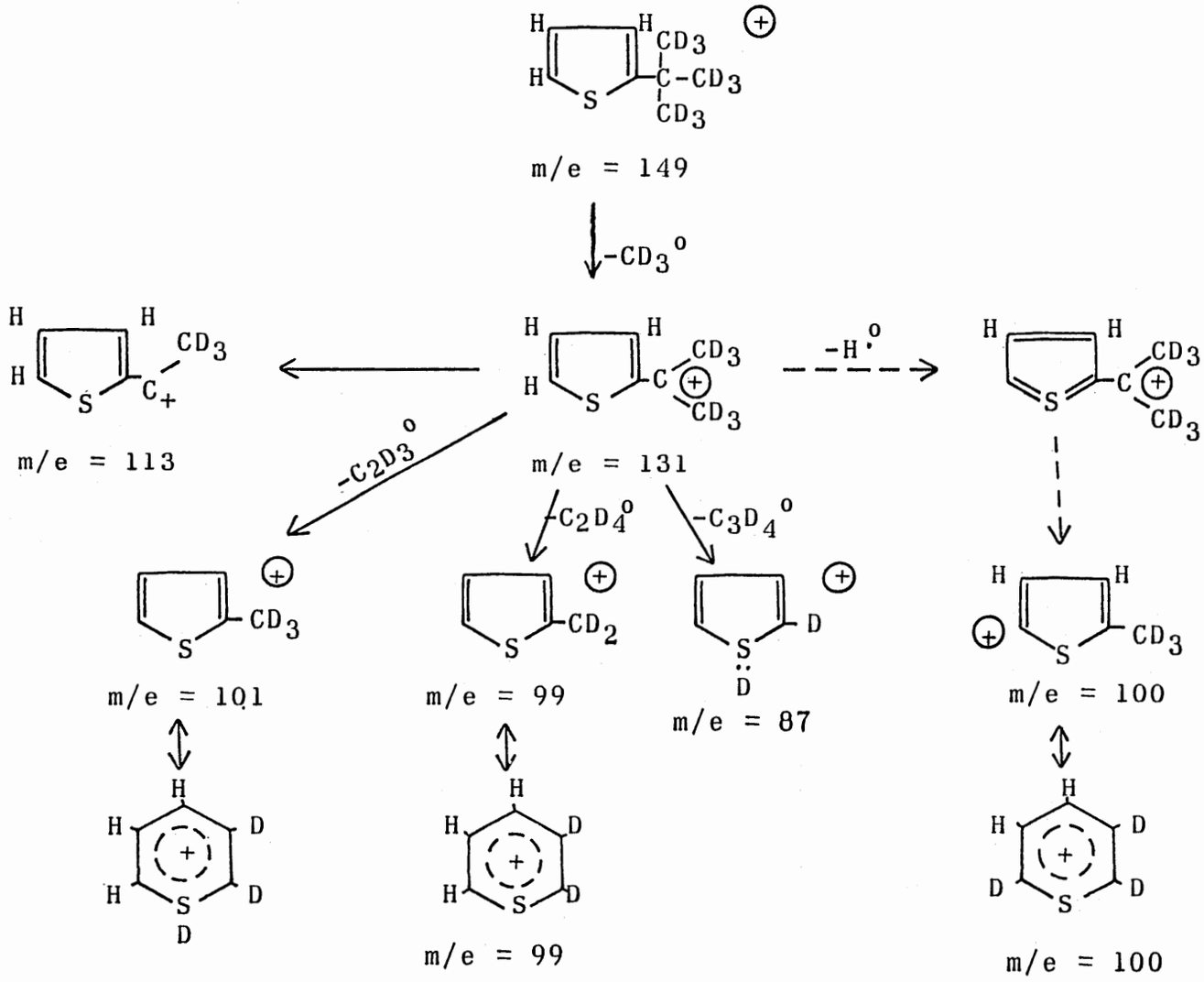


Figure 9.--Some Fragmentation Paths of the Labeled Mono-t-Butylthiophenes

The removal of the hydrogen is shown from the 5-position in the formation of m/e 130 from m/e 131. Due to the influence of the sulfur atom the 5-position is activated 100 to 1 compared to the 3-position provided that the 2-position is substituted with an alkyl group (41). This suggests that the loss of the hydrogen from the 5-position would be favored. However, loss of hydrogen could be random in a high energy process. Except for the ions at m/e 100, 99, 87 and 66 the major fragments form about the same ion intensities in the 70 electron volt spectra.

2. Low voltage data

A plot of the low ionization voltage versus intensity of the fragment ion appearing at low voltage for the mono-t-butylthiophenes and mono(t-butyl-$^{2}H_{9}$)thiophenes are shown in Figure 10 and Figure 2, respectively. The data at low ion intensities are near the limit of detection and these points are probably accurate to only $\pm$ 0.5 electon volt.

The parent ion production curve and the m/e 131 ion production curve are quite similar for the two labeled isomers. This suggests that formation of the parent ion (m/e 149) and the ion at m/e 131 are probably identical processes for the two isomers, and do not involve ring substitution differences. The m/e's at 100, 99, and 87 have approximately the same appearance potential for each isomer. This indicates that there is a common precursor for these three ions.

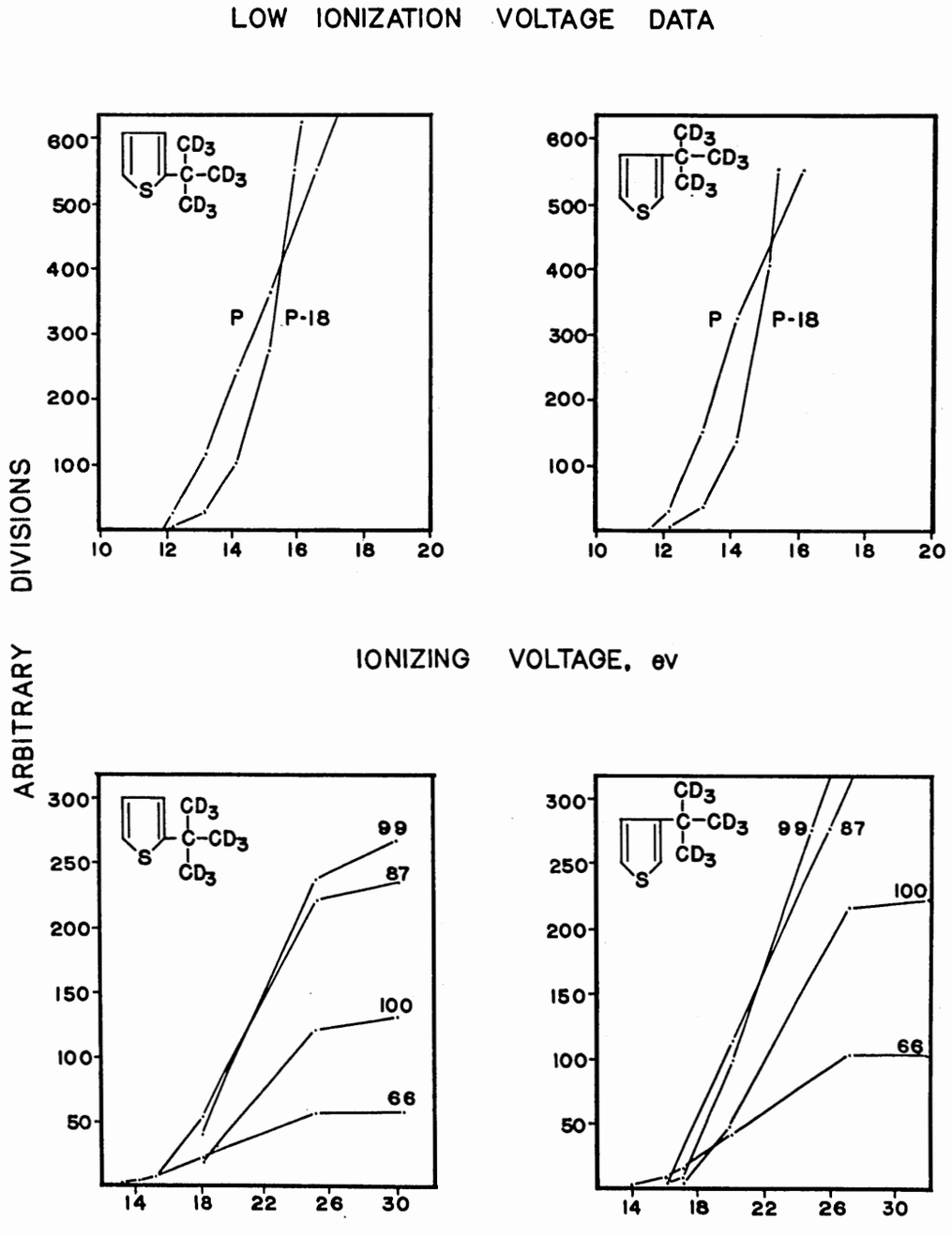


Figure 10

Low Ionization Voltage Data for 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)thiophene

The m/e 66 ion appears four electron volts higher for the 3-isomer than for the 2-isomer. This is considerable energy since one electron volt equals 23.03 kilocalories per mole. This gross difference in electron voltage must indicate a significant contribution from the substitutional position.

Comparing the low voltage data of the mono-(t-butyl-$^2H_9$)thiophenes with the mono-t-butylthiophenes reveals some interesting information and/or inconsistencies. The presence of m/e 100 and m/e 99 peaks in the labeled mono-t-butylthiophenes are not expected, since the corresponding ions at m/e 98 and m/e 97 for the unlabeled mono-t-butylthiophenes were apparently observed but not reported (42). Also, the m/e 85 ($C_4H_3DS^+$) and m/e 64 ($C_4D_8^+$) peaks in the low voltage spectra of the labeled mono-t-butylthiophenes are absent. The corresponding ions at m/e 84 and m/e 56 in the unlabeled mono-t-butylthiophenes were prominent.

The formation of the thiapyrillium ion (m/e=99) appears to be the most favored process after formation of the m/e 131 ion. The charged ion at m/e 87 forms with about the same ease as m/e 99 forms. The 87^+ ion is in an excited state and could be stabilized by the deuterium sharing the nonbonding electrons of sulfur.

Ion production of the t-butyl group from the 3-isomer is greater than from the 2-isomer. However, the appearance potential of the 2-t-isomer is 4 electron volts lower than

the 3-t-isomer. This difference in appearance potential and ion production of the two isomers at intermediate voltages indicates several mechanisms for the formation of the two ions, with varying amounts of each process participating in ion formation. Approximately equal ion intensities of the 2-t- and 3-t-isomers at 70 electron volts indicate that the excess energy available at this voltage averages out the processes that are producing ions.

The ion production of the m/e 100 species ($C_5D_3H_2S^+$) is greater for the 3-isomer than for the 2-isomer. The key to the formation of the m/e 100 ion probably lies in the conformation that the species assumes when the t-butyl group is in the 3-position. Secondly, the interactions between the sulfur and the deuterium can be presumed to be at a minimum when the t-butyl group is in the 3-position. By use of models (Figure 8) the deuteriums on the t-butyl group by favorable rotation can be located near the hydrogen atoms on the 2- and 4-positions of the thiophene ring. In an excited state species it is conceivable then that both of the hydrogens could be exchanged by deuterium. Alternatively, a carbon-carbon interaction could occur between a carbon of the t-butyl group and a ring carbon (2 or 4).

3. Doubly charged ions

Doubly charged ions contribute 1.25% of the total ion intensity in the spectrum of 3-(t-butyl-$^2H_9$)thiophene,

whereas, doubly charged ions in the spectrum of 2-(t-butyl-$^2H_9$)thiophene contribute 0.68% of the total ion intensity to its spectrum. Table 4 compares the doubly charged ions observed for each compound. The peak at m/e 74.5 in the 2-(t-butyl-$^2H_9$)thiophene represents a doubly charged parent ion of mass 149. The contribution of this doubly charged parent ion to the total parent ion intensity is approximately 1/1000 of that contributed by the singly charged ion. No peak at m/e 74.5 was observed in the 3-(t-butyl-$^2H_9$)-thiophene. The first fragmentation of the doubly charged molecule ion supports the process $149^{++} \rightarrow 131^{++} + CH_3^{o}$; and the existence of a doubly charged ion at m/e 131. Doubly charged m/e 131 ions are observed for both isomers.

At m/e 43.5 a peak was observed in the 2-(t-butyl-$^2H_9$)thiophene spectrum. This corresponds to the m/e 87^{++} ion.

Foster (18) suggested that doubly charged ions would appear at 131^{++}, 127^{++}, and 123^{++} in the deuterium labeled compounds which correspond to 125^{++}, 123^{++}, and 121^{++} observed in the unlabeled mono-t-butylthiophenes. The suggested ions were observed in both compounds. The following processes were defined:

$$131^{++} \rightarrow 127^{++} + D_2$$

$$127^{++} \rightarrow 123^{++} + D_2$$

$$123^{++} \rightarrow 119^{++} + D_2$$

TABLE 4

DOUBLY CHARGED IONS OF LABELED MONO-t-BUTYLTHIOPHENES

m/e	Doubly Charged Ions	
	2-(t-butyl-$^2H_9$)-thiophene	3-(t-butyl-$^2H_9$)-thiophene
37.5	75^{++}	---
38.5	77^{++}	---
41.5	83^{++}	---
43.5	87^{++}	---
47.5	---	95^{++}
53.5	107^{++}	107^{++}
54.5	109^{++}	109^{++}
55.5	111^{++}	111^{++}
56.5	113^{++}	113^{++}
58.5	117^{++}	117^{++}
59.5	119^{++}	119^{++}
60.5	121^{++}	121^{++}
61.5	123^{++}	123^{++}
62.5	125^{++}	125^{++}
63.5	127^{++}	127^{++}
64.5	129^{++}	129^{++}
65.5	131^{++}	131^{++}
66.5	---	133^{++}
68.5	137^{++}	137^{++}
69.5	139^{++}	139^{++}
70.5	141^{++}	141^{++}
71.5	143^{++}	143^{++}
72.5	145^{++}	145^{++}
73.5	147^{++}	147^{++}
74.5	149^{++}	---

The doubly charged ions indicate an unusual series of losses of H_2 and D_2. This is thought to be mostly loss of D_2 since the raio of deuterium to hydrogen is 9 to 3. If this loss is prevalent with doubly charged ions, a certain amount of D_2 loss or H_2 loss must occur with the corresponding singly charged ions.

4. Metastable ion decompositions

A metastable ion is one that decomposes after nearly complete acceleration from the ion source, but before complete mass separation. The product ion from such a decomposition gives rise to a somewhat diffuse peak in the spectrum below its actual m/e, and is called a metastable peak or metastable ion. These metastable ions are quite useful in eludicating ion decomposition pathways. Many reactions producing major ions are not represented by such "metastable" peaks in the spectrum. Also, the presence of a peak representing a metastable ion decomposition to form a particular fragment ion only shows that some of the normal peak for this ion in the spectrum is formed by this particular pathway. Not necessarily all of it is formed in this way. In the conventional single-focusing mass spectrometer the product ion, m_2, from the decomposition of precursor ion, m_1, is most likely to be found at a mass m^*, where $m^* = \frac{m_2^2}{m_1}$ (43).

The metastables observed in the spectra of 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene are not as numerous as those observed in the spectra of 2-t-butylthiophene and 3-t-butylthiophene. One of the explanations that can be offered is that upon calculation of metastables for a number of suggested pathways the metastable mass appeared under a peak and thus could not be observed. Table 5 indicates those metastable ions whose mass number is nearly an integral value and cannot be distinguished from the peak at this m/e value.

Secondly, these spectra were obtained using the electrometer detection system instead of the electron multiplier. The electronic noise is increased when operating in the electrometer mode. This creates difficulty in locating diffuse metastable ions of low intensity.

Experimental values of metastable peaks did not correlate with the calculated values of expected fragmentation processes. Fragmentation patterns were developed by correlation of the labeled mono-t-butylthiophenes with the unlabeled mono-t-butylthiophenes.

Table 5 indicates fragmentation processes for which metastable ions were calculated. Further studies will be required to delineate the fragmentation path represented by each metastable ion observed in the spectrum. Observed metastables are listed in Table 6.

