THE STEREOCHEMISTRY OF SULFONIUM SALTS

ROBERT L. CARET

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THE STEREOCHEMISTRY OF SULFONIUM SALTS

by

ROBERT L. CARET

B. A., Suffolk University, 1969

A THESIS

Submitted to the University of New Hampshire

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Department of Chemistry

May, 1974
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The author dedicates this thesis to his wife and parents whose love, understanding, and continuous support have made possible the achievement of this goal.
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ABSTRACT

THE STEREOCHEMISTRY OF SULFONIUM SALTS

by

ROBERT L. CARET

Optically active dialkylaryl sulfonium salts were prepared from optically active sulfoxides by alkylation followed by treatment with dialkylcadmium or Grignard reagents.

The mechanistic pathway of the reaction was investigated and was found to be one of inversion at sulfur. Having determined this, the absolute configuration of several sulfonium salts were assigned, for the first time, by correlation to the starting sulfoxide.

It was also shown that the chiroptic properties (ORD and CD spectra) of these salts could be obtained and related to the configuration about sulfur; a positive Cotton effect corresponding to the $R$-configuration and a negative Cotton effect to the $S$-configuration.

The stereospecificity of the reaction was shown to be dependent on the reaction time, temperature, and organometallic. In particular, great care should be taken to exclude halide from the reaction mixture. The use of distilled dialkylcadmium reagents for a 20-min period at room tempera-
ture, and the subsequent isolation of the sulfonium salt with a non-nucleophilic anion provided satisfactory conditions for both chemical and optical yield; ca. 50% and 80%, respectively.

The synthesis of triaryl- and alkyldiarylsulfonium salts was not completely successful. Although the chemical yields were satisfactory, the optical yields in all cases were zero. This was attributed to a low barrier to pyramidal inversion around sulfur.

The synthesis of trialkylsulfonium salts was never accomplished using this method. Varying the organometallic, leaving group, reaction time, and reaction temperature had no effect on the final outcome.

A number of investigations into the modes of decomposition and racemization of the title compounds were undertaken.
HISTORICAL

The sulfonium ion (1) has four ligands, if one includes the lone pair of electrons, attached to a central sulfur atom.

The non-planarity of the sulfonium ion was first demonstrated in 1900 by the successful resolution of methyl-ethylthetine bromide (2) by Pope and Peachy.¹ In the same year, Smiles² reported the resolution of both enantiomers of methylethylphenacylsulfonium bromide (3).

![Chemical structures](image-url)
The X-ray structure of triethylsulfonium iodide (4), published in 1940\(^3\), unequivocally established a pyramidal geometry to the sulfonium ion. Further proof of this geometry appeared one year later with the publication of the X-ray structure of trimethylsulfonium iodide (5).\(^4\)

![Chemical Structure 1](image1)

More recently, the structures of 1-acetonyl-1-thionia-5-thiacyclooctane perchlorate (6)\(^5\) and phenylsulfoxonium iodide (7)\(^6\) have been determined; 6 was shown to exhibit a pyramidal geometry about sulfur, while 7 was shown to be tetrahedral.

![Chemical Structure 2](image2)
Thermal and hydrolytic instability preclude the extensive natural occurrence of sulfonium compounds. The small number that have been found in nature include dimethyl-β-propiothetin (8) found in some marine algae, S-methylmethionine (9) present in many vegetables, and methyldiethylsulfonium hydroxide (10) found in dog urine.7

\[
\begin{align*}
8 & : \quad \text{CH}_3 \quad \text{S} \quad \text{CH}_2\text{CH}_2\text{COOH} \\
9 & : \quad \text{CH}_3 \quad \text{S} \quad \text{CH}_2\text{CH}_2\text{CHCOOH} \\
10 & : \quad \text{CH}_3 \quad \text{S} \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

The sulfonium ion has been found to be very important in methyl-group transfer in certain biological systems. S-Adenosylmethionine (11), for example, can transfer the methyl group attached to sulfur to a variety of acceptors.8,9,43 Only one isomer of 11, drawn below, exhibits any biological activity. Although the amino acid center is known to have the L-configuration, the configuration at sulfur is unknown.10
Sulfonium compounds have been used as dyes, lubricants, emulsifying agents, and wetting agents. A number have been shown to exhibit antifungal activity and many have been employed as biological toxicants, plant defoliants, and plant-growth-inhibitors. More recently, sulfonium compounds have found use in the preparation of anion exchange resins.7

The absolute configuration of a sulfonium salt has never been determined unambiguously. Trost and Hammen11 have assigned the (+)-S and (-)-R configurations to the two enantiomers of adamantylallylethylsulfonium tetrafluoroborate (12) by correlation with S-2-pentanol (13-S) (Scheme I). The conversion of 12-S to 14-R proceeds via a [2,3] sigmatropic rearrangement of the intermediate ylid 16. The reactive conformations necessary for the conversion of 16 to 14 are
SCHEME I

$$\text{CH}_2\text{CH}_3, \text{BF}_4^- \rightarrow \text{Ad-S} \rightarrow \text{C} \rightarrow \text{H}$$

12-S

$$\text{CH}_2\text{CH}=\text{CH}_2$$

14-R

$$\text{CH}_2\text{CH}_2\text{CH}_3$$

13-S

15-R

Ad = \includegraphics[width=0.1\textwidth]{cyclohexyl}
illustrated below. Of the reactive conformations possible for the two isomers, the one illustrated for the S-isomer minimizes non-bonded interactions whereas that illustrated for the R-isomer maximizes these interactions. The S-configuration was assigned to the starting salt on this basis.
In 1971, Kobayashi et al.\textsuperscript{12} published the synthesis and absolute configuration of methylethylphenyloxosulfonium mercuritriiodide (17). All attempts to oxidize methylethylphenylsulfonium mercuritriiodide (18) to 17, which would allow the direct assignment of the configuration of 18, failed (eq. 1).\textsuperscript{13}

\[
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{CH}_3 \quad \text{S} \quad \text{HgI}_3^- \\
\end{array} + 
\begin{array}{c}
\text{[O]} \\
\end{array} 
\rightarrow 
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{CH}_3 \quad \text{S} \quad \text{O} \\
\end{array} + 
\begin{array}{c}
\text{HgI}_3^- \\
\end{array}
\]

18 17

The racemization of sulfonium salts has been shown to proceed by three different pathways\textsuperscript{14} (Scheme II): Path A, dissociation-recombination (Sn1); Path B, pyramidal inversion; Path C, nucleophilic displacement (Sn2).

Balfe and co-workers investigated the racemization of the l-methylethylphenacylsulfonium salts (19a) and (19b).\textsuperscript{15} They found that 19a was optically stable at room temperature in acetone, but 19b completely racemized after 139 hr under the same conditions. They concluded that the mercuritetrati iodide ion which can dissociate to mercuritriiodide and iodide ion, racemized the sulfonium salt via Path C, nucleophilic displacement (Sn2), as a result of nucleophilic attack by the iodide ion.
SCHEME II

\[ R^2R^3S + (R')^t(X)^- \]

\[ R^2R^3S \leftrightarrow R^1X \]
Darwish et al.\textsuperscript{16} found that the racemization of p-methoxybenzylethylmethylsulfonyl perchlorate (20) followed Path A, dissociation-recombination (Sn1), accompanied by solvolysis or internal return to give racemic sulfonyl salt. They reasoned that the stability of the p-methoxybenzyl cation accounted for the favorability of this pathway for 20.
The large majority of sulfonium salts have been shown to racemize through Path B, pyramidal inversion. Darwish and Tourigny\textsuperscript{17,18} studied the racemization of $\tau$-butylethylmethylsulfonium perchlorate (21) and its analogs 22 and 23. Path C, nucleophilic displacement (Sn2), was ruled out as the perchlorate ion is known to be non-nucleophilic. The electron-withdrawing nature of the methoxy group in 22 and the electron-releasing nature of the methyl group in 23 would result in a decrease in the rate of racemization of 22 compared to 21 and an increase in rate for 23 vs. 21 if Path A, dissociation-recombination (Sn1), were followed. If Path B, pyramidal inversion, was the route, both 22 and 23 should racemize faster than 21 due to their increased steric bulk. The relative rates of racemization of 21:22:23 are 1:1.7:3.8 indicating pyramidal inversion as the major pathway for racemization.
Other salts that have been shown to racemize by pyramidal inversion include 1-adamantylethylmethylsulfonium perchlorate (24), benzylethylmethylsulfonium perchlorate (25), p-nitrobenzylethylmethylsulfonium perchlorate (26), and methylethylphenacylsulfonium perchlorate (27).
In 1973, Darwish and Scott determined the rate constants for inversion of a number of monoaryl- and diaryl-sulfonium salts (28a-h). They found a marked steric effect on the rate of racemization but very little change in the rates due to electronic effects (Table I).