TABLE 5

CALCULATED METASTABLE PEAKS IN THE MASS SPECTRA OF THE LABELED MONO-t-BUTYLTHIOPHENES

Calculated Metastable m/e	Process Probably Occurring	Total Ion Intensity	
		2-t-	3-t-
115.35	$149^+ \rightarrow 131^+ + 18^0$ (CD_3)	0.006	0.006
147.20	$149^+ \rightarrow 148^+ + 1^0$ (H)		
48.60	$149^+ \rightarrow 85^+ + 64^0$ (C_4H_8)		
46.35	$149^+ \rightarrow 83^+ + 66^0$ (C_4H_9)		
92.1	$148^+ \rightarrow 116^+ + 32^0$ (C_2D_4)		
92.1	$148^+ \rightarrow 116^+ + 32^0$ (S)		
87.3	$144^+ \rightarrow 112^+ + 32^0$ (C_2D_4)		
87.3	$144^+ \rightarrow 112^+ + 32^0$ (S)		
78.02	$131^+ \rightarrow 101^+ + 30^0$ (C_2D_3)		
74.97	$131^+ \rightarrow 99^+ + 32^0$ (C_2D_4)		
71.97	$131^+ \rightarrow 97^+ + 34^0$ (H_2S)		
57.91	$131^+ \rightarrow 87^+ + 40^0$ (C_3H_4)		
73.09	$129^+ \rightarrow 97^+ + 32^0$ (S)		
73.09	$129^+ \rightarrow 97^+ + 32^0$ (C_2D_4)		
71.2	$127^+ \rightarrow 95^+ + 32^0$ (S)		
71.2	$127^+ \rightarrow 95^+ + 32^0$ (C_2D_4)		
57.91	$116^+ \rightarrow 88^+ + 28^0$ (C_2D_2)		

Note: The corresponding processes in the unlabeled mono-t-butylthiophenes show a metastable ion.

TABLE 6

METASTABLES OBSERVED IN THE SPECTRA OF
2-(t-BUTYL-$^2H_9$)THIOPHENE AND 3-(t-BUTYL-$^2H_9$)THIOPHENE

2-(t-Butyl-$^2H_9$)thiophene	3-(t-Butyl-$^2H_9$)thiophene
m/e	m/e
45.8	39.9
54.8	41.8
55.8	44.8
61.8	45.8
67.6	76.5
88.5	85.5
98.7	86.8
115.4	98.8
148.7	115.4
	129.8
	131.8
	148.8

5. Proposed future studies

In the formation of the m/e 100 a hydrogen is removed from the ring. It would be of interest to determine which hydrogen is lost when the m/e 100 ion is formed. This would give a definite insight into the conformation of the ion species and aid in defining pathways for the m/e 100 ion. Three of the molecules necessary for this study would be 2-*t*-butylthiophene-3-$^2H_1$, 2-*t*-butylthiophene-5-$^2H_1$, 3-*t*-butylthiophene-2-$^2H_1$, 3-*t*-butylthiophene-4-$^2H_1$, and 3-*t*-butylthiophene-5-$^2H_1$.

The synthesis of these molecules would involve the preparation of the appropriate bromo-mono-*t*-butylthiophene, a Grignard reaction and hydrolysis of the Grignard with deuterium oxide.

If the *t*-butylcarbon atom were to be labeled with carbon-13, then it could be readily ascertained if the ring to α-carbon bond was maintained when cleavage of the m/e 131 ion to form m/e 99 ion occurred. If the carbon-13 was randomized, as it would be by the formation of a cationated cyclopropane complex, then the resulting m/e 97 species should contain the label one-third of the time. If the m/e 87 ion is a simple cleavage ion involving only two deuterium shifts, then none of the labeled carbon-13 should appear in the m/e 87 species. Deuterium labeling would not be necessary in the *t*-butyl group, only C-13 labeling in the carbon alpha to the ring would be required.

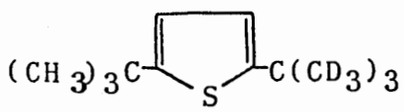
The synthesis of the ^{13}C compound would involve a Grignard reaction of 2-bromothiophene and addition of t-butyl chloride -α-^{13}C. Hydrolysis would yield both isomers labeled with ^{13}C in the alpha position.

Further studies of the fragmentation patterns, metastable ions, doubly charged ions and fragment ions of low m/e values are anticipated. This additional work might lead to other useful labeling experiments.

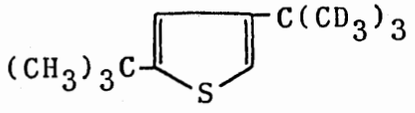
E. Interpretation of Mass Spectral Data for Di-t-butylthiophenes

From examination of the high voltage mass spectra of 2,5-di(t-butyl-4-$^{2}H_9$)thiophene and 2,4-di(t-butyl-4-$^{2}H_9$)-thiophene several striking differences were apparent. Partial mass spectral data are given in Table 7 for the labeled and unlabeled di-t-butylthiophenes. Complete mass spectral data for each of the labeled isomers is in the Appendix. Mass spectral data for the unlabeled isomers have been previously reported (18).

The molecular structure of the labeled di-t-butylthiophenes are as follows:



2,5-di(t-butyl-5-$^{2}H_9$)-thiophene



2,4-di(t-butyl-4-$^{2}H_9$)-thiophene

TABLE 7

PARTIAL MASS SPECTRAL DATA OF THE DI-t-BUTYLTHIOPHENES

m/e	Total Ion Intensity (labeled) 2,5-di-t	2,4-di-t	Probable Ion	Total Ion Intensity (unlabeled) 2,5-di-t	2,4-di-t	Probable Ion
57	0.091	3.551	$C_4H_9^+$	0.70	7.525	$C_4H_9^+$
65	0.504	0.208	---	1.41	1.118	---
66	0.330	2.588	$C_4D_9^+$	0.283	0.234	---
69	0.680	1.012	$C_5HD_4^+$	0.990	2.326	---
85	0.767	0.555	$C_4H_3DS^+$	0.795	0.673	$C_4H_5S^+$
86	1.818	2.109	$C_4H_4DS^+$	0.082	0.060	---
87	0.302	0.336	$C_4H_3D_2S^+$	0.134	0.060	---
91	0.324	0.381	$C_7H_7^+$	1.573	1.250	$C_7H_7^+$
97	2.124	0.184	$C_7HD_6^+$	0.954	0.902	$C_5H_5S^+$
125	0.313	0.258	---	0.571	0.769	$C_7H_9S^+$
126	0.474	0.487	$C_7H_8DS^+$	0.065	0.084	---
131	0.250	0.305	$C_7H_3D_6S^+$	0.065	0.048	---
139	0.380	0.266	$C_8H_5D_3S^+$	0.312	0.132	---
151	0.094	0.159	---	2.350	0.926	$C_9H_{11}S^+$
154	1.161	0.699	$C_9H_8D_3S^+$	0.024	0.036	---
157	1.422	0.370	$C_9H_5D_6S^+$	---	---	---
165	0.013	0.056	---	1.539	0.855	$C_{10}H_{13}S^+$
166	0.046	0.025	---	5.596	0.571	$C_{10}H_{14}S^+$
172	5.606	0.555	$C_{10}H_8D_6S^+$	---	---	---
181	0.091	0.008	---	24.447	23.079	$C_{11}H_{17}S^+$
187	13.237	7.655	$C_{11}H_{11}D_6S^+$	---	---	---
190	14.224	19.415	$C_{11}H_8D_9S^+$	---	---	---
196	0.011	0.012	---	3.593	3.426	$C_{12}H_{20}S^+$
205	4.185P	3.699P	$C_{12}H_{11}D_9S^+$	---	---	---

1. Major fragment ions

Two major differences appear in the spectra of the two labeled isomers. The peaks at m/e 172 (P-33) correspond to the loss of two methyls (CH_3^o and CD_3^o) and the ions are different in intensity by a factor of two, the 2,5-isomer being the larger. The second difference is that the intensity of the t-butyl carbonium ion (m/e 57, m/e 66) is 14 times more intense for the 2,4-isomer. The ion distributions of the unlabeled di-t-butylthiophenes parallel that obtained from the corresponding labeled di-t-butylthiophenes.

The parent ion intensities (m/e 205) are almost identical for the 2,5-compound and the 2,4-compound. The first fragmentation process to form the ion (m/e = 181^+) of largest intensity in the unlabeled di-t-butylthiophenes was the loss of a methyl group. In the labeled molecules two possibilities exist for loss of a methyl group from the parent ion. A loss of a methyl group to give a fragment ion of mass 190 (P-15) or a loss of methyl $-^2H_3$ group to give a fragment ion of mass 187 (P-18) are plausible. For the 2,5-compound the loss of CH_3 or CD_3 to give m/e 190 and m/e 187 are almost equivalent processes based on total ion intensities. A 1% difference in favor of the methyl loss may be contributed to isotopic effects, difference in bond energies ($C-CD_3$ being greater than $C-CH_3$) and experimental error.

A preferred loss of methyl to give the m/e 190 (base peak) was observed for the 2,4-isomer. This was indicated by a comparison of the total ion intensity of m/e 187 to m/e 190. The difference observed between the 2,4-isomer and the 2,5-isomer is related to the structure of the molecule (Figure 11). The type of ion formed from the 2,5-isomer by loss of a methyl is energetically favored. The loss of the second methyl or methyl-$^2H_3$ is a preferred mode of fragmentation for the 2,5-isomer based on intensity measurements. This forms the fragment ion at m/e 172. This process is favored about 10 to 1 for the 2,5-isomer when compared to the 2,4-isomer. Absence of P-30 and P-36 peaks from the spectrum indicates that successive losses of two methyls or two methyls-$^2H_3$ groups from the same t-butyl group does not occur. For the 2,5-isomer, one methyl group is first lost from the t-butyl group in the 2-position to give the peak of highest intensity at P-15 (base peak). The next loss is a methyl-$^2H_3$ group from the 5-position. The opposite process also occurs, first as the loss of $-CD_3$ followed by the loss of $-CH_3$. Isotopic labeling firmly established this process. This is striking proof of the value of using isotopically labeled molecules to define pathways.

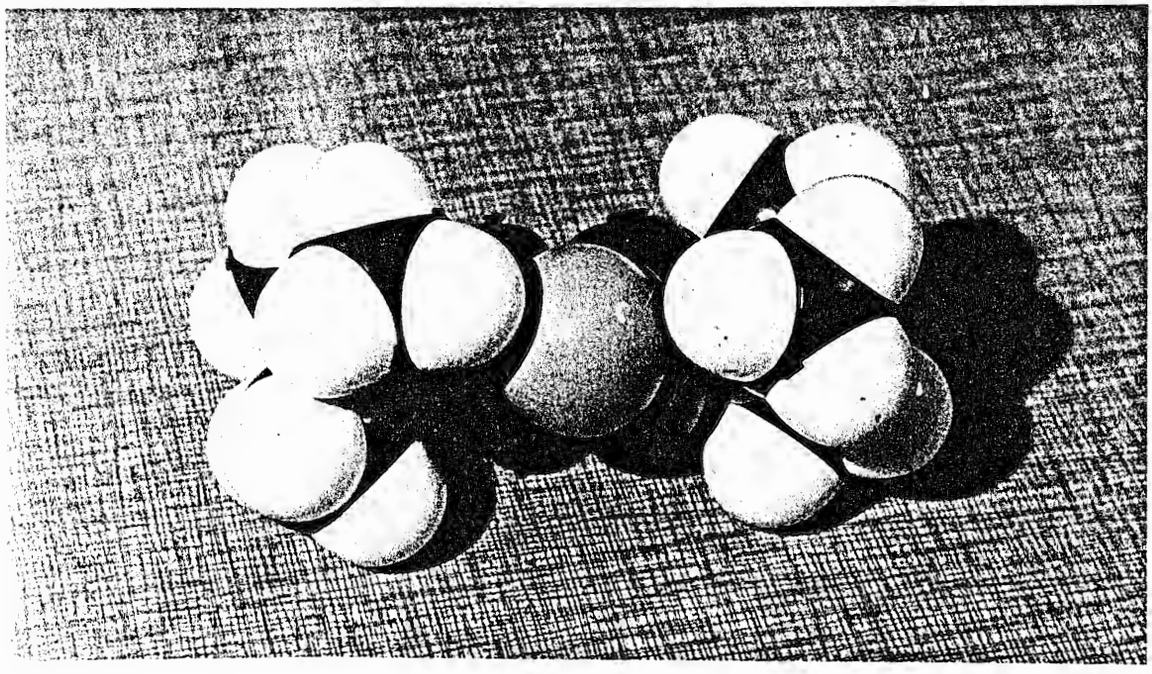
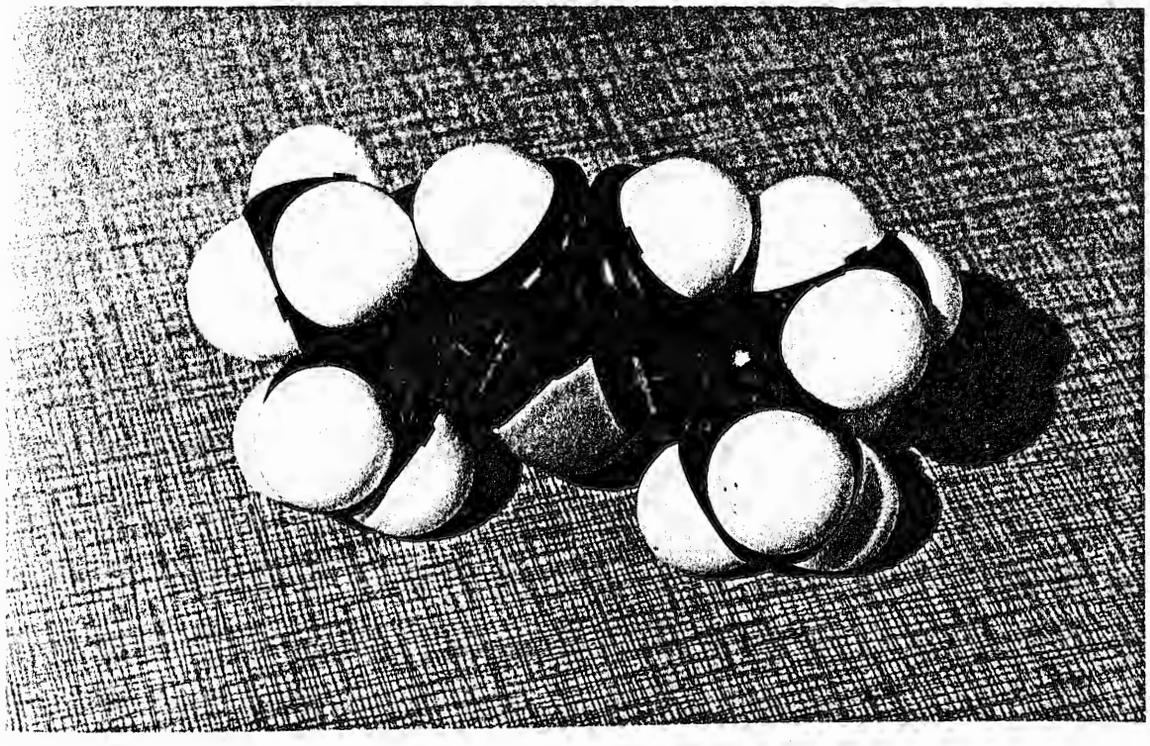