Fava and co-workers have investigated the racemization of the cyclic sulfonium salts 29, 30 and 31. Employing many of the same arguments presented in earlier discussions, they concluded that a pyramidal inversion pathway was the major route of racemization in this series.

More recently, Fava et al. have investigated the racemization of trans-3-methyl-3-thioniabicyclo[4.3.0]nonane iodide (32).
<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>R</th>
<th>R'</th>
<th>k^a</th>
</tr>
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<tbody>
<tr>
<td>28a</td>
<td>H</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>1</td>
</tr>
<tr>
<td>28b</td>
<td>OCH₃</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>1.61</td>
</tr>
<tr>
<td>28c</td>
<td>OH</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>1.86</td>
</tr>
<tr>
<td>28d</td>
<td>NO₂</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>1.19</td>
</tr>
<tr>
<td>28e</td>
<td>H</td>
<td>n-C₃H₇</td>
<td>C₂H₅</td>
<td>11.2</td>
</tr>
<tr>
<td>28f</td>
<td>H</td>
<td>n-C₄H₉</td>
<td>C₂H₅</td>
<td>9.51</td>
</tr>
<tr>
<td>28g</td>
<td>OCH₃</td>
<td>Ph</td>
<td>CH₃</td>
<td>9.82</td>
</tr>
<tr>
<td>28h</td>
<td>OCH₃</td>
<td>Ph</td>
<td>C₂H₅</td>
<td>70.8</td>
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^aRelative rate constants in methanol at 50°
Through pyramidal inversion (Path A, Scheme III) proton \( ^1H \) becomes \( ^2H \) and \( ^3H \) becomes \( ^4H \) whereas \( ^2H \) and \( ^3H \) would exchange if Path B (Scheme III) were involved. Nmr analysis of \( 32-(d_3) \) showed the exchange of \( ^1H-^2H \) and \( ^3H-^4H \) proving conclusively that pyramidal inversion is the only route involved in the racemization of this compound.

The barriers to pyramidal inversion for a large number of sulfonium salts have been arrived at both through theoretical calculations and experimental measurements; they lie in the range of \( \Delta H^\ddagger = 25-29 \text{ kcal/mole} \).14,19,22-24,46

The use of sulfonium ylids in organic synthesis has been the focal point of a large amount of research over the past few years.

Trost and co-workers have successively employed the cyclopropyldiphenylsulfonium ylid (33) in the synthesis of a variety of organic intermediates25; these include cyclobutanones26,27, \( \gamma \)-butyrolactones26, spiropentanes27, and oxaspiropentanes26,28,29 (Scheme IV).
SCHEME III

B

\[
\begin{align*}
\text{H}^1 & \quad \text{H}^3 \\
\text{H}^2 & \quad \text{H}^4 \\
\text{S} & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}^2 & \quad \text{H}^4 \\
\text{H}^3 & \quad \text{H}^1 \\
\text{S} & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}^2 & \quad \text{H}^3 \\
\text{H}^1 & \quad \text{H}^4 \\
\text{S} & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}^2 & \quad \text{H}^3 \\
\text{H}^1 & \quad \text{H}^4 \\
\text{S} & \quad \text{CH}_3
\end{align*}
\]
SCHEME IV

R2CO → R2CO

H⁺ → R2CO

R2CO + R2CO → R2CO

H₂O₂ → R₂CO

HO⁻ → R₂CO

Scheme IV illustrating the conversion of various chemical structures to another.
Nucleophilic alkyldiene transfer by sulfonium ylids has been employed in the synthesis of cyclopropanes and oxiranes. Cyclopropane formation through stereospecific intramolecular methylene transfer in the synthesis of 34 from 35 illustrates the synthetic utility of this reaction (eq. 2); the formation of 36, expected through an intermolecular 1,2-attack was not observed.

The possibility of chirality transfer from sulfur to carbon through chiral sulfonium ylids has been investigated by Trost and Hammen. Although quenching of the optically active salt (37) with deuteriofluoroboric acid proceeded with almost no loss of optical activity, condensations of this ylid gave very low yields of optical induction (Scheme V). The [2,3] sigmatropic rearrangement of 12-S to 14-R illustrated in Scheme I, however, proceeded with a minimum of 94% optical induction.
SCHEME V

```
\[ \text{CH}_2\text{CH}_3 \quad \alpha_D 17.4^\circ -27.3^\circ \]

\[ \text{DBF}_5 \quad \rightarrow \quad \text{DCH}_2\text{S} \quad \alpha_D 16.1^\circ \]

\[ \text{PhCHO} \quad \rightarrow \quad \text{PhCH=CCOOC}_2\text{H}_5 \quad \alpha_D 0^\circ \]

\[ \text{CN} \quad \rightarrow \quad \text{CN} \quad \alpha_D 0.78^\circ \]

\[ \text{CH}_2\text{CH}_3 \quad \alpha_D 17.4^\circ -27.3^\circ \]
```
Trost et al. extended their study of the [2,3] sigmatropic rearrangement to its utility in natural product synthesis. They found that optical activity could be induced through the use of chiral solvents in the rearrangement step. The optical induction was on the order of 5-12% in the cases studied. Achiral S-Methyl-S,S-bis-(γ,γ-dimethylallyl)sulfonium tetrafluoroborate (38) could be rearranged to the chiral sulfide (39) in good yields. Using this basic scheme, cyclopropyl compounds such as 41, which are direct precursors of squalene and phytoenes, could be prepared from the easily obtainable achiral precursors 40. Work in this area is still in progress.
Corey and co-workers have found a highly effective and efficient method of oxidizing primary and secondary alcohols to carbonyl compounds through the intermediate formation of alkoxy sulfonium salts (eq. 3).

\[
H_2NC\text{I} + (\text{CH}_3)_2S \rightarrow (\text{CH}_3)_2S^{+}-\text{NH}_2,\text{Cl}^- \xrightarrow{\text{R}_2\text{CHOH}} (\text{CH}_3)_2S^{+}-\text{O-CHR}_2,\text{Cl}^- \\
\text{Et}_3\text{N} \xrightarrow{-25^\circ} \text{R}_2\text{CO}
\]

(3)

Johnson and McCants found that alkylation and subsequent hydrolysis of R-benzyl p-tolyl sulfoxide (42-R) yielded the sulfoxide of inverted configuration, 42-S; 42-R \rightarrow 43-R \rightarrow 42-S (Scheme VI). Alkylation of 42-S followed by hydrolysis, 42-S \rightarrow 43-S \rightarrow 42-R, completed the cycle. These results proved that the alkylation proceeded with retention of configuration and the hydrolysis with 100% inversion of configuration at sulfur. The latter step, involving inversion at sulfur, is analogous to most nucleophilic substitution reactions at tetravalent tricoordinate sulfur.