Figure 11a

Molecular Models of 2,5-di(t-Butyl-5-$^{2}H_{9}$)thiophene



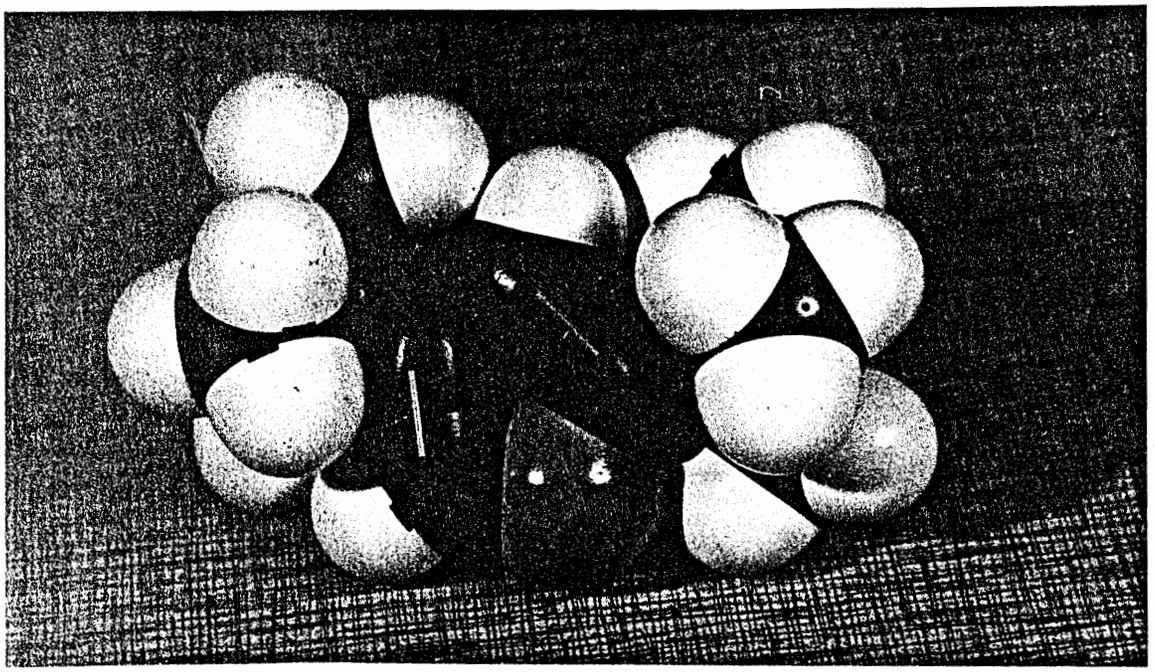
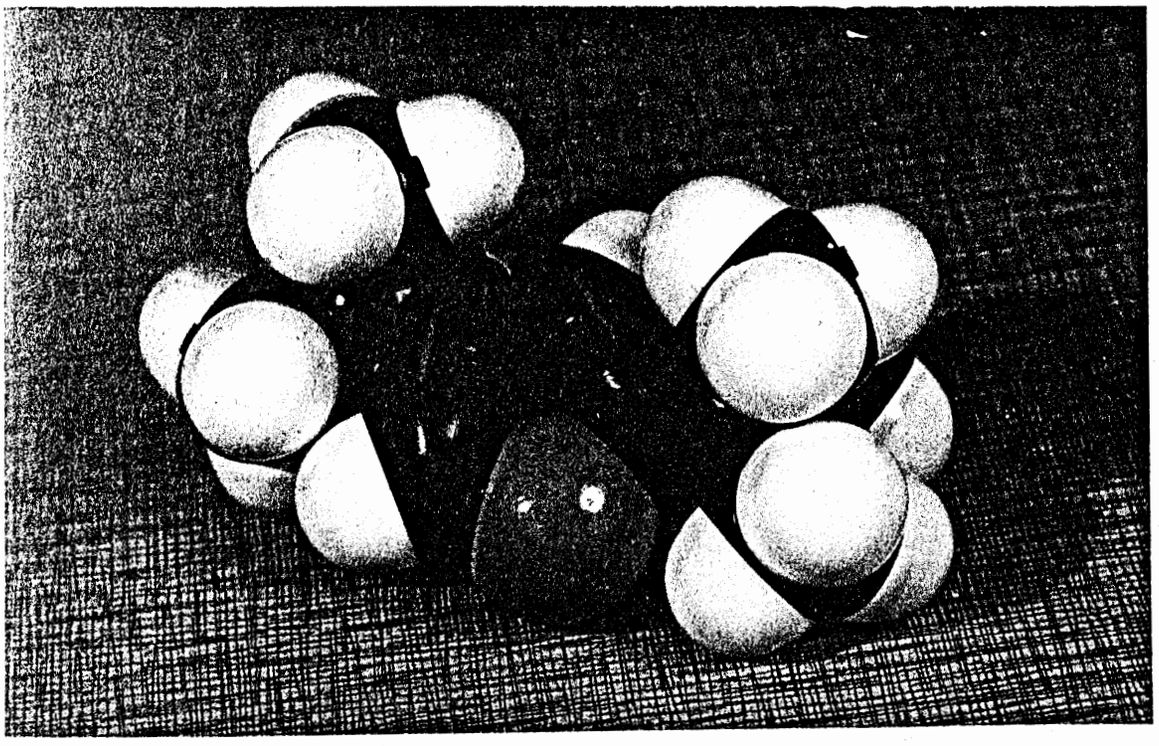


Figure 11b

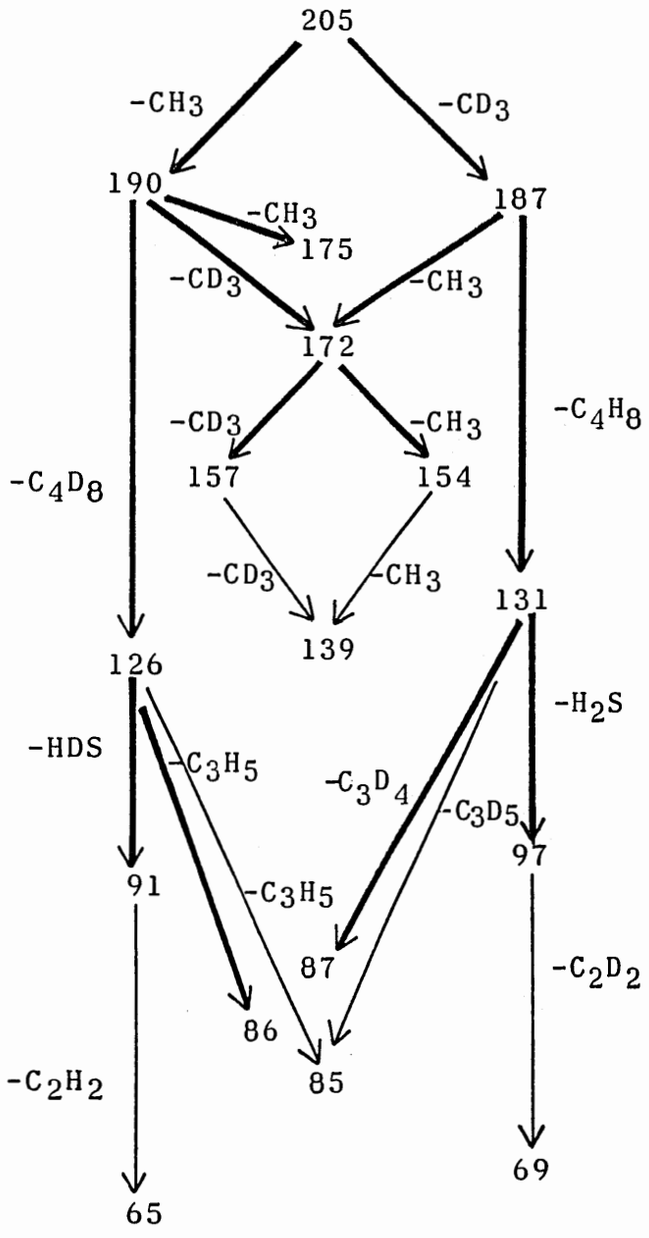
Molecular Models of 2,4-di(t-Butyl-4-$^{2}H_{9}$)thiophene



The difference in intensity observed between the two isomers is directly related to the position of the t-butyl group on the thiophene ring. The formation of the ions can be explained based on the electronic influence of the sulfur atom, steric effects and the presence of two allylic systems. Competing reactions are occurring in the fragmentation processes of the two isomers. Stabilization occurs for the 2,5-isomer upon loss of two methyls (CD_3^o and CH_3^o) due to the formation of two allylic carbonium ions whose electrons undergo delocalization to form a non-classical ion. The stability of the m/e 172 ion makes this a highly favored fragmentation and the intensity is much higher in the two isomer than in the 2,4-isomer. This delocalization is not as readily attained in the 2,4-isomer. The loss of the t-butyl group in the 2,4-isomer is the more favored process. The loss occurs somewhat more readily from the 2-position than from the 4-position. Loss in the 2-position is favored. There is little preference for loss of the t-butyl group in the 2,5-isomer since the two positions are equivalent except for isotopic labeling in one of the t-butyl groups. A slight isotope effect is observed based on total ion intensity since a greater amount of m/e 66 is lost. In the 2,4-isomer the total ion intensity of m/e 57 is greater than m/e 66. Loss of m/e 57 is favored over m/e 66 due to steric hinderance and possibly

preferred ion structures. The m/e 66 ion occupies a larger volume of space than the m/e 57 ion. Loss of the t-butyl group relieves the strain in the molecule to some extent.

Loss of a third methyl group (CH_3 or CD_3) may occur to give m/e 157 or m/e 154. This loss is favored to a greater extent in the 2,5-isomer than in the 2-4-isomer, since the 2,4-isomer prefers to lose a t-butyl group. A suggested fragmentation pattern for the formation of these ions is shown in Figure 12. The pathways indicated for the formation of the various ions should be regarded as possible pathways and not as defined pathways. Delocalization of the electrons occurs to give an alkylaromatic system of greater stability. Non-classical ion formation to give structures of greater stability can be written for most of the fragment ions. In the fragmentation scheme shown in Figure 12 many other processes could occur to give the charged ions by other routes. Emphasis must also be placed on the fact that observation of the presence of a given m/e does not allow us to assign a structure. Speculation is permitted and a pathway is tentatively established.



m/e	Probable Ion
65	$C_5H_5^+$
69	$C_5HD_4^+$
85	$C_4H_3DS^+$
86	$C_4H_4DS^+$
87	$C_4H_3D_2S^+$
91	$C_7H_7^+$
97	$C_7HD_6^+$
126	$C_7H_8DS^+$
131	$C_7H_3D_6S^+$
139	$C_8H_5D_3S^+$
154	$C_9H_8D_3S^+$
157	$C_9H_5D_6S^+$
172	$C_{10}H_8D_6S^+$
175	$C_{10}H_5D_9S^+$
187	$C_{11}H_{11}D_6S^+$
190	$C_{11}H_8D_9S^+$
205	$C_{12}H_{11}D_9S^+$

Note: Processes shown by heavy lines are proven by metastables.

Figure 12

Some Fragmentation Paths of the Labeled di-t-Butylthiophenes

2. Low voltage data

Graphical plots of low voltage data are shown in Figure 13. Production of the parent ions and parent minus 15 ions for the two isomers appear to be identical processes since their appearance potential and rate of formation are about equal. In the 2,5-isomer P-15 and P-18 ion productions differ slightly. This difference can be related to the strength of the bond since more energy is required to break the $C-CD_3$ bond than the $C-CH_3$ bond. In the 2,4-isomer the loss of methyl (P-15) from the 2-position is preferred over loss of methyl-$^2H_3$ from the 4-position. This firmly establishes a difference in delocalization of the charge on the two positions. This is related to the orbital bonding possibilities of the sulfur atom which interacts with the deuteriums of a CD_3 group thus facilitating the loss of the CH_3 group.

Low voltage data shows that the 172 ion of the 2,4-compound has a slightly higher appearance potential than the 2,5-compound. This indicates a possible difference in the mechanism of the formation of the 172^+ ion for the two isomers. The production of the 172^+ ion is enhanced for the 2,5-isomer. As indicated previously the 172^+ ion is stabilized by a delocalized system of electrons and a conjugated alkylaromatic system is formed.

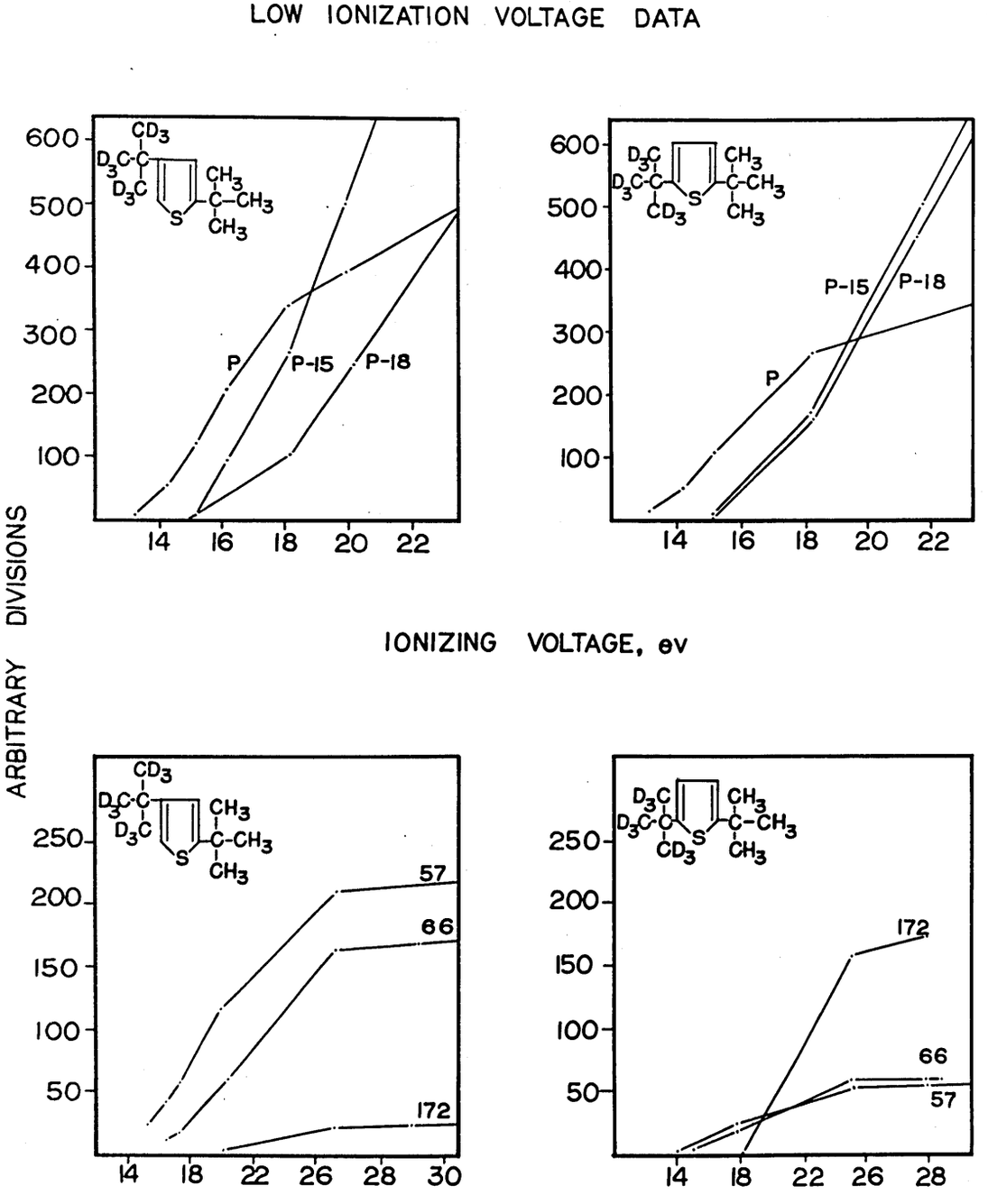


Figure 13

Low Ionization Voltage Data for 2,5-di(t-Butyl-5-$^{2}H_{9}$)-thiophene and 2,4-di(t-Butyl-4-$^{2}H_{9}$)thiophene

There is a preferred loss of the t-butyl group from the 2,4-compound. The appearance potential of the 66^+ ion is higher than the 57^+ ion in the 2,4-isomer. The data suggests that slightly more energy is required to remove the t-butyl group from the 4-position. The appearance potential of the 57^+ and 66^+ ions are essentially the same for the t-butyl group in the 2,5-isomer. The slight difference is probably due to isotope effects, a difference in bond strength and experimental errors.

The 2,5-isomer preferentially ejects two methyls to form m/e 172, whereas the 2,4-isomer prefers loss of m/e 57 or m/e 66 to form m/e 148 or m/e 139. Depending upon the structure of the labeled di-t-butylthiophene each isomer seems to have a preferred pathway. The pathway selected by the fragmenting species is the one which will produce fragment ions with the electrons delocalized thus giving a structure of greater stability than the stability of the fragmenting ions. The alkylthiophene fragmentation pathways differ from those of the alkylbenzenes, due to the influence of the sulfur atom in the thiophene ring.

3. Doubly charged ions

Doubly charged ions are prevalent in the spectra of the labeled di-t-butylthiophenes. Table 8 compares the doubly charged ions observed for each compound.

TABLE 8

DOUBLY CHARGED IONS OF LABELED DI-t-BUTYLTHIOPHENES

m/e	Doubly Charged Ions	
	2,5-di(t-butyl-5-$^2H_9$)-thiophene	2,4-di(t-butyl-4-$^2H_9$)-thiophene
38.5	---	77
39.5	---	79
45.5	---	81
50.5	---	101
51.5	103	103
52.5	105	105
53.5	107	107
54.5	109	109
55.5	111	111
56.5	113	113
57.5	115	115
58.5	117	117
59.5	119	119
60.5	121	---
61.5	123	123
62.5	125	125
63.5	127	127
64.5	129	129
65.5	131	131
66.5	133	133
67.5	135	135
68.5	137	---
69.5	139	139
70.5	141	141

TABLE 8 (Continued)

m/e	Doubly Charged Ions	
	2,5-di(t-butyl-5-$^{2}H_9$)-thiophene	2,4-di(t-butyl-4-$^{2}H_9$)-thiophene
71.5	143	143
72.5	145	145
73.5	147	147
74.5	149	149
75.5	151	151
76.5	153	153
77.5	155	155
78.5	157	157
79.5	159	159
80.5	161	161
81.5	163	163
82.5	165	165
83.5	167	167
84.5	169	169
85.5	171	171
86.5	173	173
87.5	175	175
88.5	177	177
89.5		179
90.5		181
91.5		183
92.5		185
93.5	187	187
94.5	189	189
95.5	191	191
102.5	205	205

The peak at m/e 102.5 in both isomers represents doubly charged parent ions at 205^+. For the first fragment ion, peaks at 93.5^+ are observed in the spectra of both isomers representing a doubly charged ion at 187^+. The doubly charged ions indicate an unusual series of losses of H_2 and D_2. This is thought to be mostly loss of D_2 since the ratio of deuterium to hydrogen is 18 to 2. If this loss is prevalent with doubly charged ions, a certain amount of D_2 loss or H_2 loss must occur with the corresponding singly charged ions.

4. Metastable ion decompositions

Metastable ions are prominent in the spectra of the 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)-thiophene. The spectrum of the 2,5-di(t-butyl-5-$^2H_9$)-thiophene has been examined in detail for metastable decompositions. The well defined metastable processes are listed in Table 9. The fragmentation routes in which metastable ions have been observed are indicated by heavy solid lines in Figure 12. The observed metastable peaks were more intense for the processes involving loss of CD_3 or other deuterated species, than loss of CH_3 or non-deuterated species. This increased intensity can be correlated with the fact that more energy is required to release a CD_3 group than a CH_3 group. A species absorbs more energy in the C-D bonds and the resulting ion carries

less excess energy. Most of the pathways in the fragmentation of the labeled di-t-butylthiophenes have been established by metastable peaks (Figure 12).

TABLE 9

OBSERVED METASTABLES IN THE FRAGMENTATION OF LABELED DI-t-BUTYLTHIOPHENES

m*	m_i	→	m_f	+	neutral	
176.3	205		190		CH_3^o	
170.8	205		187		CD_3^o	
155.9	190		172		CD_3^o	
158.4	187		172		CH_3^o	
161.4	190		175		CH_3^o	
152.9	187		169		CD_3^o	
83.7	190		126		$C_4D_8^o$	
91.9	187		131		$C_4H_8^o$	
143.5	172		157		CH_3^o	Probable
138.1	172		154		CD_3^o	Probable
58.8	126		86		$C_3H_4^o$	
57.8	131		87		$C_3D_4^o$	
65.6	126		91		HDS^o	
71.8	131		97		H_2S^o	

IV. EXPERIMENTAL

A. Preparation of 2-(t-Butyl-$^2H_9$)thiophene and 3-(t-Butyl-$^2H_9$)thiophene

A dry 250 ml. three-neck round-bottom flask was provided with a mercury-sealed stirrer, a dropping funnel with a pressure equalizing tube and a condenser carrying a drying tube. In the reaction flask were placed 3.0 g. (0.125 mole) of magnesium turnings, a small crystal of iodine and approximately 100 ml. of anhydrous ether. The stirrer was started and a small quantity (1 g.) of 2-bromothiophene was added. The reaction started immediately as indicated by a turbidity and a change in color from red to yellow. Once the reaction had started 16.93 g. (0.11 mole) of 2-bromothiophene was added dropwise. The reflux rate was kept moderate during the addition of the bromide. The reaction mixture was refluxed for four hours after the bromide addition was completed. The Grignard reagent was then transferred to another reaction flask equipped as previously described. No excess magnesium was present in the Grignard reagent.

When the temperature of this mixture was cooled to 0^oC, 10 g. (0.10 mole) of t-butyl chloride-$^2H_9$ was added

during a period of 1.5 hours. Next the reaction mixture was stirred at room temperature for four hours and then refluxed for ten hours.

The reaction mixture was hydrolyzed by the addition of dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted three times with ether. The organic layer and ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed by use of a rotary evaporator and the residue distilled. The product was collected at 68°C at 25 mm. and weighed 3.8 g. which corresponded to a 27% yield. Gas chromatography indicated by retention time data the presence of the 2-isomer and the 3-isomer. The isomers were separated from each other by preparative gas chromatography as described on pages 85-86.

Mass spectra indicated the desired labeled 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene had been obtained and mixed isotopic labeling had not occurred.

B. Preparation of Unlabeled 2,5-di-t-Butylthiophene

1. Synthesis of mixture of isomeric t-butylthiophenes

a. Interaction of thiophene and t-butyl alcohol in the presence of sulfuric acid

A 100-ml. three-neck round-bottom flask was equipped with a reflux condenser which had a thermometer suspended inside, a mercury-seal stirrer and a dropping

funnel with pressure equalizing tube. In the reaction flask were placed 16.8 g. (0.21 mole) of thiophene and 15.54 g. (0.21 mole) of t-butyl alcohol. The reaction mixture was heated to 60°C and 27 g. of 75% sulfuric acid was added at a slow rate so that the temperature of the reaction mixture was maintained between 60-70°C throughout the addition of the sulfuric acid. The addition required approximately forty-five minutes. Next, the reaction mixture was heated for two hours between 60-70° C with constant stirring.

On cooling to room temperature, the organic layer was separated from the sulfuric acid layer and washed with 10% sodium hydroxide solution several times. After drying over calcium chloride overnight, the organic material was filtered and distilled at reduced pressure. The fraction boiling at 53-55°C at 13 mm. was a mixture equivalent to 16 g. of 2-t-butylthiophene and 3-t-butylthiophenes which represented a 57.1% conversion and the product collected from 101-105°C at 12 mm. was a mixture equivalent to 8 g. of isomeric di-t-butylthiophenes.

b. Interaction of thiophene and t-butyl chloride in the presence of stannic chloride (26)

A dry five-liter three-neck round-bottom flask was provided with a mercury-seal stirrer, a dropping funnel with a pressure equalizing tube and a reflux condenser which had a thermometer suspended inside with a calcium chloride drying tube attached. The reaction flask was charged with

2.2 liters of dry carbon disulfide, 168 g. (2.0 moles) of thiophene and 222 g. (2.4 moles) of t-butyl chloride. The reaction mixture was cooled to 0°C and maintained at this temperature during the dropwise addition of 627 g. (2.4 moles) of stannic chloride. The addition time was approximately three hours. After the stannic chloride addition was completed, the ice bath was removed and the reaction mixture was stirred until it was dark red in color. Six to eight hours of stirring at room temperature was necessary to complete the reaction.

The reaction mixture was hydrolyzed by pouring it over a mixture of crushed ice and hydrochloric acid. The mixture was stirred and then the organic layer was separated and washed with water until the red color had disappeared and the organic layer was light yellow. The organic layer was dried with anhydrous magnesium sulfate overnight. After filtration and removal of the solvent by use of the rotary evaporator the residue was vacuum distilled. A fraction boiling at 53-55°C at 12 mm. or 162-170°C at atmospheric pressure consisted of a mixture of 2-t-butylthiophene and 5-t-butylthiophene. The second fraction collected from 100-102°C at 12 mm. or 220-225°C at atmospheric pressure was a mixture of the di-t-butylthiophenes. The yield of the isomeric t-butylthiophenes varied depending on the length of time the reaction mixture was stirred at room temperature. The yield ranged from 23.5% to 32% (66-90 g.)

of 2-t-butylthiophene and 3-t-butylthiophene and 3-7% (12-28 g.) for the isomeric di-t-butylthiophenes. The gas chromatogram indicated a ratio of 3.44 to 1 of the 2-t-butylthiophene to the 3-t-butylthiophene.

c. Interaction of 2-thienylmagnesium bromide and t-butyl bromide (27)

A dry 500-ml. three-neck round-bottom flask was provided with a mercury-seal stirrer, a dropping funnel with a pressure equalizing tube and a condenser with a drying tube attached. In the reaction flask were placed 6.00 g. (0.25 mole) of magnesium turnings, a small crystal of iodine and 125 ml. of anhydrous ether. The stirrer was started and a small quantity of 2-bromothiophene was added. Once the reaction had started, as indicated by the development of a turbidity and a change in color from red to yellow, 40.75 g. (0.25 mole) of 2-bromothiophene was added dropwise at a rate sufficient to maintain gentle reflux of the ether. The addition time was approximately two hours. After all the 2-bromothiophene had been added the reaction mixture was stirred and refluxed for two hours. At this point, the reaction mixture was cooled to $0^{o}C$ and 35 g. (0.25 mole) of t-butyl bromide was added dropwise. Care was exercised during the addition of the t-butyl bromide to maintain the temperature of the reaction mixture at $0^{o}C$. The addition time was approximately one hour. Next the reaction mixture was stirred for four hours while the reaction mixture warmed

up to room temperature and then was heated for eight hours to maintain a moderate reflux of the ether.

The reaction flask was cooled in an ice bath and the stirred, chilled reaction mixture was hydrolyzed by the dropwise addition of approximately 50 ml. of 10% hydrochloric acid solution.

The organic layer was separated from the aqueous layer and the latter was extracted three times with 100-ml. portions of ether. The organic layer and ether extracts were then combined and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by means of a rotary evaporator. The residue was distilled under reduced pressure. The yield of the 2-t-butylthiophene and 3-t-butylthiophene boiling at 52 and 55°C at 12 mm. was 9 g., which corresponded to a 26% yield. The yield of the isomeric di-t-butylthiophenes boiling at 100-102°C at 12mmm. was 2 g., which corresponded to a 4% yield. The gas chromatographic retention time data indicated the above isomers.

2. Separation of isomeric t-butylthiophenes

The initial fractionation of the mixture of isomeric t-butylthiophenes was accomplished by use of an eighteen-inch Vigreux column. This fractionation roughly separated 100 g. of mono-t-butylthiophenes boiling at 164-175°C from 25 g. of di-t-butylthiophenes boiling at 210-225°C. Two methods of separation were used to obtain the mono-t-

butylthiophenes in better than 99.95% purity. Fractional distillation, using a spinning-band column, and gas chromatographic separation, using a preparative scale gas chromatograph (Varian A-700) were employed successfully in the separation of the mono-t-butylthiophenes. The di-t-butylthiophenes were separated in better than 99.95% purity by use of a preparative scale gas chromatograph.

a. Separation by use of the spinning-band column

A typical distillation is described for separation of a mixture containing 76.7% 2-t-butylthiophene and 23.3% 3-t-butylthiophene. The operation of the annular "Teflon" spinning-band column (Nester-Faust) was carried out in general as specified in the instruction manual.

A 50-ml. pot was charged with 20 ml. of the mixture. In the initial distillation boiling occurred in the pot at a temperature of 167°C, corresponding to a pot transformer setting of 74. In other distillations the transformer was set initially at this predetermined value. Boil-up occurred in forty minutes. The liquid was allowed to travel two-thirds the length of the column and the stirrer was then turned on slow speed (30 on transformer setting) and the column and head transformer were set at 63 and 95, respectively (numbers determined from first distillation). About one hour was required for the liquid to reflux off the tip of the reflux valve. The stirrer was then turned up to a high speed (transformer setting 50). The head temperature

gradually increased and exceeded the temperature at the top of the column. An 8-10° temperature differential between the head temperature and top-of-column temperature gave optimum purity. The reflux rate was maintained at 12-15 drops per minute and the column was allowed to equilibrate for two hours at total reflux. A reflux ratio of 9 to 1 was then established. One milliliter of sample was collected for each 20 minutes of sample collection. Ten milliliters of pure 2-t-butylthiophene (99.9%), then three milliliters of 2-t-butylthiophene (95%) and finally 7 milliliters (residue) of 2-t-butylthiophene and 3-t-butylthiophene (68.6%) were obtained in one distillation. Time required for collection of the sample for one distillation was 4.5 hours.

The 2-t-butylthiophene fractions of 95% and better purity were combined and redistilled to obtain 99.9% 2-t-butylthiophene. A total of 52 grams of pure 99.9% 2-t-butylthiophene was obtained. Several residues containing 31.4% 2-t-butylthiophene and 68.6% 3-t-butylthiophene were combined and distilled to furnish 8 grams of pure 3-t-butylthiophene (99.9%). The gas chromatogram charts #1, #2, and #3 indicate the original mixture, pure 2-t-butylthiophene, and pure 3-t-butylthiophene, respectively.

During the separation of the fractions, the distillation purity of the mono-t-butylthiophenes was checked by use of a Varian 1520B gas chromatograph equipped with a 10%

Apiezon J on Chromosorb P 60-80 mesh column 10 feet long and 1/4 inch in diameter. Optimum conditions for the separation of the 2-t-butylthiophene from the 3-t-butylthiophene were as follows:

Column Temp.	Flow Rate	Detector Temp.	Sample Size
140°C	120 ml/min	230°C	2 μl

Notes:

(1) The thermocouple well was sealed to the pot with sealing wax to prevent leakage.

(2) The head and the pot were wrapped with glass wool to prevent heat loss.

(3) The motor was raised to position the stirrer at the midpoint of the flask at boil-up. At 163° the band expands several inches and will drag against the bottom of the pot unless it is raised.

(4) Initially, a few milliliters of sample (low-boiling forerun) must sometimes be removed in order to obtain a head temperature of 162°.

(5) The optimum settings were as follows for collection of pure 2-t-butylthiophene:

Transformer Settings			Pyrometer Reading				
Pot	Column	Head	Pot	Bottom	Middle	Top	Head
75	65	95	171	161	165	156	163

b. Gas chromatographic separations

A Varian A-700 autoprep with automatic injector and collector assembly was available for use. Four different preparative columns were investigated for the separation of the isomeric mixture of t-butylthiophenes and optimum

conditions for separation of the four isomers were obtained for each column. The following preparative columns were evaluated for this particular separation. All preparative columns were 20 feet long and 3/8 inch in diameter.

Column Description

Liquid Phase	Per Cent	Support	Mesh Size
QF-1	30	Chromosorb P	60-80
QF-1	15	Chromosorb P	60-80
SE-30	30	Chromosorb W	60-80
Apiezon J	30	Firebrick	40-60

The optimum conditions for the separation of 2-t-butylthiophene from 3-t-butylthiophene were obtained using the SE-30 column. However, the liquid phase was dissolved by the t-butylthiophenes. This disadvantage prevented the use of this column for separating large amounts of the t-butylthiophenes.

The Apiezon J column allowed adequate separation but the retention time was too long to allow a feasible separation. Also, much peak broadening on the Apiezon J column was observed for the mono-t-butylthiophenes.

The QF-1 (15%) column allowed adequate separation of the mono-t-butylthiophenes but this separation could only be maintained with a sample size of 25 µl or less.

The QF-1 (30%) column was selected as the best column available for the separation. All four isomers were

separated within one hour and 15 minutes. The maximum sample to be introduced was 100 μl for the mono-t-butylthiophenes and a 50 μl sample in the case of the di-t-butylthiophenes. Larger sample size did not permit adequate separation of 2-t-butylthiophene from 3-t-butylthiophene and 2,5-di-t-butylthiophene from 2,4-di-t-butylthiophene. Gas chromatogram charts #4 and #5 indicate the separation of the mono-t-butylthiophenes and the di-t-butylthiophenes, respectively.

3. Preparation of 2,5-di-t-Butylthiophene and 2,4-di-t-Butylthiophene

a. Interaction of 2-t-butylthiophene with t-butyl chloride in the presence of stannic chloride

A 100-ml. three-neck round-bottom flask was equipped with a reflux condenser carrying a drying tube, a mercury-seal stirrer and a dropping funnel with a pressure-equalizing tube attached. In the reaction flask were placed 50 ml. of dry carbon disulfide, 7.3 g. (0.052 mole) of 2-t-butylthiophene, and 4.8 g. (0.052 mole) of t-butyl chloride. To this reaction mixture 14.52 g. (0.056 mole) of stannic chloride was added dropwise during the period of fifteen minutes. The red reaction mixture was stirred at room temperature for forty-eight hours.

The reaction mixture was hydrolyzed by pouring it over a mixture of crushed ice and hydrochloric acid. The mixture was stirred and the organic layer was separated

and washed several times with water until the red color of the organic layer had disappeared. The light yellow organic layer was dried over anhydrous magnesium sulfate. After filtration and removing of the solvent by use of the rotary evaporator the residue was distilled at reduced pressure. The material collected from 100-102°C at 12 mm. equalled 6 g. and corresponded to a 58.8% yield of the isomeric di-t-butylthiophenes. Gas chromatography indicated a ratio of 4.85 to 1 for the 2,5-di-t-butylthiophene compared to the 2,4-di-t-butylthiophene.

b. Interaction of t-butyl chloride with 5-t-butyl-2-thienylmagnesium bromide

The intermediate necessary for this preparation, namely, 2-bromo-5-t-butylthiophene, was prepared by modification of the method described by Cagniant (38) for the preparation of 2-bromo-5-ethylthiophene. The preparation was carried out in the following manner.

A dry 200-ml. one-neck round-bottom flask containing a magnetic stirring bar was equipped with a reflux condenser carrying a calcium chloride drying tube. In the reaction flask were placed 60 ml. of carbon tetrachloride (distilled from potassium hydroxide and dried over phosphorus pentoxide), 14 g. (0.1 mole) 2-t-butylthiophene, and 19.84 g. (0.112 mole) of N-bromosuccinimide. The mixture was stirred and refluxed for forty-eight hours.