Johnson and Phillips have shown that alkoxy sulfonium salts react with a variety of alkoxides to undergo rapid alkoxy group exchange followed by a) base-catalyzed collapse to carbonyl compounds and sulfides or b) α-rearrangements analogous to the Pummerer reaction (Scheme VII); the pre-
ponderance of the α-rearranged reaction appeared to be a function of the stability of the carbonium ion formed via elimination of alkoxide from the ylid intermediate.

The reduction of alkoxy sulfonium salts with sodium borohydride has also been investigated by Johnson and Phillips. They found that the salts were smoothly and efficiently converted to the parent sulfides with either alcohol or tetrahydrofuran as solvent. The proposed mechanism is illustrated in eq. 4.

\[
\text{CH}_3\text{S}\text{CH}_3 + \text{NaBH}_4 \rightarrow \text{CH}_3\text{H}_3\text{SCH}_3 \quad \text{eq. 4}
\]

The reaction of alkoxy sulfonium salts with nitrogen and carbon nucleophiles has been shown to yield products (20-90%) arising from nucleophilic attack at sulfur (Scheme VIII). In contrast, the reaction of pyridine with diaryl-etheroxysulfonium salts (eq. 5) proceeds through nucleophilic attack at carbon preferentially yielding the sulfoxide of retained configuration.
SCHEME VIII

\[ \text{cyclopentadienyl anion} \]

\[ X = \text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2, \text{PhCH}_2\text{CH}_2\text{NH}^-, \text{ClO}_4^-\text{(CH}_3\text{CH}_2)_2\text{NHCH}_2\text{CH}_2\text{NH}^-, \]

\[ \text{cyclopentadienyl anion} \]

\[ Y = \text{(CH}_3\text{CH}_2)_2\text{N(CH}_2)_3\text{NH}^-, \text{ClO}_4^-\text{(CH}_3\text{CH}_2)_2\text{NHCH}_2\text{CH}_2\text{NH}^-, \text{(CH}_3\text{OOOC)}_2\text{C}^- \]
Trialkylsulfonium salts have been shown to undergo an \( \text{E}_2 \) elimination in the presence of alkoxides (eq. 6)\(^{42}\), while dialkylaryl- and diarylalkylsulfonium salts have been treated with hydroxide ion yielding an aryl alkyl or diaryl sulfide resulting from nucleophilic attack at carbon (eqs. 7,8).\(^{43}\)
Base catalyzed hydrogen-deuterium exchange reactions have been carried out on the cyclic sulfonium salts 32, 44, 45, and 46. Protons cis to the methyl on sulfur (trans to the lone pair of electrons) have been shown to undergo exchange 30-100 times faster than their trans counterparts.
Trialkylsulfonium salts were shown at the turn of the century to be chiral, since they could be resolved.\textsuperscript{1,2} In 1966, Andersen and Papanikolaou\textsuperscript{45} attempted the first synthesis of optically active triarylsulfonium salts. Several triarylsulfonium salts were obtained from the reaction of arylmagnesium bromides with diarylethoxysulfonium salts prepared from the corresponding optically active sulfoxides (eq. 9). Although the chemical yields were satisfactory, the optical yields in all cases were zero. Since triarylsulfonium salts have never been resolved, and since, at that time, it was not known whether or not the triarylsulfonium ion was pyramidal in nature and hence capable of chirality, the reason for the optical inactivity was not obvious. A low barrier to pyramidal inversion was the favored explanation. Subsequently, 9,9-dimethyl-10-phenylthioxanthylum perchlorate (47) was synthesized.\textsuperscript{46} The diastereotopic nature of the gem-dimethyl group was manifest in the nmr spectrum of 47.
Variable temperature nmr measurements were performed and the gem-dimethyl group was seen to coalesce at 200±5° in benzophenone. This led to a $\Delta G^\ddagger$ value of 25 kcal/mole for the pyramidal inversion barrier in 47. It was concluded that the triarylsulfonium ion is non-planar and might well undergo pyramidal inversion too rapidly at room temperature to allow their isolation in an optically active form (eq. 10).
In 1971, Andersen\textsuperscript{47} reported the first asymmetric synthesis of optically active sulfonium salts. The alkylation of optically active alkyl \( p \)-tolyl sulfoxides with triethyl-oxonium tetrafluoroborate followed by reaction with distilled dialkylcadmium reagents yielded optically active dialkylaryl-sulfonium salts (eq. 11). Although the reaction was assumed to proceed with inversion and has been drawn in this way, the stereochemistry of attack was unknown.

\[
\begin{align*}
R, \text{CH}_3; R', \text{CH}_3\text{CH}_2 \\
R, \text{CH}_3(\text{CH}_2)_3; R', \text{CH}_3 \\
\text{(11)}
\end{align*}
\]

Ladd\textsuperscript{48a-c} continued this work and prepared several dialkyl-\( p \)-tolylsulfonium salts via the cadmium reaction; these salts are listed below:
Through the work of Ladd and Andersen, it was shown that by starting with two different sulfoxides of known chirality that they could be converted into the structurally identical sulfonium salts of opposite stereochemistry.* This was done with two different pairs of reactions (eqs. 12-15).

*The results indicate identical stereochemistry in all cases.
This thesis will continue the work of Andersen and Ladd on the synthesis and stereochemistry of optically active sulfonium salts prepared from sulfoxides and organometallics.
RESULTS AND DISCUSSION

Optically active dialkylarylsulfonium salts can be prepared from optically active alkyl aryl sulfoxides by alkylation followed by treatment with dialkylcadmium reagents (eq. 16).\textsuperscript{47,48a-c}

\[
\begin{align*}
\text{Ar} - S - R^1 & \quad \text{O} \\
& \quad R_2^3 O^+ \\
\text{Ar} - S - R^1 & \quad \text{O} - R^2 \\
& \quad R^3 Cd \\
\text{Ar} - S - R^1 & \quad R_2^3 Cd
\end{align*}
\]

The original aim of this research was to synthesize stereospecifically, as in eq. 16, optically active sulfonium salts from organomagnesium compounds, a route which had not been successful previously.

Initially, in order to get better acquainted with the system and to determine the best conditions for the reaction, a racemic sulfonium salt was synthesized from a racemic sulfoxide. Alkylation of (+)-n-butyl p-tolyl sulfoxide with triethylxonium tetrafluoroborate, followed by treatment with ethereal ethylmagnesium bromide for 1 hr at -78° gave (+)-ethyl-n-butyl-p-tolylsulfonylum bromide which was subsequently converted to the tetraphenylborate salt (48) (eq. 17).
With the knowledge that organomagnesium compounds could be employed in the reaction (eq. 16), the preparation of several optically active dialkylaryl sulphonium salts from their optically active sulfoxide precursors was undertaken. \textit{R-}(+)	extit{-Ethyl p-tolyl sulfoxide was converted to \textit{(-)-ethyl-n-butyl-p-tolyl sulphonium 2,4,6-trinitrobenzenesulphonate (TNBS\textsuperscript{-}) [(-)-49] by alkylation with triethyloxonium tetrafluoroborate and reaction with n-butylmagnesium bromide (eq. 18).}
Since the absolute configuration of the sulfonium salt was unknown, the stereochemistry of the substitution process was likewise unknown*, but was depicted as inversion of configuration analogous to most substitution reactions at tricoordinate tetravalent sulfur.37a-c

Similarly, (-)-methyl-n-butyl-p-tolylsulfonium tetraphenylborate [(-)-50], and (+)-methylethyl-p-tolylsulfonium tetraphenylborate [(+)-51] were prepared from R-(+)-methyl p-tolyl sulfoxide and R-(+)-ethyl p-tolyl sulfoxide, respectively.

\[
\text{(-)-50} \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{Ph}_4 \text{B}^-
\end{array} \quad \text{CH}_3 
\]

\[
\text{(+)-51} \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \text{CH}_3 \\
\text{Ph}_4 \text{B}^-
\end{array} 
\]

Combined with the work of Ladd⁴⁸a-c and Andersen⁴⁷, it was now evident (eqs. 19-22 and Table II) that by starting with two different sulfoxides of known chirality and transforming them into the structurally identical sulfonium salt, it was evident that the reaction does indeed proceed with inversion of configuration at sulfur.

*Although at the time of these reactions the stereochemistry of attack was not known, we have subsequently shown that the reaction does indeed proceed with inversion of configuration at sulfur.
that the two processes follow the same stereochemistry. The results indicate identical stereochemistry within each pair and presumably between pairs; in addition the sulfonium salt's sign of rotation is independent of the anion.

\[
\begin{align*}
\text{CH}_3\text{S}^{\ominus} & \xrightarrow{1) \text{Et}_3\text{OBF}_4} \text{CH}_2\text{CH}_3 \quad \text{(19)} \\
\text{CH}_3\text{CH}_2\text{S}^{\ominus} & \xrightarrow{1) \text{Et}_3\text{OBF}_4} \text{CH}_3\text{S}^{\ominus} \quad \text{(20)} \\
\text{CH}_2(\text{CH}_2)_3\text{S}^{\ominus} & \xrightarrow{1) \text{Et}_3\text{OBF}_4} \text{CH}_3\text{S}^{\ominus} \quad \text{(21)} \\
\text{CH}_3\text{S}^{\ominus} & \xrightarrow{1) \text{Et}_3\text{OBF}_4} \text{CH}_3\text{S}^{\ominus} \quad \text{(22)} \\

1) \text{Et}_3\text{OBF}_4 & \xrightarrow{2) \text{Et}_2\text{Cd} \text{ or } \text{Me}_2\text{Cd} \text{ or } \text{MeMgBr}} \text{P-Tol} \\
2) \text{Me}_2\text{Cd} \text{ or } \text{MeMgBr}} \text{P-Tol} \\
\end{align*}
\]
TABLE II

![Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>(X(^-))(^a)</th>
<th>([\alpha]_{\text{D}}^{23})</th>
<th>Yield (%)(^b)</th>
<th>Conditions(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-51</td>
<td>CH(_3)</td>
<td>C(_2)H(_5)</td>
<td>Ph(_4)B(^-)</td>
<td>+7.84°</td>
<td>9</td>
<td>A</td>
</tr>
<tr>
<td>(-)-49</td>
<td>C(_2)H(_5)</td>
<td>n-C(_4)H(_9)</td>
<td>TNBS(^-)</td>
<td>-6.18°</td>
<td>11</td>
<td>A</td>
</tr>
<tr>
<td>(-)-50</td>
<td>CH(_3)</td>
<td>n-C(_4)H(_9)</td>
<td>Ph(_4)B(^-)</td>
<td>-17.48°</td>
<td>9</td>
<td>A</td>
</tr>
<tr>
<td>(-)-52</td>
<td>CH(_3)</td>
<td>C(_2)H(_5)</td>
<td>TNBS(^-)</td>
<td>-5.6°</td>
<td>57</td>
<td>B</td>
</tr>
<tr>
<td>(+)-53</td>
<td>CH(_3)</td>
<td>n-C(_4)H(_9)</td>
<td>TNBS(^-)</td>
<td>+7.6°</td>
<td>74</td>
<td>B</td>
</tr>
<tr>
<td>(+)-52</td>
<td>CH(_3)</td>
<td>C(_2)H(_5)</td>
<td>TNBS(^-)</td>
<td>+19.24°</td>
<td>ca. 10</td>
<td>C</td>
</tr>
<tr>
<td>(-)-53</td>
<td>CH(_3)</td>
<td>n-C(_4)H(_9)</td>
<td>TNBS(^-)</td>
<td>-6.55°</td>
<td>&quot;</td>
<td>C</td>
</tr>
<tr>
<td>(+)-51</td>
<td>CH(_3)</td>
<td>C(_2)H(_5)</td>
<td>Ph(_4)B(^-)</td>
<td>+4.84°</td>
<td>&quot;</td>
<td>C</td>
</tr>
<tr>
<td>(-)-50</td>
<td>CH(_3)</td>
<td>n-C(_4)H(_9)</td>
<td>Ph(_4)B(^-)</td>
<td>-10.69°</td>
<td>&quot;</td>
<td>C</td>
</tr>
<tr>
<td>50</td>
<td>CH(_3)</td>
<td>n-C(_4)H(_9)</td>
<td>Ph(_4)B(^-)</td>
<td>-</td>
<td>11</td>
<td>A</td>
</tr>
</tbody>
</table>

\(^a\)TNBS\(^-\) = 2,4,6-Trinitrobenzenesulfonate. \(^b\)Overall yield from sulfoxide. \(^c\)A - prepared by R. L. Caret; RMgX, -78°, 1 hr. B - prepared by K. K. Andersen; R\(_2\)Cd (distilled), room temperature, 10-50 hr. C - prepared by D. L. Ladd; R\(_2\)Cd (undistilled), room temperature, 20 min.
The results from Table II also suggest that the distilled dialkylcadmium reagents provide much higher chemical yields of the sulfonium salts although under all three reaction conditions the optical yields are of the same magnitude. It was decided to employ the distilled dialkylcadmium reagents whenever possible.

The question of main concern at this point involved the stereochemical pathway of the reaction, the determination of which would allow the first direct assignment of the absolute configuration to a sulfonium salt.

Sulfonium salts can be divided into four general classes: triaryl-, alkyldiaryl-, dialkylaryl-, and trialkylsulfonium salts. Thus far, all efforts had been centered on the dialkylaryl sulfonium salts and it was decided to look into the synthesis of one or more of the other classes with the possibility of finding a more suitable system for investigation.

(+)-Phenyl p-tolyl sulfoxide was converted to (+)-phenyl-o-tolyl-p-tolylsulfonium tetraphenylborate (54) by means of the Grignard reaction. The triaryl sulfonium salt formed in much higher yield (46%) and was more easily isolated than the dialkylaryl sulfonium salts previously prepared. Following this reaction, R-(+)-phenyl p-tolyl sulfoxide was alkylated with triethyloxonium tetrafluoroborate and treated with di-o-tolylcadmium to give phenyl-o-tolyl-p-tolylsulfonium tetraphenylborate (54) (eq. 23). The salt isolated, however, exhibited no optical activity.
Similarly, when R-(+)-phenyl p-tolyl sulfoxide was converted to ethylphenyl-p-tolylsulfonium tetraphenylborate (55), through alkylation with trimethyloxonium tetrafluoroborate and treatment with diethylcadmium, only racemic salt was isolated (eq. 24).

These results were not surprising. Both the work of Andersen et al.\textsuperscript{46} on 9,9-dimethyl-10-phenylthioxanthylum perchlorate (47) and the more recent work of Darwish and Scott\textsuperscript{19} on the rate constants for inversion of several mono- and diarylsulfonium salts indicated that triarylsulfonium
salts would pyramidally invert too rapidly at room temperature to allow their isolation in an optically active form, while the alkyldiarylsulfonium salts could be isolated in an optically active state but would invert at a sufficiently rapid rate as to make their racemization a serious problem: \( \text{Ar}_3\text{S}^+, t_{1/2} = 15 \text{ min} \) and \( \text{Ar}_2\text{RS}^+, t_{1/2} = 2.4 \text{ hr} \) in methanol at 25\(^\circ\).

The optical instability of both the triaryl- and alkyldiarylsulfonium salts and the chemical instability of the alkyldiarylsulfonium salts* forced the abandonment of these systems in favor of the trialkyl- and/or dialkylaryl-sulfonium salt systems.