Upon cooling, the succinimide was removed from the reaction mixture by suction filtration. The organic layer was washed with 5% potassium hydroxide solution and dried over anhydrous magnesium sulfate. The solvent was removed by use of the rotary evaporator. The residue was distilled at reduced pressure. The yield of the 2-bromo-5-t-butylthiophene boiling at 96-98°C at 15 mm. was 15.6 g. This corresponded to a 71% conversion. The purity of the product was shown by gas chromatography to be 99.9% or better.

A dry 250-ml. three-neck round-bottom flask was provided with a mercury-seal stirrer, a dropping funnel with a pressure equalizing tube and a condenser carrying a drying tube. In the reaction flask were placed 1.20 g. (0.05 mole) of magnesium turnings, a small crystal of iodine and approximately 125 ml. of anhydrous ether. The stirrer was started and a small quantity (1 g.) of 2-bromo-5-t-butylthiophene was added. The reaction mixture was warmed and the reaction started, as indicated by a turbidity and a change in the color from red to yellow. When the reaction had started 9.95 g. of 2-bromo-5-t-butylthiophene was added dropwise. The reflux rate was kept moderate during the addition of the bromide. The reaction mixture was stirred and refluxed for two hours after the bromide addition was completed.

When the temperature of this mixture was cooled to 0°C, 4.6 g. (0.05 mole) of t-butyl chloride was added dropwise. The addition time was approximately forty-five minutes.

While being stirred the reaction mixture was allowed to warm up to room temperature during a period of four hours and then refluxed for sixteen hours.

After cooling to $0^{o}C$ the Grignard addition product was hydrolyzed by the dropwise addition of approximately 50 ml. of 10% hydrochloric acid solution. The organic layer was separated from the aqueous layer and the aqueous layer was extracted three times with 50-ml. portions of ether. The organic layer and ether extracts were combined and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration the solvent was removed by use of the rotary evaporator and the residue was distilled under reduced pressure. The forerun, boiling at $68^{o}C$ at 25 mm., weighed 1.885 g. By comparison of gas chromatographic retention times the forerun was 2-t-butylthiophene. The material boiling at $115-117^{o}$ at 25 mm. weighed 1.855 g., and corresponded to an 18.3% yield and was shown by gas chromatographic retention times to consist of 2-t-butylthiophene, 2,5-di-t-butylthiophene, 2,4-di-t-butylthiophene and 2-bromo-5-t-butylthiophene.

C. Preparation of 2,5-di(t-Butyl-5-$^{2}H_{9}$)thiophene and 2,4-di(t-Butyl-4-$^{2}H_{9}$)thiophene

A dry 250 ml. three-neck round-bottom flask was provided with a mercury-seal stirrer, a dropping funnel with a pressure equalizing tube and a condenser carrying a drying

tube. In the reaction flask were placed 3.0 g. (0.125 mole) of magnesium turnings, a small crystal of iodine and approximately 100 ml. of anhydrous ether. The stirrer was started and a small quantity (1 g.) of 2-bromo-5-t-butylthiophene was added. The reaction started after 15 minutes, as indicated by a turbidity and a change in color from red to yellow. When the reaction had started 23.1 g. (0.11 mole) of 2-bromo-5-t-butylthiophene was added dropwise. The reflux rate was kept moderate during the addition of the bromide. The reaction mixture was stirred and refluxed for four hours after the bromide addition was completed. The Grignard reagent was then transferred to another reaction flask equipped as previously described. No excess magnesium was present in the Grignard reagent.

When this mixture was cooled to $0^{o}C$, 10 g. (0.1 mole) of t-butyl chloride-$^{2}H_{9}$ was added during a period of 1.5 hours. Next, the reaction mixture was stirred at room temperature for four hours and then refluxed for ten hours.

The reaction product was isolated in an analogous manner as described on page 89. The forerun boiling at 68^{o} at 25 mm. weighed 1 g. The material boiling at 115-$117^{o}C$ at 25 mm. weighed 7.7 g. and corresponded to a 39% yield. Gas chromatography indicated by retention time data that the following compounds were present: 2-isomer, 2,5-isomer and the 2,4-isomer. The 2,5-isomer was separated from the 2,4-isomer by preparative gas chromatography as

described on page 85. The mass spectral analysis indicated the desired labeled 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,4-di(t-butyl-4-$^2H_9$)thiophene had been obtained and that mixed isotopic labeling had not occurred.

D. Friedel-Crafts Alkylation of Mono-t-Butylthiophenes using t-Butyl chloride-$^2H_9$

1. Alkylation of 2-t-butylthiophene with t-butyl chloride-$^2H_9$

A mixture of 4.8 g. (0.052 mole) of the labeled t-butyl chloride-$^2H_9$ and 7.3 g. (0.052 mole) of 2-t-butylthiophene in 50 ml. of carbon disulfide reacted with 14.52 g. (0.036 mole) stannic chloride in exactly the same way as described in the synthesis of the unlabeled di-t-butylthiophenes (page 86).

The reaction product was isolated in an analogous manner. The product boiled at 105°C at 13 mm. and equalled 4.5 g. This corresponded to a 44.1% yield.

Gas chromatographic analysis showed that the two isomeric di-t-butylthiophenes were present. These two isomers were present in a ratio of 4.85 to 1 and were separated by preparative gas chromatography. Conditions for the separation are exactly the same as those described for the unlabeled di-t-butylthiophenes (page 89).

The mass spectral analysis of the two fractions indicated that mixed isotopic labeling had occurred. The

2,5-isomer consisted of 2,5-di-t-butylthiophene, 2,5-di(t-butyl-5-$^2H_9$)thiophene and 2,5-di(t-butyl-2,5-$^2H_{18}$)thiophene. The 2,4-isomer consisted of 2,4-di-t-butylthiophene, 2,4-di(t-butyl-4-$^2H_9$)thiophene and 2,4-di(t-butyl-2,4-$^2H_{18}$)-thiophene.

2. Alkylation of 3-t-butylthiophene with t-butyl chloride-$^2H_9$ in the presence of stannic chloride

A 100-ml. three-neck round-bottom flask was equipped with a reflux condenser with a calcium chloride drying tube attached, a mercury-seal stirrer and a dropping funnel with a pressure equalizing tube. In the flask were placed 40 ml. of anhydrous carbon disulfide, 4.25 g. (0.03 mole) 3-t-butylthiophene, and 5.0 g. (0.054 mole) t-butyl chloride-$^2H_9$. To this reaction mixture 14.4 g. (0.056 mole) of stannic chloride was added dropwise during a period of thirty minutes. The red reaction mixture was stirred for nine days at room temperature.

The reaction mixture was hydrolyzed by pouring it into a mixture of crushed ice and concentrated hydrochloric acid. The mixture was stirred. The organic layer was separated and washed with water until the red color of the organic layer disappeared. The light-yellow organic layer was dried with anhydrous magnesium sulfate. After filtration and removal of the solvent by use of the rotary evaporator, the residue was distilled at reduced pressure. The forerun boiling at 55°C at 12 mm. corresponded to pure

3-t-butylthiophene and weighed 2.0 g. The 2,4-di(t-butyl-2-$^2H_9$)thiophene weighed 1 g. and distilled at 105°C at 12 mm. This corresponded to a 16.3% yield. The gas chromatogram indicated a single substance corresponding to a retention time equivalent to the 2,4-isomer. The mass spectra and the nuclear magnetic resonance spectra indicated 50% of the product contained an extra deuterium 2,4-di(t-butyl-2-$^2H_9$)thiophene-5-^2H or 2,4-di(t-butyl-$^2H_9$)-thiophene-3-^2H .

E. Mass Spectral Operating Conditions

Consolidated Electrodynamics Corporation (CEC) single focus mass spectrometer model 21-104 was used in obtaining all mass spectral data. The instrument was equipped with the CEC heated inlet system operated at an oven temperature of 165°C, and the temperature of the ionization chamber was controlled automatically at 250°C. The ionizing voltage was 70 e. v. The ionizing current of 10 microamperes was used for all spectra. The repeller settings of the instrument were (1)=7.2 and (2)=10.1. The slit width was 4 mils and the electrostatic scanning rate was 9 with a recording chart rate of 1/4 inch per second. For each sample run 2 lambda (0.002 μl) of liquid was injected. The electron multiplier was set at 160 volts/stage for all compounds run, except 2,4-di(t-butyl-4-$^2H_9$)thiophene, 2-(t-butyl-$^2H_9$)thiophene

and 3-(t-butyl-$^2H_9$)thiophene. These compounds were run using the electrometer mode detection.

Relative intensities of peaks in a mass spectrum are expressed as percent of the largest, or base peak. Total ion intensity of peaks in a mass spectrum are expressed as percent of the sum of the relative intensities of all the peaks in the spectrum from m/e 37 to m/e . The mass spectra data in tabulated form for all compounds analyzed are in the appendix.

Low ionization voltage data were obtained on all compounds reported here. The initial onset method of Smith (44) was used and the appearance potential of benzene (9.52 ev) reported by Morrison and Nicholson (45) was used to correct the meter ionization voltage to absolute electron volts.

F. Gas Chromatographic Operating Conditions

The gas chromatograph Varian model 1520B was used for all analytical correlations. The analytical column used for analysis of mono-t-butylthiophenes and di-t-butylthiophenes was a 10% Apiezon J on Chromosorb P 60-80 mesh column 10 feet long and 1/4 inch in diameter. This column allowed separation of all four isomers. A thermal conductivity detector was used in all analyses.

Percentage compositions and isomer ratios were determined by obtaining the chromatogram, cutting out the

peaks and weighing each peak on a Mettler balance. The percent of each isomer present was then calculated.

All of the preparative gas chromatographic separations were performed on the Varian A-700 autoprep. All samples were injected manually. The preparative column used was a 30% QF-1 on 60-80 mesh Chromosorb P. The column was conditioned at 250^{o}C with a flow rate of 60 ml/min. for 12 hours after the separation of several grams of material.

V. SUMMARY

The desired 2-(_t_-butyl-$^2H_9$)thiophene and 3-(_t_-butyl-$^2H_9$)thiophene were synthesized by the following procedure: (a) Interaction of 2-thienylmagnesium bromide and _t_-butyl chloride-$^2H_9$ forming both the 2- and 3-isomers; (b) Separation of the two isomers by preparative gas chromatography; (c) The isotopic purity of 2-(_t_-butyl-$^2H_9$)-thiophene was 96.3% and for the 3-(_t_-butyl-$^2H_9$)thiophene was 96.7%.

The desired 2,5-di(_t_-butyl-5-$^2H_9$)thiophene and 2,4-di(_t_-butyl-4-$^2H_9$)thiophene were synthesized by the following procedure: (a) Interaction of 5-_t_-butyl-2-thienylmagnesium bromide and _t_-butyl chloride-$^2H_9$ forming both the 2,5-isomer and the 2,4-isomer; (b) Separation of the two isomers by preparative gas chromatography; (c) The isotopic purity of the 2,5-di(_t_-butyl-5-$^2H_9$)thiophene was 98.72% and the 2,4-di(_t_-butyl-4-$^2H_9$)thiophene was 95.22%.

The Friedel-Crafts alkylation of 2-_t_-butylthiophene with _t_-butyl chloride-$^2H_9$ yielded 2,5-di-_t_-butylthiophene, 2,5-di(_t_-butyl-5-$^2H_9$)thiophene, 2,5-di(_t_-butyl-2,5-$^2H_{18}$)-thiophene, 2,4-di-_t_-butylthiophene, 2,4-di(_t_-butyl-4-$^2H_9$)-thiophene, and 2,4-di(_t_-butyl-2,4-$^2H_{18}$)thiophene. The

Friedel-Crafts alkylation of 3-t-butylthiophene with t-butyl chloride-$^2H_9$ yielded a product containing equal amounts of 2,4-di(t-butyl-2-$^2H_9$)thiophene and 2,4-di(t-butyl-2-$^2H_9$)-thiophene-5-$^2H_1$.

Mass spectral studies of 2-(t-butyl-$^2H_9$)thiophene and 3-(t-butyl-$^2H_9$)thiophene indicated the following: (a) Confirmed direct losses of methyl-$^2H_3$ from the t-butyl group; (b) Preferred successive losses of methyl-$^2H_3$ groups occurred in the fragmentation of the 2-isomer, whereas loss of the t-butyl group is the preferred fragmentation route in the 3-isomer; (c) Positional substitution is an important influence on the mode of fragmentation of the various isomers. The steric relationships of the t-butyl group to the rest of the molecule differs depending upon the location (2 or 3) of the t-butyl group. The favored interaction between the deuterium of the t-butyl group and the sulfur atom is related to the location of the t-butyl group.

Mass spectral studies of 2,5-di(t-butyl-5-$^2H_9$)-thiophene and 2,4-di(t-butyl-4-$^2H_9$)thiophene indicated the following: (a) Confirmed that two successive losses, one of methyl and one of methyl-$^2H_3$ occurred; (b) Preferential losses of methyl and methyl-$^2H_3$ are favored in the 2,5-isomer, whereas loss of a t-butyl group is favored in the 2,4-isomer to a considerable extent and apparently occurs with almost equal probability from either position.

The fragmentation of the 2,5-isomer differs from the 2,4-isomer in ion production and in the intensity of the ions formed at high voltage. These differences may be related to steric effects and interaction of the deuteriums of the t-butyl group with the sulfur atom. Additional study of the existing data presented is expected to yield considerable information on the fragmentation pathways.

REFERENCES

1. Hartough, H. D., editor. The Chemistry of Heterocyclic Compounds. Thiophene and Its Derivatives. Interscience Publishers, Inc., New York, 1952, pp. 132-141.

2. Kinney, I. W. and Cook, G. L. Anal. Chem. 24, 1391-1396 (1952).

3. Foster, N. G., Hirsch, D. E., Kendall, R. F. and Eccleston, R. H. United States Department of Interior, Bureau of Mines Report of Investigations, No. 6433 (1964), pp. 1-38.

4. Foster, N. G., Hirsch, D. E., Kendall, R. F. and Eccleston, B. H. United States Department of Interior, Bureau of Mines Report of Investigations, No. 6671 (1965); pp. 1-31.

5. Cook, G. L. and Foster, N. G. Proc. Am. Petrol. Inst. 41, Sec. III, 199-214 (1961).

6. Rylander, P. N., Meyerson, S. and Grubb, H. M. J. Am. Chem. Soc. 78, 57799-5802 (1956).

7. Hanuš, V. and Čermák, V. Coll. Czech. Commuc. 24, 1602-1607 (1959).

8. Koutecký, J. Coll. Czech. Commun. 24, 1602-1607 (1959).

9. Zwolinski, Bruno J., et al. Selected Values of Properties of Hydrocarbons and Related Compounds. Comprising the Tables of the American Petroleum Institute Research Project 44 extant as of Oct. 31, 1963. A. & M. Press Texas, Agricultural and Mechanical College of Texas, College Station, Texas (1963), 1, 933 tables (See #1876).

10. Cilento, Guiseppe. Chem. Rev. 60, 147-167 (1960).

11. Meyerson, S. and McCollum, J. D. J. Am. Chem. Soc. 81, 4116-4117 (1959).

12. Higgins, R. W. and Wu, E-Ming. J. of Chem. and Eng. Data 7, 447 (1962).

13. Foster, N. G. and Higgins, R. W. J. Org. Mass Spec. 1, 1-8 (1968).

14. Meyerson, S. and Rylander, R. N. J. Chem. Phys. 27, 901-904 (1957).

15. Bailey, Wm. A. Private Communication. Shell Oil Company, Houston, Texas, May 25, 1961.

16. Foster, N. G. and Higgins, R. W. "Mass Spectrometric Studies of Selected Ions in Deuterated Alkylthiophenes," presented at 14th ASTM-E-14 Committee on Mass Spectrometry meeting, May 25, 1966, Dallas, Texas.

17. Foster, N. G. and Higgins, R. W. "The Use of Isotopically Labeled Molecules in Studying Fragmentation Routes in the Mass Spectrometer," presented at the Southwest Regional meeting of the American Chemical Society, December 6-8, 1962.

18. Foster, N. G. United States Department of Interior, Bureau of Mines Report of Investigations, No. 6741 (1966), pp. 1-30.

19. Rylander, P. N. and Meyerson, S. J. Am. Chem. Soc. 78, 5799-5802 (1956).

20. Hartough, H. D., editor. The Chemistry of Heterocyclic Compounds. Thiophene and Its Derivatives. Interscience Publishers, Inc., New York (1952), pp. 159-164.

21. Gronowitz, S. In Advances in Heterocyclic Chemistry, Katritzky, A., editor, Academic Press, Inc., New York (1964), p. 1.