The trialkylsulfonium salts held particular interest. Prof. A. Kjaer and Dr. E. Kjellstrup\(^{49}\) were working on the assignment of the absolute configuration to \( 56 \), while Trost and Hammen\(^{11}\) had recently assigned the \(+\)-S and \(-\)-R configurations to adamantylallylethylsulfonium tetrafluoroborate (12). Through the use of the appropriate sulfoxide, therefore, it should be possible to assign an inversion or retention mechanism to eq. 16 according to eq. 25 and/or 26.

---

*In several instances these compounds rapidly decomposed, in a matter of minutes, to the parent sulfide.
It should also be possible, through the use of the appropriate cyclic system (e.g. eq. 27), to obtain the same information independent of the above assignments.
Trialkylsulfonium salts are known to be optically stable and several were prepared by alkylation of the corresponding sulfides (Scheme IX).

\[ R^1 - S - R^2 \xrightarrow{\text{alkylating agent}} R^1 - S^+ - R^2 \xrightarrow{\text{alkylating agent}} X^- \]

<table>
<thead>
<tr>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( R^3 )</th>
<th>( X )</th>
<th>\text{alkylating agent}</th>
<th>\text{compound}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{n-C}_4\text{H}_9 )</td>
<td>( \text{n-C}_4\text{H}_9 )</td>
<td>( \text{C}_2\text{H}_5 )</td>
<td>( \text{TBNS} )</td>
<td>( (\text{C}_2\text{H}_5)_3\text{OBF}_4 )</td>
<td>57</td>
</tr>
<tr>
<td>-( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^- )</td>
<td>( \text{CH}_3 )</td>
<td>( \text{BF}_4 )</td>
<td>( (\text{CH}_3)_3\text{OBF}_4 )</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

In contrast, the alkylation of racemic or optically active dialkyl sulfoxides (cyclic or acyclic) followed by treatment with several organometallics at varying temperatures and reaction times failed to yield any sulfonium salt (eq. 28).
The main product isolated from these reactions (eq. 28) was the parent sulfoxide, which was often isolated as a 1:1 adduct of sulfoxide and 2,4,6-trinitrobenzenesulfonylic acid, the anion used in the attempted isolation of the sulfonylum salt.

Formation of sulfoxide-acid adducts are not unknown. For example, dimethyl sulfoxide forms a 1:1 adduct with nitric acid\(^{50}\) and a 2:1 adduct with 2,4,6-trinitrobenzene-sulfonylic acid.\(^{51}\) Sulfoxide-hydrochloric acid adducts are also known.\(^{50}\)

The authentic sample of one such complex (59) was prepared from (+)-methyl-n-butyl sulfoxide and 2,4,6-trinitrobenzenesulfonylic acid (eq. 29).
A number of attempts were made to resolve racemic sulfoxides through the formation of adducts of the sulfoxide and d-10-camphorsulfonic acid (d-10CSA) (Scheme X). In all cases, only racemic material was isolated.

Scheme X

\[
\text{R}_2\text{SO} + \text{d-10CSA} \rightarrow [\text{R}_2\text{SO}; \text{d-10CSA}] \rightarrow \text{R}^\text{R}_2\text{SO}
\]

\[
\text{NaOH}
\]

\[
\text{[S}_2\text{SO; d-10CSA]} \rightarrow \text{S}^\text{R}_2\text{SO}
\]

When optically active sulfoxides were employed in the reaction (eq. 28), optically inactive sulfoxide was isolated. This fact was puzzling. If the organometallic was attacking carbon rather than sulfur as assumed, sulfoxides of retained configuration should predominate (Scheme XI).
A number of model experiments were undertaken to explain these observations.

The reaction of (+)-methoxymethyl-n-butylsulfonium tetrafluoroborate with diethylcadmium (eq. 30) indicated that propane was formed (glpc) so that attack at carbon was definitely occurring.

\[
\begin{align*}
\text{CH}_3\text{CH}_2^- &
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{S} &\rightarrow (\text{CH}_2)_3\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_3 \quad (30)
\end{align*}
\]

Triethylsulfonium tetrafluoroborate, on the other hand, was stable to treatment with dimethylcadmium; no propane or ethylene (glpc) were observed (eq. 31) and the salt was recovered in quantitative yield. The same result was
obtained on treatment with dimethylcadmium followed by the addition of an aliquot of methanol.

\[
\begin{align*}
1) \text{Me}_2\text{Cd} & \quad \text{(CH}_3\text{CH}_2)_3\text{S}^+ \\
\text{or} & \\
1) \text{Me}_2\text{Cd} & \quad \rightarrow \\
2) \text{CH}_3\text{OH} & \quad \text{No Reaction} \quad (31)
\end{align*}
\]

The alkylation of sulfoxides to alkoxy sulfonium salts is known to proceed to 70-100% completion and the work of Johnson and McCants\textsuperscript{36} (Scheme VI) also suggests that these compounds exhibit appreciable optical stability. In order to verify this latter point, \textit{R}-(-)-methyl \textit{n}-butyl sulfoxide was alkylated in methylene chloride with triethyl oxonium tetrafluoroborate (eq. 32). The optical rotation of

\[
\begin{align*}
\text{CH}_3\text{S} \equiv \text{(CH}_2)_3\text{CH}_3 & \quad \text{Et}_3\text{OBF}_4 & \quad \text{CH}_3\text{S} \equiv \text{(CH}_2)_3\text{CH}_3 \\
& \quad \rightarrow & \\
& \quad (-)\text{-60} \quad \text{BF}_4^-
\end{align*}
\]

\[
\text{NaOH} \rightarrow \quad \text{CH}_3\text{(CH}_2)_3\text{S} \equiv \text{CH}_3 \quad (32)
\]
the (-)-ethoxymethyl-n-butylsulfonium tetrafluoroborate

\([-\text{6}0]\) formed showed no change in magnitude in solution

over a 24 hr period at room temperature: \(\alpha_D^{25}\), initial

-33.7°, \(\alpha_D^{25}\), final -33.7°. Hydrolysis of \([-\text{6}0]\) with 1%

sodium hydroxide, a hydrolysis known to proceed with 90-100%

inversion of configuration at sulfur, gave the sulfoxide

of inverted configuration which was 90% optically pure based

on the optical purity of the starting sulfoxide.

The reaction was repeated with \(\text{R-}(+)\)-methyl p-tolyl

sulfoxide with the same results.

Several alkylated optically active sulfoxides were

treated with varying stoichiometric amounts of organometallic

followed by hydrolysis with either water or 1% sodium hy-

droxide. The optical rotations of the recovered sulfoxides

were recorded and the results are presented in Table III.

The model experiments led to a number of interesting

conclusions. The reaction of O-alkylated dialkylsulfoxides

with alkylmagnesium, dialkylcadmium, or dialkylmagnesium

reagents does not form trialkylsulfonium salts; if the salts

were formed, they would be stable under the reaction condi-

tions (eq. 31). Rather, the organometallic attacks carbon
to give sulfoxide of retained configuration (eq. 30). Evi-
dently, the latter reaction is slow and the racemic sulfoxide
isolated is due to the final hydrolysis which has been shown
to convert O-alkylated sulfoxides to the parent sulfoxides

with complete racemization (Table III).
<table>
<thead>
<tr>
<th>R&lt;sup&gt;1&lt;/sup&gt;S(0)R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Stoichiometric Amount of Organometallic</th>
<th>Hydrolyzing Agent</th>
<th>% Retention</th>
<th>% Inversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>0</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>50</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>0</td>
<td>NaOH</td>
<td>7</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>0.17</td>
<td>NaOH</td>
<td>32</td>
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<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>p-Tol</td>
<td>0.17</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>50</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>p-Tol</td>
<td>0.17</td>
<td>NaOH</td>
<td>18</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>1</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>50</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>1</td>
<td>NaOH</td>
<td>38</td>
</tr>
</tbody>
</table>
Indeed, when $S-(+)$-methyl $n$-butyl sulfoxide was alkylated and treated with diethylcadmium followed by hydrolysis with 1% sodium hydroxide, sulfoxide of predominantly inverted configuration was obtained.

Other systems were employed in an attempt to circumvent the problem of attack at carbon (Scheme XI). When $N$-tosyl methyl phenyl sulfilimine was alkylated with methyl fluorosulfonate and treated with $n$-butylmagnesium bromide (eq. 33), none of the desired sulfonium salt was isolated. The products isolated included the parent sulfilimine, $N$-methyl $p$-toluenesulfonamide, and methyl phenyl sulfoxide.

\[
\begin{align*}
S & \quad N \quad Tos \\
\text{CH}_3 - S - \text{Ph} & \quad \rightarrow \quad \text{CH}_3 - S - \text{Ph} \\
\text{CH}_3 - S - \text{Ph} & \quad \rightarrow \quad \text{CH}_3 - S - \text{Ph} + \text{FSO}_3^- \\
\text{FSO}_3^- & \quad \text{FSO}_3^-
\end{align*}
\]

The reaction was repeated with $N$-tosyl phenyl ethyl sulfilimine with analogous results.

It was known that $O$-adamantyl sulfonium salts could be prepared, isolated, and characterized.\textsuperscript{52} Employing the method of Mislow and Lewis\textsuperscript{52}, several of these salts were prepared and are listed in Scheme XII.
Scheme XII

Treatment of 61 with diethylcadmium over a 20-min period at room temperature (eq. 34) gave the desired sulfonium salt in very low yield (6%) while treatment of 62 with diethylcadmium for ca. 15 hr at room temperature (eq. 34) gave the salt (64) in quantitative yield.

\[ \text{CH}_3\text{CH}_2\text{Cd} \quad \text{Et}_2\text{Cd} \]

61, \( X = \text{ClO}_4 \)
62, \( X = \text{SbF}_6 \)
When \( \text{63} \) was treated with diethylcadmium under the same conditions, however, none of the desired product was obtained (eq. 35). Several attempts were made in this regard but in no instance was any trialkylsulphonium salt isolated (Scheme XIII); the products (nmr, tlc) consisted of the parent sulfoxide, adamantanol, and several unidentified side products.

Scheme XIII

\[
\begin{align*}
\text{R}^1 \quad \text{S} \quad \text{R}^2 & \quad 1. \text{AdBr,AgX} \\
\text{R}^3 & \quad 2. \text{R}_2 \text{Cd} \\
\text{R}^1 \quad \text{S} \quad \text{R}^2 & \quad \text{X} \\
\text{CH}_3 & \quad \text{CH}_3 & \text{C}_2\text{H}_5 & \text{ClO}_4 \\
n-\text{C}_4\text{H}_9 & \quad n-\text{C}_4\text{H}_9 & \text{C}_2\text{H}_5 & \text{ClO}_4 \\
\text{CH}_3 & \quad n-\text{C}_4\text{H}_9 & \text{C}_2\text{H}_5 & \text{ClO}_4 \\
-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^- & \quad \text{C}_2\text{H}_5 & \text{BF}_4
\end{align*}
\]
The failure to synthesize trialkylsulfonium salts forced the adoption of the dialkylaryl sulfonium salt species as the prime system for investigation.

The diastereomeric sulfoxides 65 and 66 were chosen as substrates for the reaction since they not only fulfilled the basic requirement of being alkyl aryl sulfoxides, but also converted the problem concerning the stereochemical reaction pathway from one involving a determination of the absolute configuration of a chiral, acyclic, sulfonium salt, with which a correlation could be made to the starting sulfoxide, into one involving the experimentally easier assignment of configuration to cis-trans cyclic stereoisomers.

Sulfoxides 65 and 66 had been prepared and separated previously, but their configurations had never been assigned. 53, 54

The synthesis, separation, and assignment of configuration to 65 and 66 was performed in conjunction with Dr. I. K. Nielsen. 55,*

*Refer to footnote 55 for details of this portion of the work.
The appropriate sulfoxide 65 or 66 was alkylated to the corresponding alkoxy sulfonium salt (70 or 71) by trimethyl oxonium tetrafluoroborate in nitromethane. Nmr showed formation of only one alkoxy sulfonium salt from its sulfoxide precursor in most cases. The small amount of epimerization occasionally observed is attributed to the presence of water which was not completely excluded from the starting sulfoxide. The salts, obtained as oils, were purified by repeated precipitation from methylene chloride by ether followed by several washings with ether.

Separate treatment of 70 and 71 with either dimethylcadmium (distilled) or methylmagnesium bromide gave the sulfonium salts 68 and 69 which were isolated as the tetrafluoroborates (oils) and subsequently converted to the tetraphenylborates (solids). Nmr analysis of the tetrafluoroborate sulfonium salts obtained from the reactions yielded the cis:trans ratios based on the relative areas of a clearly resolved S-CH\textsubscript{3} singlet and C-CH\textsubscript{3} doublet for each isomer. The reactions are shown by eq. 36 and the results are tabulated in Table IV.
The results given in Table IV are divided into three groups: (A) the reactions of 70 and 71 with methylmagnesium bromide at -78° for 1 hr; (B) the reactions with distilled dimethylcadmium at room temperature for 20 min; (C) those with dimethylcadmium at room temperature for 1 hr. Except for B-1 and B-2, where moisture caused some isomerization, the alkylation of the cis and trans isomers of (+)-2-methyl-2,3-dihydrobenzothiophene 1-oxide (65 and 66) gave only one isomer, assumed to have retained configuration at sulfur, and did so in good yield. Treatment of 70 or 71 with the organometallic reagent gave, in all cases, mixtures of the cis and trans isomers of (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate (68 and 69) in 30 to 50% yields.

Reactions B-1 and B-2 proceeded with complete inversion at sulfur; $70 + 71 \neq 68 + 69$. The cis:trans ratios
### TABLE IV

**Reaction Products**

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Starting Sulfoxide</th>
<th>Methoxysulfonium Salt % Yld (70:71)</th>
<th>Sulfonium Salt % Yld, (69:68)</th>
<th>% Yield of 67,65 and 66</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sup&gt;c&lt;/sup&gt;-1</td>
<td>65</td>
<td>75 (100:0)</td>
<td>45 (90:10)</td>
<td>20&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>A&lt;sup&gt;c&lt;/sup&gt;-2</td>
<td>65</td>
<td>79 (100:0)</td>
<td>50 (95:5)</td>
<td>16&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>A&lt;sup&gt;c&lt;/sup&gt;-3</td>
<td>66</td>
<td>81 (0:100)</td>
<td>40 (50:50)</td>
<td>60&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>A&lt;sup&gt;c&lt;/sup&gt;-4</td>
<td>66</td>
<td>79 (0:100)</td>
<td>30 (35:65)</td>
<td>70&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>B&lt;sup&gt;e&lt;/sup&gt;-1</td>
<td>65</td>
<td>77 (95:5)</td>
<td>31 (92:8)</td>
<td>55&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>B&lt;sup&gt;e&lt;/sup&gt;-2</td>
<td>66</td>
<td>62 (15:85)</td>
<td>32 (15:85)</td>
<td>50&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>C&lt;sup&gt;g&lt;/sup&gt;-1</td>
<td>66</td>
<td>100 (0:100)</td>
<td>45 (15:85)</td>
<td>36&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields determined by nmr analysis.  
<sup>b</sup>A mixture of 65 and 66 was obtained in all cases.  
<sup>c</sup>Methylmagnesium bromide, -78°, 60 min.  
<sup>d</sup>Greater than 90% 67.  
<sup>e</sup>Dimethylcadmium, room temp., 20 min.  
<sup>f</sup>Greater than 90% 65 and 66.  
<sup>g</sup>Dimethylcadmium, room temperature, 60 min.
were completely reversed in going from starting material to product. Reaction C-1, which involved an increase in reaction time, exhibited an increase in the chemical yield but a slight drop in the stereospecificity; fifteen percent of the sulfonium salt was of retained configuration.