22. Kutz, W. M. and Corson, B. B. J. Am. Chem. Soc. 68, 1477-1479 (1946).

23. Ceasar, P. D. J. Am. Chem. Soc. 70, 3623 (1948).

24. Appleby, W. G., Sartor, A. F., Lee, S. H., and Kapranos, S. W. J. Am. Chem. Soc. 70, 1552-1555 (1948).

25. Pines, Herman, Kvetinkas, Bruno, and Vesely, J. A. J. Am. Chem. Soc. 72, 1568-1571 (1950).

26. Sy, Michel, Buu-Hoi, NG. Ph. and Xuong, NG. D. J. Chem. Soc. 1975-1978 (1954).

27. Cagniant, M. Paul and Cagniant, Denise. Bull. Soc. Chim. France, 1152-1163 (1956).

28. Goldfarb, Ya. L. and Konstantinov, P. A. Bull. Akad. Sci. USSR, Div. Chem. Sci. USSR (Eng. Transl.) 113-118 (1957).

29. Wynberg, Hans and Wiersum, U. E. J. Org. Chem. 30, 1058-1060 (1956).

30. Weinmayr, V. M. J. Am. Chem. Soc. 72, 918 (1950).

31. Bak, B., J. Org. Chem. 21, 797 (1956).

32. Gronowitz, S., Moses, P. and Hakonsson, R., Arkiv. Kemi., 15, 45 (1962).

33. Orza, J. M. and Sarompas, R. Anales. Real. Soc. Espan. Fis. Quim. Ser. B, 58, 295 (1962). Through Chem. Abst., 58, 1066 (1962).

34. Pak, Y. Y. Unpublished Master's Thesis, Dept. of Chem., Texas Woman's University (1963).

35. Lee, F. Unpublished Master's Thesis, Dept. of Chem., Texas Woman's University (1964).

36. Chen, M. Unpublished Master's Thesis, Dept. of Chem., Texas Woman's University (1966).

37. Hartough, H. D., editor. The Chemistry of Heterocyclic Compounds. Thiophene and Its Derivatives. Interscience Publishers, Inc., New York, (1952), pp. 132-141.

38. Cagniant, M. Paul and Cagniant, Denise. Bull. Soc. Chim. France, 713-719 (1952).

39. Olah, George A. Friedel-Crafts and Related Reactions. Interscience Publishers, Inc., New York (1964), Vol. II, Part 1, pp. 1-18.

40. Bartlett, Paul D. Nonclassical Ions, W. A. Benjamin, Inc., New York (1965), pp. 78-85.

41. Hartough, H. D., editor. The Chemistry of Heterocyclic Compounds. Thiophene and Its Derivatives. Interscience Publishers, Inc., New York (1952), pp. 145, 146.

42. Foster, N. G. Private Communication. Texas Woman's University, Denton, Texas. May 20, 1968.

43. Biemann, Klauss. Mass Spectroscopy. Organic Chemical Applications. McGraw-Hill Book Co., Inc., New York (1962), pp. 153-157.

44. Smith, L. G. Phys. Rev. 51, 263-275 (1937).

45. Morrison, J. D. and Nicholson, A. J. F. J. Chem. Phys. 20, 1021 (1952).

APPENDIX A

POLYISOTOPIC MASS SPECTRAL DATA

LABELED t-BUTYLTHIOPHENES

General Operating Conditions

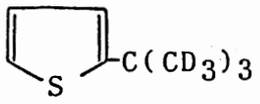
1. Magnet current: 4.0, 7.3 amp.
   (scan overlap made on the basis of m/e 39, 41, and 43)
2. Accelerating voltage: 3200 v.
3. Ionizing voltage: 70 e. v.
4. Ionizing current: 10 amp.
5. Repeller settings: No. 1) 7.2; No. 2) 10.1
6. Temperature of ionization chamber: 250°C
7. Oven temperature: 165°C
8. Slit width: 4 mils
9. Electrostatic scanning rate: 9
10. Recording chart rate: 1/4 inch per second

Key to Spectral Peaks

P: Parent molecule ion

m: Metastable peak

d: Doubly charged ion



2-(t-butyl-$^2H_9$)thiophene

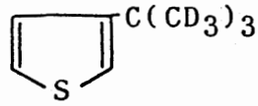
M.W. = 149

Date: 4-23-68

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.215	0.73	57.1	0.840	2.85
37.5d	0.003	0.01	58.0	0.595	2.02
38.0	0.598	2.03	58.1	0.413	1.40
38.5d	0.003	0.01	58.5d	0.012	0.04
39.0	1.488	5.05	59.0	0.380	1.29
40.0	1.247	4.23	59.5d	0.006	0.02
41.1	1.857	6.30	60.0	0.368	1.25
41.5d	0.003	0.01	60.5d	0.012	0.04
42.0	3.557	12.07	61.0	0.218	0.74
43.0	0.725	2.46	61.1	0.118	0.40
43.5d	0.006	0.02	61.5d	0.035	0.12
44.0	0.094	0.32	61.8m	0.012	0.04
44.1	0.660	2.24	62.0	0.663	2.25
45.0	2.976	10.10	62.1	0.256	0.87
45.1	1.577	5.35	62.5d	0.059	0.20
45.8m	0.059	0.20	63.0	0.280	0.95
46.0	1.518	5.15	63.5d	0.091	0.31
46.1	5.018	17.03	64.0	0.342	1.16
47.0	0.192	0.65	64.5d	0.100	0.34
47.1	0.192	0.65	65.0	0.410	1.39
48.0	0.168	0.57	65.5d	0.118	0.40
48.1	0.071	0.24	66.0	0.245	0.83
49.0	0.156	0.53	66.1	0.457	1.55
49.1	0.035	0.12	66.5d	0.012	0.04
50.0	0.339	1.15	67.0	0.725	2.46
51.0	0.519	1.76	67.6m	0.024	0.08
52.0	0.678	2.30	68.0	0.589	2.00
53.0	0.928	3.15	68.5d	0.006	0.02
53.5d	0.012	0.04	69.0	0.678	2.30
54.0	0.536	1.82	69.1	0.690	2.34
54.5d	0.012	0.04	69.5d	0.006	0.02
54.8m	0.006	0.02	70.0	0.448	1.52
55.0	0.536	1.82	70.5d	0.018	0.06
55.5d	0.024	0.08	71.0	0.197	0.67
55.8m	0.038	0.13	71.1	0.286	0.92
56.0	0.601	2.04	71.5d	0.012	0.04
56.5d	0.012	0.04	72.0	0.206	0.70
57.0	0.595	2.02	72.1	0.124	0.42

2-(t-butyl-$^2H_9$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
72.5d	0.100	0.34	108.0	0.024	0.08
73.0	0.180	0.61	109.0	0.071	0.24
73.5d	0.018	0.06	110.0	0.112	0.38
74.0	0.433	1.47	111.0	0.928	3.15
74.5d	0.006	0.02	112.0	0.383	1.30
75.0	0.141	0.48	113.0	0.654	2.22
76.0	0.130	0.44	114.0	0.162	0.55
77.0	0.106	0.36	115.0	0.100	0.34
78.0	0.059	0.20	115.4m	0.006	0.02
79.0	0.130	0.44	116.0	0.053	0.18
80.0	0.292	0.99	117.0	0.024	0.08
81.0	0.330	1.12	118.0	0.012	0.04
82.0	0.268	0.91	119.0	0.012	0.04
83.0	0.251	0.85	120.0	0.012	0.04
83.5m	0.006	0.02	121.0	0.018	0.06
84.0	0.262	0.89	122.0	0.006	0.02
85.0	0.351	1.19	123.0	0.018	0.06
86.0	0.304	1.03	124.0	0.030	0.10
87.0	2.171	7.37	125.0	0.027	0.09
88.0	0.554	1.88	126.0	0.030	0.10
88.5m	0.006	0.02	127.0	0.139	0.47
89.0	0.192	0.65	128.0	0.174	0.59
90.0	0.100	0.34	129.0	0.466	1.58
91.0	0.024	0.08	130.0	1.892	6.42
92.0	0.47	0.16	131.0	29.468	100.00
93.0	0.059	0.20	132.0	3.734	12.67
94.0	0.062	0.21	133.0	1.435	4.87
95.0	0.386	1.31	134.0	0.168	0.57
96.0	0.637	2.16	135.0	0.018	0.06
97.0	0.380	1.29	140.0	0.006	0.02
98.0	0.197	0.67	141.0	0.012	0.04
98.7m	0.006	0.02	145.0	0.024	0.08
99.0	3.035	10.30	146.0	0.053	0.18
100.0	1.400	4.75	147.0	0.133	0.45
101.0	0.501	1.70	148.0	0.625	2.12
102.0	0.124	0.42	148.7m	0.041	0.14
103.0	0.053	0.18	149.0	6.769P	22.97P
104.0	0.041	0.14	150.0	0.981	3.33
105.0	0.035	0.12	151.0	0.374	1.27
106.0	0.012	0.04	152.0	0.106	0.36
107.0	0.012	0.04	153.0	0.009	0.03



3-(t-butyl-$^2H_9$)thiophene

M.W. = 149

Date: 4-23-68

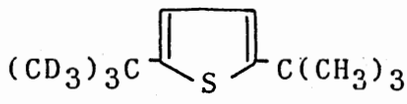
m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.251	0.90	57.1	0.371	1.33
38.0	0.616	2.21	58.0	0.516	1.55
39.0	1.567	5.62	58.1	0.349	1.25
39.9m	0.006	0.02	58.5d	0.011	0.04
40.0	1.325	4.75	59.0	0.382	1.37
41.0	1.685	6.04	59.5d	0.006	0.02
41.8m	0.011	0.04	60.0	0.360	1.29
42.0	3.894	13.96	60.5d	0.011	0.04
43.0	0.379	1.36	61.0	0.215	0.77
44.0	0.112	0.40	61.1	0.140	0.50
44.1	0.602	2.16	61.5d	0.042	0.15
44.8m	0.006	0.02	62.0	0.430	1.54
45.0	3.776	13.54	62.1	0.268	0.96
45.1	1.754	6.29	62.5d	0.070	0.25
45.8m	0.006	0.02	63.0	0.273	0.98
46.0	1.308	4.69	63.5d	0.215	0.77
46.1	5.288	18.96	64.0	0.321	1.15
47.0	0.220	0.79	64.5d	0.243	0.87
47.1	0.190	0.68	65.0	0.396	1.42
47.5	0.006	0.02	65.5d	0.312	1.12
48.0	0.128	0.40	66.0	0.251	0.90
48.1	0.042	0.15	66.1	0.577	2.07
49.0	0.167	0.60	66.5d	0.022	0.08
49.2m	0.006	0.02	67.0	0.689	2.47
50.0	0.340	1.22	68.0	0.499	1.79
51.0	0.466	1.67	68.5d	0.011	0.04
52.0	0.586	2.10	69.0	0.516	1.85
53.0	0.809	2.90	69.1	0.541	1.94
53.5d	0.006	0.02	69.5d	0.011	0.04
54.0	0.466	1.67	70.0	0.402	1.44
54.5d	0.011	0.04	70.5d	0.022	0.08
55.0	0.418	1.50	71.0	0.140	0.50
55.5d	0.053	0.19	71.1	0.117	0.42
56.0	0.365	1.31	71.5d	0.011	0.04
56.5d	0.011	0.04	72.0	0.167	0.60
57.0	0.421	1.51	72.5d	0.156	0.56

3-(t-butyl-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
73.0	0.184	0.66	105.0	0.053	0.19
73.1	0.162	0.58	106.0	0.011	0.04
73.5d	0.017	0.06	107.0	0.006	0.02
74.0	0.123	0.44	108.0	0.014	0.05
75.0	0.087	0.31	109.0	0.081	0.29
76.0	0.031	0.11	110.0	0.109	0.39
76.1	0.084	0.30	111.0	0.820	2.94
76.5m	0.006	0.02	112.0	0.413	1.48
77.0	0.064	0.23	113.0	0.569	2.04
78.0	0.047	0.17	114.0	0.154	0.55
79.0	0.106	0.38	115.0	0.092	0.33
80.0	0.254	0.91	115.4m	0.006	0.02
81.0	0.340	1.22	116.0	0.059	0.21
82.0	0.301	1.08	117.0	0.025	0.09
82.5m	0.006	0.02	118.0	0.011	0.04
83.0	0.237	0.85	119.0	0.017	0.06
84.0	0.254	0.91	120.0	0.008	0.03
85.0	0.500	1.79	121.0	0.017	0.06
85.5m	0.006	0.02	122.0	0.008	0.03
86.0	0.524	1.88	123.0	0.022	0.08
86.8m	0.006	0.02	124.0	0.033	0.12
87.0	2.675	9.59	125.0	0.031	0.11
88.0	0.655	2.35	126.0	0.028	0.10
89.0	0.215	0.77	127.0	0.139	0.50
90.0	0.053	0.19	128.0	0.198	0.71
91.0	0.017	0.06	129.0	0.452	1.62
92.0	0.022	0.08	129.8m	0.011	0.04
93.0	0.053	0.19	130.0	1.866	6.69
94.0	0.059	0.21	131.0	27.890	100.00
95.0	0.312	1.12	131.8m	0.098	0.35
96.0	0.516	1.85	132.0	3.428	12.29
97.0	0.312	1.12	133.0	1.328	4.76
98.0	0.220	0.79	134.0	0.156	0.56
98.8m	0.017	0.06	135.0	0.017	0.06
99.0	3.894	13.96	137.0	0.011	0.04
100.0	1.813	6.50	143.0	0.006	0.02
101.0	0.633	2.27	144.0	0.011	0.04
102.0	0.156	0.56	145.0	0.022	0.08
103.0	0.059	0.21	146.0	0.056	0.20
104.0	0.053	0.19	147.0	0.145	0.52

3-(t-butyl-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
148.0	0.639	2.29	151.0	0.365	1.31
148.8m	0.042	0.15	152.0	0.006	0.02
149.0	6.738P	24.16P	153.0	0.006	0.02
150.0	0.976	3.50			



2,5-di(t-butyl-5-$^{2}H_9$)-thiophene

M.W. = 205

Date: 4-11-68

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
38.0	0.189	1.33	55.5d	0.009	0.06
38.8m	0.001	0.01	56.0	0.309	2.17
39.0	2.102	14.78	56.5d	0.004	0.03
39.8m	0.001	0.01	56.8m	0.001	0.01
40.0	0.667	4.69	57.0	0.091	0.64
40.8m	0.013	0.09	57.1	0.757	5.32
41.0	3.815	26.82	57.5d	0.001	0.01
41.8m	0.001	0.01	58.1	0.275	1.94
42.0	1.674	11.77	58.5d	0.004	0.03
42.8m	0.001	0.01	58.8m	0.001	0.01
43.0	0.388	2.73	59.0	0.495	3.48
44.0	0.033	0.23	59.1	0.070	0.49
44.1	0.432	3.04	59.5d	0.004	0.03
44.8m	0.001	0.01	60.0	0.154	1.08
45.0	1.107	7.78	60.1	0.104	0.73
45.1	0.741	5.21	60.5d	0.009	0.06
45.8m	0.001	0.01	61.0	0.142	1.00
46.0	0.582	4.09	61.1	0.107	0.75
46.1	2.927	20.58	61.5d	0.013	0.09
47.0	0.157	1.10	61.8m	0.001	0.01
47.1	0.115	0.81	62.0	0.521	3.66
48.0	0.091	0.64	62.1	0.135	0.95
48.1	0.084	0.59	62.5d	0.013	0.09
49.0	0.081	0.57	63.0	0.260	1.83
49.1	0.107	0.75	63.1	0.024	0.17
50.0	0.235	1.65	63.5d	0.009	0.06
50.1	0.040	0.28	64.0	0.128	1.28
51.0	0.532	3.74	64.1	0.020	0.14
51.5d	0.004	0.03	64.5d	0.009	0.06
52.0	0.358	2.52	65.0	0.504	3.54
52.5d	0.004	0.03	65.1	0.070	0.49
53.0	0.743	5.22	65.5d	0.009	0.06
53.5d	0.001	0.01	65.8m	0.028	0.20
54.0	0.322	2.26	66.0	0.330	2.32
54.5d	0.004	0.03	66.1	0.792	5.57
55.0	0.487	3.42	66.5d	0.009	0.06

2,5-di(t-butyl-5-$^{2}H_{9}$)thiophene

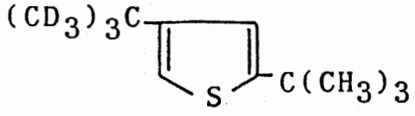
m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
67.0	0.376	2.64	83.5d	0.091	0.64
67.1	0.050	0.35	84.0	0.376	2.64
67.5d	0.058	0.41	84.2m	0.001	0.01
68.0	0.400	2.81	84.5d	0.128	0.90
68.2	0.001	0.01	85.0	0.767	5.39
68.5d	0.107	0.75	85.5d	0.482	3.39
69.0	0.680	4.78	86.0	1.818	12.78
69.5d	0.010	0.70	86.5d	0.235	1.65
70.0	0.829	5.83	87.0	0.302	2.12
70.5d	0.102	0.72	87.5d	0.041	0.29
71.0	0.293	2.06	88.0	0.102	0.72
71.5d	0.037	0.26	88.5d	0.004	0.03
71.8m	0.004	0.03	89.0	0.070	0.49
72.0	0.454	3.19	90.0	0.155	1.09
72.5d	0.046	0.32	91.0	0.324	2.28
73.0	0.124	0.87	92.0	0.236	1.66
73.1	0.107	0.75	93.0	0.322	2.26
73.5d	0.017	0.12	93.5d	0.070	0.49
74.0	0.226	1.59	94.0	0.330	2.32
74.1	0.078	0.55	94.5d	0.017	0.12
74.5d	0.028	0.20	95.0	0.383	2.69
75.0	0.178	1.25	95.5d	0.017	0.12
75.5d	0.041	0.29	96.0	0.343	2.41
76.0	0.252	1.77	97.0	2.124	14.93
76.5d	0.046	0.32	98.0	0.293	2.06
77.0	0.400	2.81	99.0	0.346	2.43
77.5d	0.028	0.20	100.0	0.223	1.57
78.0	0.432	3.04	101.0	0.124	0.87
78.2m	0.001	0.01	102.0	0.067	0.47
78.5d	0.017	0.12	102.5d	0.004	0.03
79.0	0.445	3.13	103.0	0.064	0.45
79.5d	0.004	0.03	104.0	0.100	0.70
80.0	0.371	2.61	105.0	0.152	1.07
80.5d	0.004	0.03	106.0	0.137	0.96
81.0	0.376	2.64	107.0	0.137	0.96
81.5d	0.009	0.06	108.0	0.132	0.93
82.0	0.223	1.57	109.0	0.165	1.16
82.3m	0.009	0.06	110.0	0.174	1.22
82.5d	0.037	0.26	111.0	0.236	1.66
83.0	0.019	0.13	112.0	0.230	1.62

2,5-di(t-butyl-5-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
113.0	0.230	1.62	153.0	0.219	1.54
114.0	0.178	1.25	154.0	1.161	8.16
115.0	0.078	0.55	155.0	0.252	1.77
116.0	0.114	0.80	156.0	0.196	1.38
117.0	0.121	0.85	157.0	1.422	10.00
118.0	0.137	0.96	158.0	0.186	1.31
119.0	0.157	1.10	159.0	0.095	0.67
120.0	0.141	0.99	160.0	0.023	0.16
121.0	0.111	0.78	160.8m	0.004	0.03
122.0	0.112	0.79	161.0	0.020	0.14
123.0	0.164	1.15	161.1	0.013	0.09
124.0	0.164	1.19	162.0	0.024	0.17
125.0	0.313	2.20	163.0	0.009	0.06
126.0	0.474	3.33	164.0	0.004	0.03
127.0	0.152	1.07	165.0	0.013	0.09
128.0	0.112	0.79	166.0	0.046	0.32
129.0	0.087	0.61	167.0	0.053	0.37
130.0	0.115	0.81	168.0	0.061	0.43
131.0	0.250	1.76	169.0	0.091	0.64
132.0	0.054	0.38	170.0	0.569	4.00
133.0	0.041	0.29	171.0	1.343	9.44
134.0	0.041	0.29	171.8m	0.004	0.03
135.0	0.090	0.49	172.0	5.606	39.43
136.0	0.132	0.93	172.8m	0.004	0.03
137.0	0.226	1.59	173.0	0.706	4.96
138.0	0.299	2.10	174.0	0.302	2.12
139.0	0.380	2.67	175.0	0.043	0.30
140.0	0.191	1.27	176.0	0.009	0.06
141.0	0.080	0.56	177.0	0.001	0.01
142.0	0.178	1.25	181.0	0.091	0.64
143.0	0.071	0.50	182.0	0.128	0.90
144.0	0.090	0.63	183.0	0.124	0.87
145.0	0.073	0.52	184.0	0.111	0.78
146.0	0.020	0.14	185.0	0.148	1.04
147.0	0.033	0.23	186.0	0.733	5.15
148.0	0.041	0.29	186.8m	0.004	0.03
149.0	0.028	0.20	187.0	13.237	93.06
150.0	0.043	0.30	188.0	1.733	12.18
151.0	0.094	0.66	189.0	1.683	11.83
152.0	0.120	0.84	189.8m	0.004	0.03

2,5-di(t-butyl-5-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
190.0	14.224	100.00	201.0	0.009	0.06
191.0	1.774	12.47	202.0	0.009	0.06
192.0	0.693	4.87	203.0	0.041	0.29
193.0	0.083	0.58	204.0	0.370	2.60
194.0	0.004	0.03	204.8m	0.004	0.03
195.0	0.001	0.01	205.0	4.185P	29.42P
196.0	0.014	0.10	206.0	0.593	4.17
197.0	0.017	0.12	207.0	0.230	1.62
198.0	0.020	0.14	208.0	0.027	0.19
199.0	0.020	0.14	209.0	0.001	0.01
200.0	0.017	0.12			



2,4-di(t-butyl-4-$^2H_9$)thiophene

M.W. = 205 Date: 4-11-68

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
38.0	0.252	1.30	54.5d	0.008	0.04
38.5d	0.002	0.01	55.0	0.633	3.26
39.0	2.301	11.85	55.5d	0.016	0.08
39.5d	0.002	0.01	56.0	0.480	2.47
40.0	0.672	3.46	56.5d	0.035	0.18
40.8m	0.012	0.06	56.8m	0.033	0.17
41.0	4.679	24.10	57.0	3.551	18.29
41.8m	0.002	0.01	57.5d	0.004	0.02
42.0	1.930	9.94	57.8m	0.012	0.06
42.8m	0.002	0.01	58.0	0.144	0.74
43.0	1.231	6.34	58.1	0.371	1.91
44.0	0.029	0.15	58.5d	0.004	0.02
44.1	0.443	2.28	58.8m	0.008	0.04
44.8m	0.016	0.08	59.0	0.456	2.35
45.0	1.401	7.26	59.5d	0.004	0.02
45.1	1.060	5.46	60.0	0.146	0.75
45.5d	0.002	0.01	60.1	0.093	0.48
45.8m	0.016	0.08	61.5d	0.029	0.15
46.0	0.491	2.53	61.8m	0.008	0.04
46.1	3.551	18.29	62.0	0.699	3.60
47.0	0.138	0.71	62.1	0.204	1.05
47.1	0.134	0.69	62.5d	0.058	0.30
48.0	0.76	0.39	63.0	0.346	1.78
48.1	0.041	0.21	63.1	0.025	0.13
49.0	0.072	0.37	63.5d	0.016	0.08
49.1	0.064	0.33	64.0	0.208	1.07
50.0	0.270	1.39	64.1	0.037	0.19
50.1	0.019	0.10	64.5d	0.016	0.08
50.5d	0.002	0.01	64.8m	0.002	0.01
51.0	0.621	3.20	65.0	0.208	2.44
52.0	0.412	2.12	65.1	0.212	1.09
52.5d	0.004	0.02	65.5d	0.012	0.06
53.0	0.672	3.46	65.8m	0.019	0.10
53.5d	0.002	0.01	66.0	2.588	13.33
54.0	0.315	1.62	66.5d	0.008	0.04

2,4-di(t-butyl-4-$^{2}H_9$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
67.0	0.417	2.15	83.0	0.144	0.74
67.1	0.136	0.70	83.1	0.140	0.72
67.2m	0.016	0.08	83.5d	0.089	0.20
67.5d	0.099	0.51	84.0	0.250	1.29
68.1	0.408	2.10	84.5d	0.083	0.43
68.2m	0.045	0.23	85.0	0.555	2.86
69.0	1.012	5.21	85.5d	0.392	2.02
69.5d	0.262	1.35	86.0	2.109	10.86
70.0	2.126	10.95	86.5d	0.266	1.37
70.5d	0.260	1.34	87.0	0.336	1.73
71.0	0.417	2.15	87.5d	0.019	0.10
71.1	0.454	2.34	88.0	0.099	0.51
71.5d	0.008	0.40	88.5d	0.002	0.01
72.0	1.087	5.60	89.0	0.085	0.44
72.5d	0.115	0.59	89.5d	0.002	0.01
73.0	0.159	0.82	90.0	0.109	0.56
73.1	0.167	0.86	90.5d	0.002	0.01
73.5d	0.025	0.13	91.0	0.381	1.96
74.0	0.159	0.82	91.5d	0.002	0.01
74.1	0.029	0.15	92.0	0.299	1.54
74.5d	0.049	0.25	92.5d	0.004	0.02
75.0	0.179	0.92	93.0	0.287	1.48
75.5d	0.054	0.28	93.5d	0.037	0.19
76.0	0.025	0.13	94.0	0.307	1.58
76.1	0.247	1.27	94.5d	0.004	0.02
76.5d	0.045	0.23	95.0	0.241	1.24
77.0	0.414	2.13	95.5d	0.002	0.01
77.5d	0.019	0.10	96.0	0.225	1.16
77.8m	0.002	0.01	97.0	0.184	0.95
78.0	0.798	4.11	98.0	0.322	1.66
78.5d	0.016	0.08	99.0	0.351	1.81
79.0	0.448	2.31	100.0	0.254	1.31
79.5d	0.006	0.03	100.1	0.159	0.82
80.0	0.371	1.91	101.0	0.136	0.70
80.5d	0.004	0.02	102.0	0.066	0.34
81.0	0.318	1.64	102.5d	0.004	0.02
81.5d	0.008	0.04	103.0	0.062	0.32
82.0	0.175	0.90	104.0	0.089	0.46
82.1	0.217	1.12	105.0	0.122	0.63
82.5d	0.019	0.10	106.0	0.107	0.55

2,4-di(t-butyl-4-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
107.0	0.126	0.65	146.0	0.010	0.05
108.0	0.130	0.67	147.0	0.002	0.06
109.0	0.111	0.57	148.0	0.025	0.13
110.0	0.151	0.78	149.0	0.023	0.12
111.0	0.214	1.10	150.0	0.037	0.19
112.0	0.212	1.09	151.0	0.159	0.82
113.0	0.214	1.10	152.0	0.076	0.39
114.0	0.171	0.88	153.0	0.103	0.53
115.0	0.085	0.44	154.0	0.699	3.60
116.0	0.330	1.70	155.0	0.252	1.30
117.0	0.111	0.57	156.0	0.023	0.64
118.0	0.111	0.57	157.0	0.370	1.98
119.0	0.136	0.70	158.0	0.159	0.29
120.0	0.105	0.54	159.0	0.076	0.13
121.0	0.107	0.55	160.0	0.103	0.02
122.0	0.111	0.57	161.0	0.699	0.08
123.0	0.148	0.76	162.0	0.252	0.70
124.0	0.171	0.88	163.0	0.124	0.10
125.0	0.258	1.33	164.0	0.384	0.06
126.0	0.487	2.51	165.0	0.056	0.06
127.0	0.163	0.84	166.0	0.025	0.21
128.0	0.097	0.50	167.0	0.004	0.11
129.0	0.066	0.34	168.0	0.025	0.13
130.0	0.101	0.52	169.0	0.035	0.18
130.9m	0.019	0.10	170.0	0.371	1.91
131.0	0.305	1.57	171.0	0.532	2.74
132.0	0.054	0.28	171.2m	0.002	0.01
133.0	0.037	0.19	172.0	0.555	2.86
134.0	0.033	0.17	173.0	0.107	0.55
135.0	0.058	0.30	174.0	0.043	0.22
136.0	0.115	0.59	175.0	0.010	0.05
137.0	0.171	0.88	176.0	0.012	0.06
138.0	0.190	0.98	177.0	0.002	0.01
139.0	0.266	1.37	178.0	0.004	0.02
140.0	0.159	0.82	178.5m	0.004	0.02
141.0	0.070	0.36	181.0	0.008	0.40
142.0	0.122	0.63	182.0	0.111	0.57
143.0	0.062	0.32	183.0	0.113	0.58
144.0	0.082	0.42	184.0	0.130	0.67
145.0	0.029	0.15	185.0	0.111	0.57

2,4-di(t-butyl-4-$^{2}H_{9}$)thiophene

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
186.0	0.441	2.22	197.0	0.016	0.08
187.0	7.655	39.43	198.0	0.019	0.10
188.0	1.087	5.60	199.0	0.019	0.10
189.0	1.738	8.95	200.0	0.012	0.06
189.8m	0.004	0.02	201.0	0.008	0.04
190.0	19.415	100.00	202.0	0.008	0.04
191.0	2.472	12.73	203.0	0.029	0.15
191.8m	0.004	0.02	204.0	0.315	1.62
192.0	0.932	4.80	205.0	3.699P	19.05P
193.0	0.111	0.57	206.0	0.544	2.80
194.0	0.012	0.06	207.0	0.208	1.07
196.0	0.012	0.06	208.0	0.025	0.13

APPENDIX B

GAS CHROMATOGRAPHIC DATA

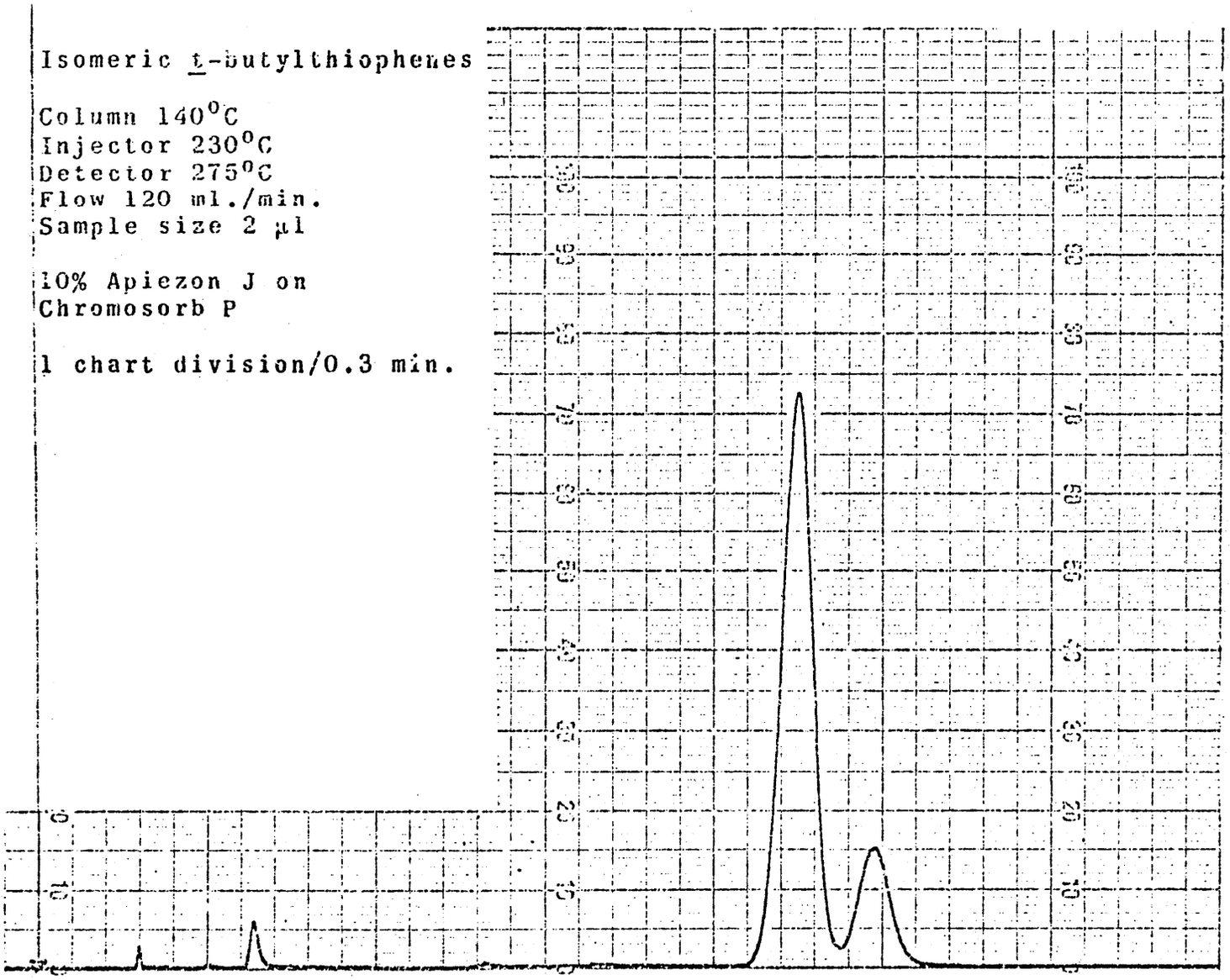

Isomeric t-butylthiophenes
Column 140°C
Injector 230°C
Detector 275°C
Flow 120 ml./min.
Sample size 2 µl
10% Apiezon J on
Chromosorb P
1 chart division/0.3 min.