Reactions A-1 and A-2 also proceeded with high stereospecificity (inversion), $70 + 68 + 69$, but A-3 and A-4 did not, $71 + 68 + 69$. The stereospecificity in the latter cases ranged from 0-30%. What caused this racemization?

Product isomerization by Grignard reagent can be ruled out since $68$ and $69$ are stable under the reaction conditions. They were recovered unchanged in quantitative yield after being treated with either the Grignard reagent or magnesium methoxide for one hour at $-78^\circ$.\textsuperscript{55}

Ligand permutation (pseudorotation) of a tetravalent tetracoordinate intermediate, a sulfurane, formed by bonding of a methyl group to the sulfur atom of $70$ or $71$, with possible coordination of the magnesium or cadmium at the methoxy carbon, could, in principle, lead to isomerization before the methoxy group departed to give $68$ or $69$. But this does not explain the loss of stereospecificity in going from reaction B-2 to C-1 where the only difference is one of reaction time.

So the explanation for isomerization seems to lie with the methoxy sulfonium salts $70$ and $71$ which might be isomerized by the basic organometallic reagent, by alkoxide
ion formed during the reaction, or by bromide ion present in the Grignard reagent. Treatment of the methoxysulfonium salt $7_2$, derived from $R$-methyl $p$-tolyl sulfoxide, $7_3$, used as a model for $7_0$ and $7_1$, with magnesium bromide and with magnesium methoxide, was carried out in order to investigate these possibilities.

When $7_2$, derived from 98% optically pure $7_3$, was stirred with magnesium methoxide for 1.5 hr at room temperature and then hydrolyzed with one per cent aqueous sodium hydroxide, a quantitative yield of $7_3$ was obtained but with 59% inversion. No methyl $p$-tolyl sulfide, $7_4$, was observed (eq. 37). The methoxide ion may attack the methoxy carbon of $7_2$, the sulfur atom, or the proton alpha to sulfur. Carbon attack leads to retention of configuration; sulfur attack leads initially to inverted $7_2$, or retained $7_3$ after hydrol-
ysis but eventually to racemization after enough alkoxide exchanges have taken place. Johnson and Phillips have shown that alkoxysulfonium salts undergo exchange with a variety of alkoxides accompanied by sulfide formation via the ylid\textsuperscript{38} (Scheme VII).

Since inversion actually predominated, this exchange reaction is negligible, as is the sulfide formation, under the \(-78^\circ\) Grignard reaction conditions but may assume some importance during the room temperature cadmium reactions.

Treatment of 72 with magnesium bromide for 1.5 hr at room temperature followed by hydrolysis as above gave a 33\% yield of 73 of 59\% retained configuration and a 46\% yield of sulfide 74 (eq. 38). Similar results had been obtained previously with (+)-ethoxybenzyl-\(p\)-tolylsulfonium tetrafluoroborate.\textsuperscript{46}

\[
\begin{array}{c}
\text{CH}_3\text{SO\textsubscript{2}C}_6\text{H}_4\text{CH}_3 \\
\downarrow \\
\text{CH}_3\text{OS}_\text{2C}_6\text{H}_4\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3\text{S\textsubscript{2}C}_6\text{H}_4\text{CH}_3 \\
\text{CH}_3\text{OS}_\text{2C}_6\text{H}_4\text{CH}_3
\end{array}
\]

(eq. 38)
Bromide ion attack on the methoxy carbon leads to 73 of retained configuration. Bromide ion attack on sulfur yields a bromosulfonium ion which, if attacked by bromide ion, would lead to 74 and bromine. A yellow-orange color formed immediately upon adding 72 to the magnesium bromide might be caused by bromine formed in this way. Of course, methoxide ion formed in these reactions adds additional reaction possibilities.

Utilizing the results from these model studies, reaction schemes XIV and XV were written which explain the observations recorded in Table IV.

Dimethylcadmium reacts with 70 or 71 (Scheme XIV) at sulfur with inversion of configuration to give 68 and 69, respectively, which are resistant towards further reaction although, given time, they will form 67 by losing an S-methyl group to a nucleophile.* The dimethylcadmium may also attack at the methoxy carbon to regenerate the precursor sulfoxide. The methoxide ion liberated in the former reaction may also react with the alkoxy sulfonium salt, as shown by the model studies, to give sulfoxide of retained configuration as well as inverted alkoxy sulfonium salt. But these processes manifest themselves only during more vigorous

*We initially attempted to isolate 68 and 69 as the sulfonium bromides. The instability of these salts was shown to be due to nucleophilic attack of bromide ion on 68 and 69 to give 67.
Scheme XIV. Dimethylcadmium Reaction Scheme.
conditions of time and temperature (C-1) and are not obvious under milder conditions (B-1 and B-2). The mixtures of 65 and 66 isolated in 36 to 55% yield must arise primarily from reaction with dimethylcadmium at carbon and upon hydrolysis of unreacted 70 or 71. While it is conceivable that 70 or 71 could form ylids 75 and 76, which lead to 67, this appears, in view of the small amount of 67 produced, to be of no importance.

The reactions of 70 and 71 with the Grignard reagent (Scheme XV) appear to be slightly more complex. Very little sulfoxide was produced, but the quantity of sulfide (67) increased dramatically as a result, in view of the model experiments, of the intermediate bromosulfonium ions 77 or 78, although the ylids 75 and 76 cannot be ruled out as possible sulfide precursors.

The results indicate that alkoxyalkylarylsulfonium salts yield dialkylarylsulfonium salts (eq. 16) with inversion of configuration at sulfur, but loss of stereospecificity may occur due to isomerization of the starting material.

In the course of this investigation it became necessary to assign the configurations of 68 and 69. This was accomplished by means of an equilibration study, a kinetic study, and 13C nmr.

1,2-Dimethyl interactions are larger in the cis isomer relative to those in the trans isomer. For this reason, the thermal equilibration of 68 and 69 (eq. 39)
Scheme XV. Methylmagnesium Bromide Reaction Scheme.
should yield a predominance of the less hindered isomer, 69. The equilibrium composition, determined by thermal equilibration of a 7:93/68:69 mixture at 110° in 96% acetic acid\textsuperscript{20}, was 60% 69 and 40% 68; 69 was assigned the trans geometry on this basis.

\begin{align*}
\begin{array}{c}
\text{68} \\
\text{69}
\end{array}
\end{align*}

The alkylation of 67 with either trimethyloxonium tetrafluoroborate in nitromethane or in methylene chloride or by methyl fluorosulfonate in methylene chloride gave in all three cases a ca. 20:80 mixture of 68:69, respectively (eq. 40). The most stable epimer is formed most rapidly.
One would expect the trans isomer to react with nucleophiles more rapidly at the S-methyl carbon than would the cis in which the carbon is more sterically crowded and therefore less accessible to nucleophilic attack. When a mixture of \(68\) and \(69\) was treated with pyridine (eq. 41) at room temperature the rate of attack on \(69\) relative to \(68\) was ca. 2:1 which is as expected based on the argument above and the assignment made by thermal equilibration.
These three studies are internally consistent. The $\Delta \Delta G^+$ for alkylation, assuming identical reaction mechanism for the formation of both isomers, is ca. 0.8 kcal/mol. The $\Delta \Delta G^0$ value for the difference in ground state energies based on the equilibration study, albeit at 110°, is ca. 0.3 to 0.2 kcal/mol. Assuming dealkylation transition states similar to those of alkylation, the predicted $\Delta \Delta G^+$ for the pyridine dealkylation is 0.5 to 0.6 kcal/mol which gives a rate ratio of ca. 2:1 as found experimentally.