CHART 1

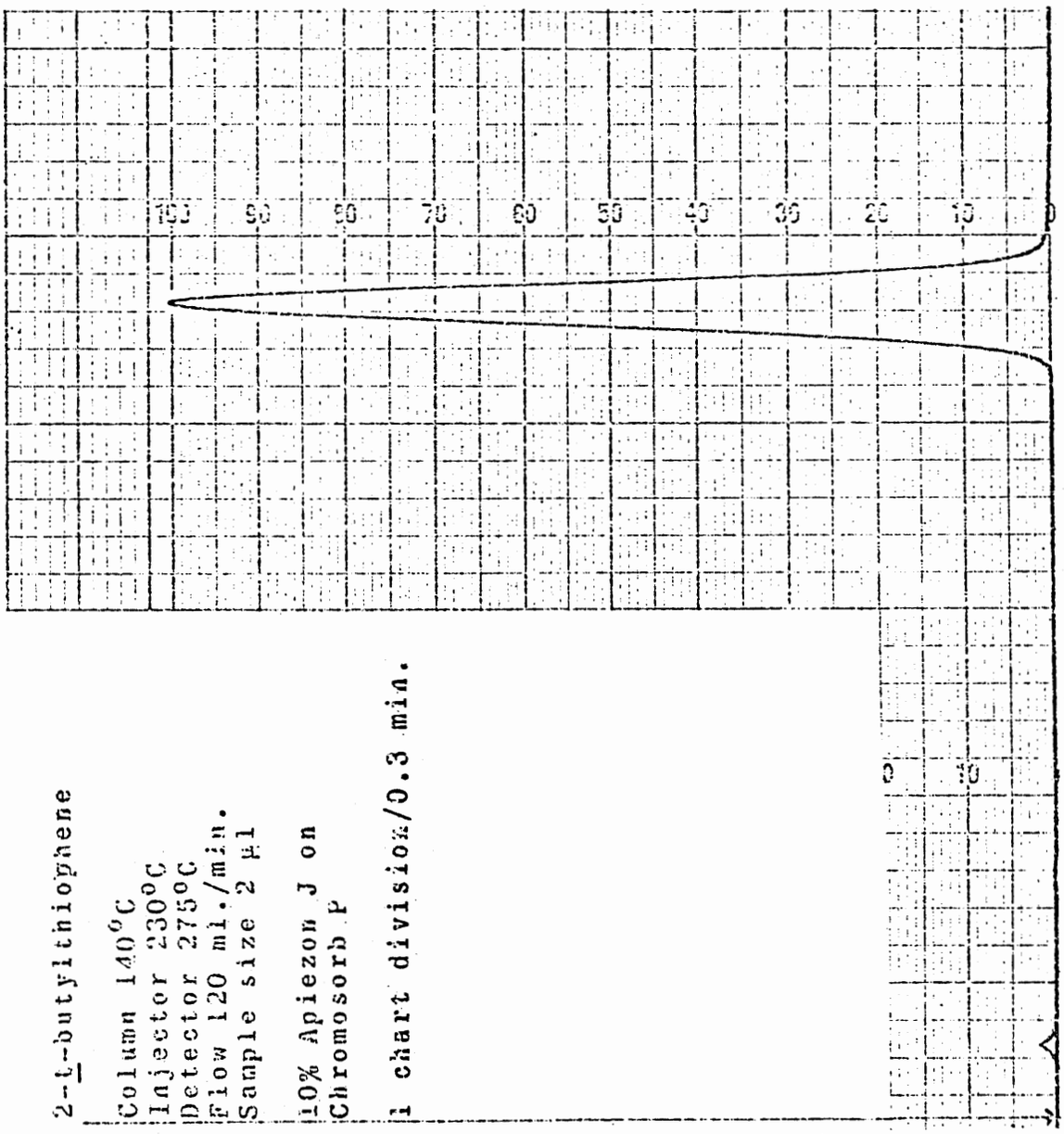

2-t-butylthiophene
Column 140°C
Injector 230°C
Detector 275°C
Flow 120 ml./min.
Sample size 2 µl
10% Apiezon J on
Chromosorb P
1 chart division/0.3 min.
100
90
80
70
60
50
40
30
20
10
0

CHART 2

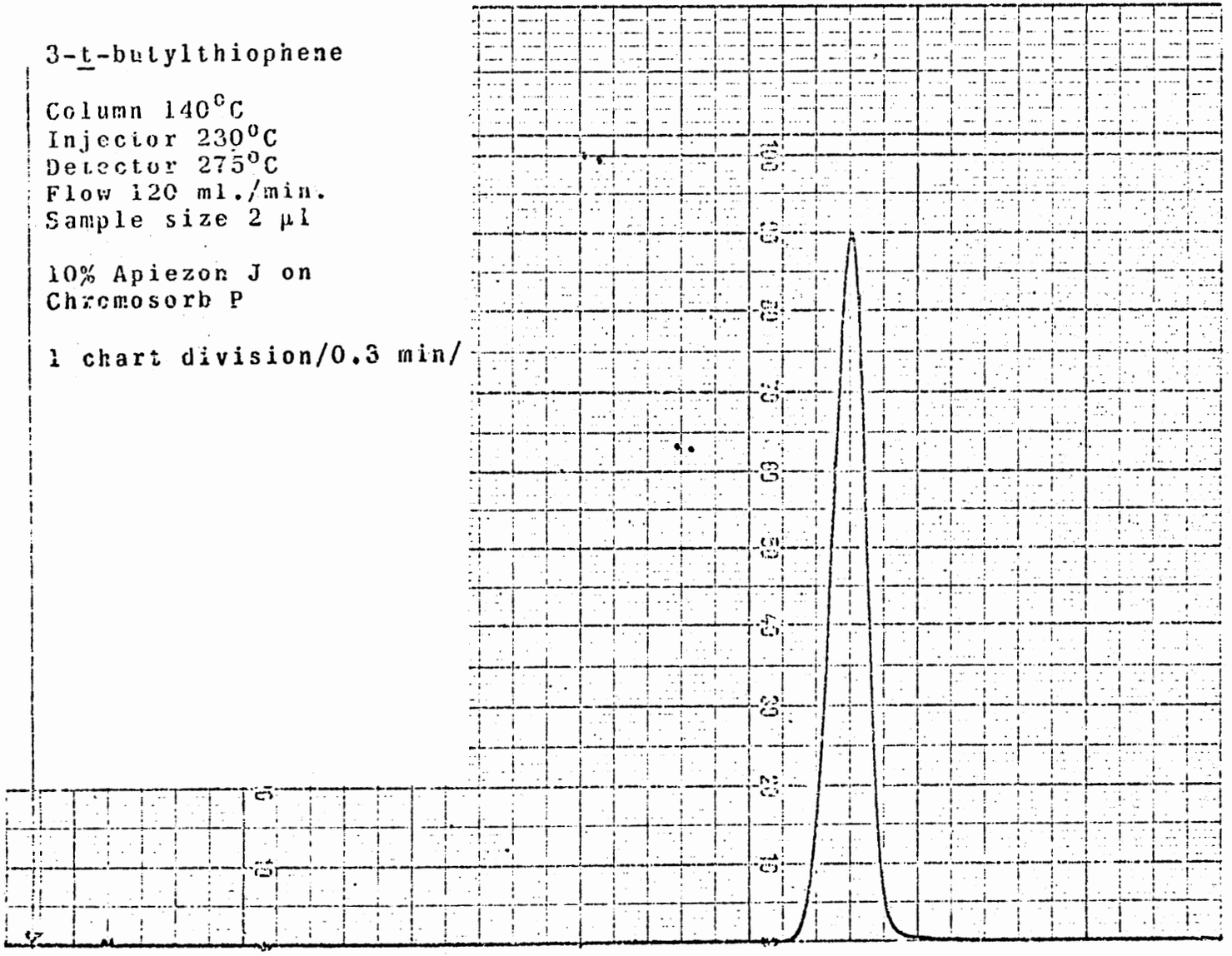
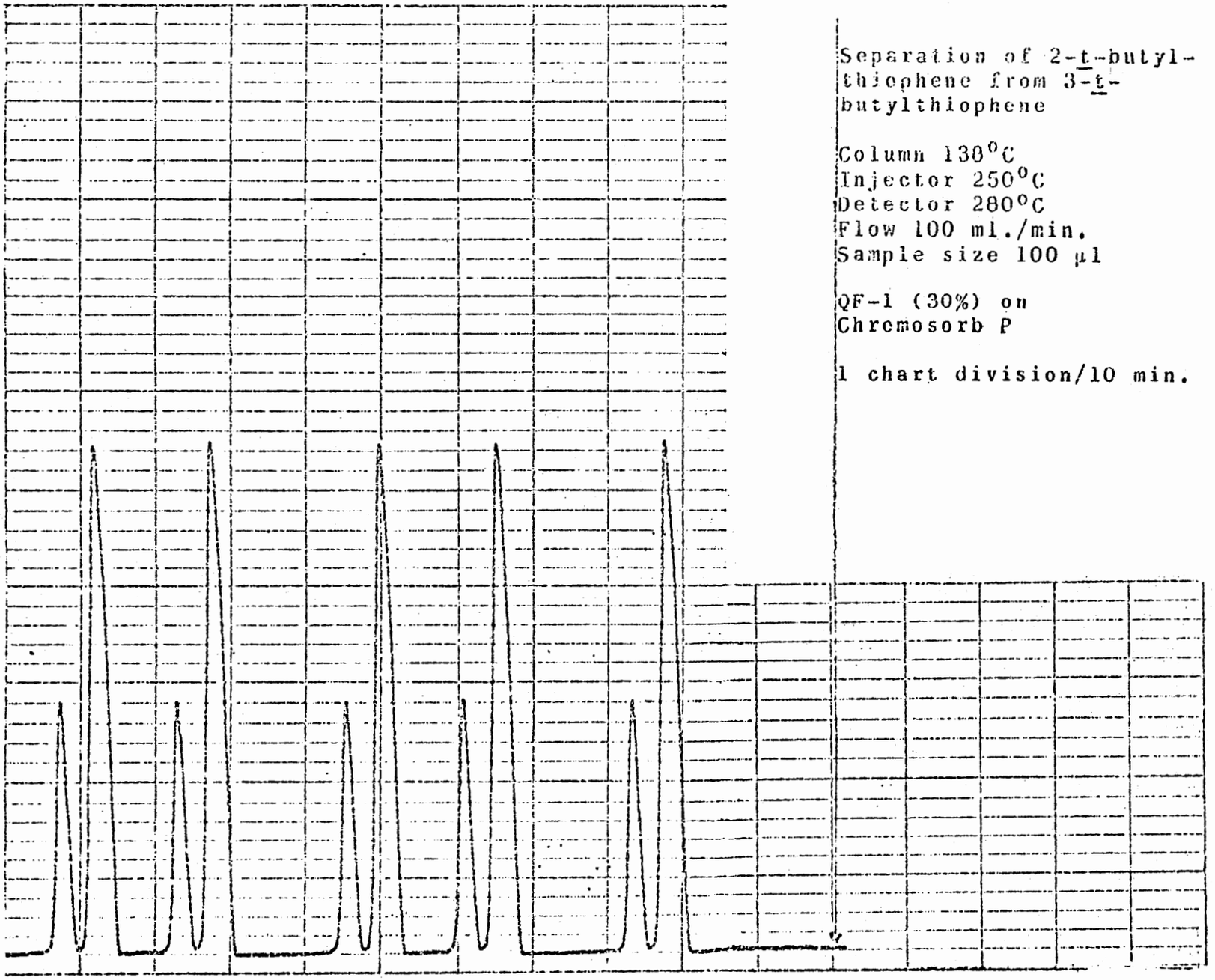

3-t-butylthiophene
Column 140°C
Injector 230°C
Detector 275°C
Flow 120 ml./min.
Sample size 2 µl
10% Apiezon J on
Chromosorb P
1 chart division/0.3 min/

CHART 3



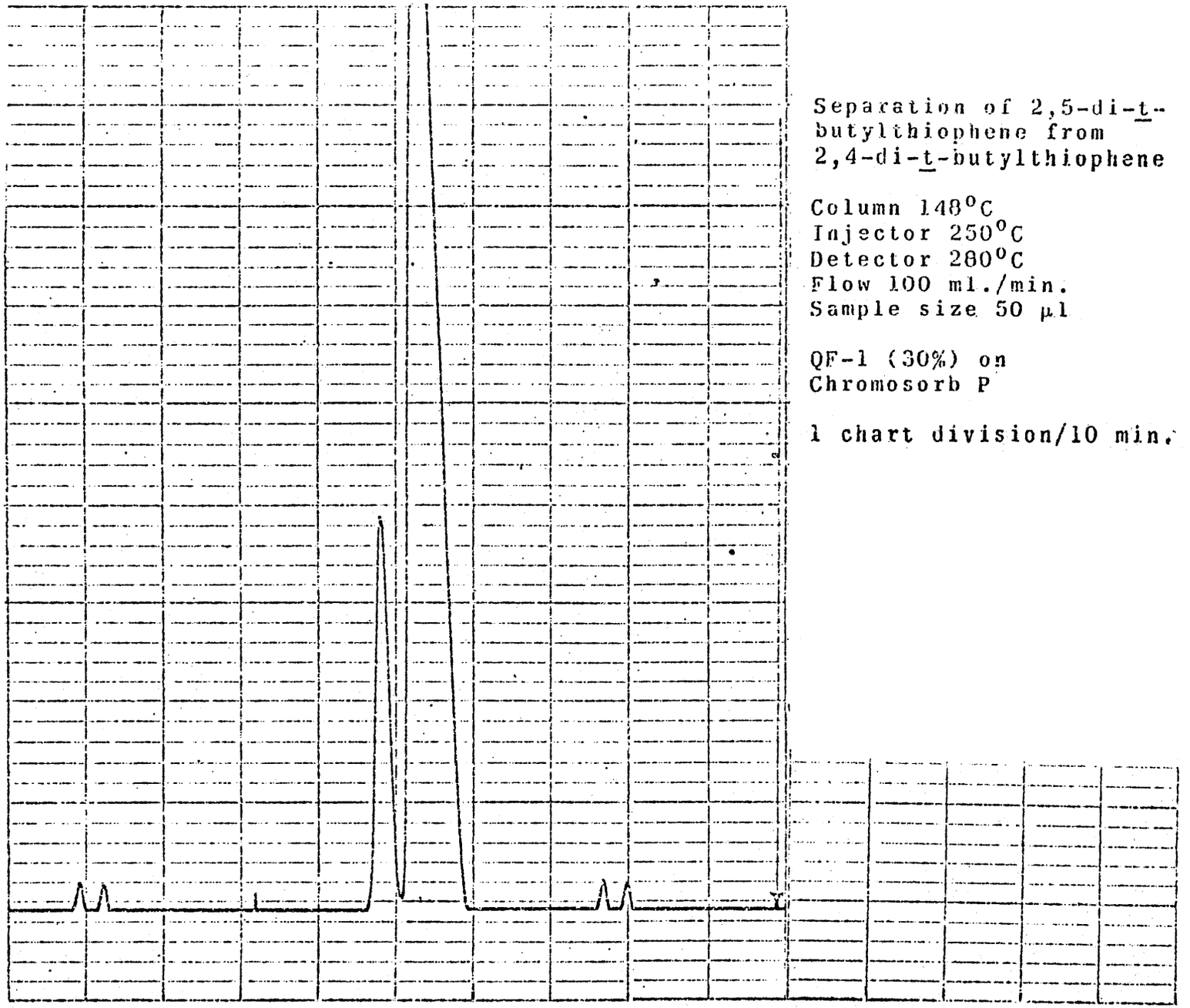
Separation of 2-t-butyl-thiophene from 3-t-butylthiophene

Column 130°C
Injector 250°C
Detector 280°C
Flow 100 ml./min.
Sample size 100 µl

QF-1 (30%) on
Chromosorb P

1 chart division/10 min.

CHART 4



Separation of 2,5-di-t-butylthiophene from 2,4-di-t-butylthiophene

Column 148°C
Injector 250°C
Detector 280°C
Flow 100 ml./min.
Sample size 50 µl

QF-1 (30%) on Chromosorb P

1 chart division/10 min.

CHART 5

VITA

Rosemary Garrett Fowler was born on July 9, 1938, in Pittsburg, Texas. In 1956 she graduated from Dainger-field High School. In 1959 she received a B. S. degree from East Texas State College, Commerce, Texas, with a major in chemistry. In 1962 the M. S. degree with a major in organic chemistry was granted by Texas Woman's University.

In 1964 studies toward a doctoral degree in radiation chemistry were initiated. During the period of her studies, she has received a Robert A. Welch Fellowship for two years, a University Fellowship for three years and scholarships from the W. H. Clark Fellowship Fund.

The author has one publication on the Synthesis of 2-(1-thiaalkyl)thiophenes. I. Journal of Organic Chemistry 27, 2168 (1962) with Robert W. Higgins. She is a member of the American Chemical Society. The author has taught for four years at Arlington State College and two years at Cisco Junior College. Rosemary Garrett was married to Lloyd Leon Fowler on April 27, 1963. They have one child, Mary Lou Fowler, who is three years old.