Due to their steric proximity, the C-CH$_3$ and S$^+$-CH$_3$ $^{13}$C nmr shifts of the cis methyl groups are expected to be upfield by ca. 6 ppm from those of the trans-isomer.$^{56}$ The value for C-CH$_3$ ($\delta_{69-68}$) was 4.89 ppm and for S-CH$_3$ ($\delta_{69-68}$), 6.82 ppm (Figure I) in agreement with the previous assignments.

Having established the stereochemical pathway of the reaction (eq. 16) as one of inversion at sulfur, it was now possible to assign the absolute configuration of the sulfonium salts prepared by this procedure. In addition, the importance of reaction time and the organometallic were clarified.

The use of distilled (halide free) dialkylcadmium reagents for a 20 min period at room temperature and isolation of the resulting sulfonium salt as the tetrafluoroborate rather than the bromide should provide the optimum conditions for both chemical and optical yields.
Figure I. $^{13}$C nmr Spectra of (+)-1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (68 and 69).

<table>
<thead>
<tr>
<th>No.</th>
<th>Intensity</th>
<th>Hz</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>2909.5</td>
<td>145.47</td>
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<tr>
<td>2</td>
<td>46</td>
<td>2901.8</td>
<td>145.08</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>5</td>
<td>58</td>
<td>2574.1</td>
<td>128.70</td>
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<td>2565.6</td>
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</tr>
<tr>
<td>7</td>
<td>80</td>
<td>2559.9</td>
<td>127.99</td>
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<tr>
<td>8</td>
<td>30</td>
<td>2554.5</td>
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<td>9</td>
<td>20</td>
<td>2544.4</td>
<td>127.21</td>
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<tr>
<td>10</td>
<td>85</td>
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<td>57.98</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>1099.0</td>
<td>54.94</td>
</tr>
<tr>
<td>12-18 DMSO-d$_6$ reference</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>48</td>
<td>569.4</td>
<td>28.47</td>
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<tr>
<td>20</td>
<td>14</td>
<td>433.1</td>
<td>21.65</td>
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<td>100</td>
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<tr>
<td>22</td>
<td>16</td>
<td>263.1</td>
<td>13.15</td>
</tr>
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</table>

[Chemical structure image]
With this in mind, the synthesis of several dialkylaryl sulfonium salts was again undertaken. In view of the high chemical yields possible (eq. 34) through use of the adamantoxyl leaving group, this reaction was attempted to determine if the optical yields were of the same order.

In this regard, \( R-(+)-\text{methyl } \text{p-tolyl sulfoxide} \) was reacted with adamantyl bromide and silver hexafluoroantimonate to yield \( (+)-\text{adamantoxyethyl-p-tolylsulfonium hexafluoroantimonate [(+)-62]} \) (eq. 42) in 53% yield. Although the treatment of \( (+)-62 \) with distilled diethylcadmium (eq. 43) provided the desired \( (+)-\text{methylethyl-p-tolylsulfonium tetrafluoroborate [(+)-64]} \) in good yield, the product had slight impurities present which could not be completely removed even after repeated recrystallization.
The optimum conditions for the preparation of optically active dialkylaryl sulfonium salts were now established:

(1) Extreme care must be taken to insure the exclusion of water from all reagents.

(2) The sulfoxide should be alkylated with simple alkyl groups.

(3) The organometallic reagent should be halide free; in this case distilled dialkylcadmium.

(4) The reaction with the dialkylcadmium reagents should be terminated after ca. 20 min.

(5) The sulfonium salt should be isolated as the tetrafluoroborate or some other non-nucleophilic anion.

These conditions were employed and several dialkylaryl sulfonium salts were prepared; the results are listed in Table V.

It is quite evident that the reaction conditions now employed provided sulfonium salts in both increased chemical and optical yields over the previous systems (Table VI).

If the results obtained in the (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate model system can be extended to the acyclic dialkylaryl sulfonium salts, the optical yields obtained from these reactions are on the order of 70-100%.

In an attempt to clarify this point, methyl p-tolyl sulfide was alkylated with triethylxonium tetrafluoroborate
<table>
<thead>
<tr>
<th>Compound</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>X</th>
<th>[α]&lt;sup&gt;25&lt;/sup&gt;</th>
<th>Configuration</th>
<th>% Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% Yield&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>BF&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>S</td>
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<td>+9.04°</td>
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<td>&quot;</td>
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<tr>
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<td>(+)-79</td>
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<td>S</td>
<td>80</td>
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<td>BPh&lt;sub&gt;4&lt;/sub&gt;</td>
<td>+10.2°</td>
<td>S</td>
<td>&quot;</td>
<td>64</td>
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</table>

<sup>a</sup>Yield of alkoxy sulfonium intermediate.  <sup>b</sup>Yield of sulfonium salt.
TABLE VI
Optically Active Dialkylarylsulfonium Salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>X</th>
<th>Configuration</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>TNBS</td>
<td>R</td>
<td></td>
<td>11</td>
<td>-6.18°b</td>
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<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>Ph&lt;sub&gt;4&lt;/sub&gt;B</td>
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<td>B</td>
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<tr>
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<td>Ph&lt;sub&gt;4&lt;/sub&gt;B</td>
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<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>BF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>R</td>
<td></td>
<td>51</td>
<td>-15.84°b</td>
<td>B</td>
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<tr>
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<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>BF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>S</td>
<td></td>
<td>59</td>
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<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Br</td>
<td>R</td>
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<td>--</td>
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<td>--</td>
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<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Configuration</td>
<td>Solvent</td>
<td>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>[α]</td>
<td>Method&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
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<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>BF&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>BF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>S</td>
<td>&quot;</td>
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<sup>a</sup>Overall yield from sulfoxide.  
<sup>b</sup>[α]<sup>25</sup> <sub>589</sub>.  
<sup>c</sup>[α]<sup>25</sup> <sub>290</sub>.  
<sup>d</sup>A, RMgX, -78°C, 1hr, initial isolation as bromide; B, R<sub>2</sub>Cd (distilled), room temperature, 20 min, initial isolation as tetrafluoroborate.
to give (+)-methylethyl-p-tolylsulfonium tetrafluoroborate (64). This salt was treated with a stoichiometric amount of d-10-camphorsulfonic acid and the nmr spectra recorded (Scheme XVI). Rapid anion exchange should provide the averaged spectra of the two diastereomeric sulfonium salts 81-Rd and 81-Sd, hopefully with sufficient magnetic nonequivalence as to exhibit separate peaks on the nmr, thereby providing a direct method of determining the optical purity of our salts. The nmr spectra exhibited only one set of peaks, however.

Scheme XVI

\[
\begin{align*}
\text{CH}_3 & \quad \text{S} \quad \text{p-Tol} \\
\text{CH}_2\text{CH}_3 & \quad \text{p-Tol} \quad \text{BF}_4^- \quad \text{d-10CS}^- \\
\text{CH}_3 & \quad \text{S} \quad \text{p-Tol} \\
\text{CH}_2\text{CH}_3 & \quad \text{p-Tol} \quad \text{p-Tol} \quad \text{CH}_3 \\
\text{CH}_2\text{CH}_3 & \quad \text{d-10CS}^- \\
\text{81-Sd} & \quad \text{81-Rd} \\
\end{align*}
\]
In an attempt to determine if the Cotton Effects of sulfonium salts can be observed and if a correlation exists between the absolute configuration of the sulfonium salt and their optical activity, the optical rotatory dispersion and circular dichroism spectra of several of the sulfonium salts were recorded. The spectra are exhibited in Figures II-XI and the results are summarized in Table VII.

The uv spectra of dialkylarylsulfonium salts exhibit an intense band (log ε ca. 4-5) at ca. 220-230 nm which will be referred to as the primary band. A secondary band (log ε ca. 3-4) appears at ca. 260-266 nm. The primary band is attributed to the well documented \(^1L_a\) transition of aromatic chromophores while the secondary band corresponds to one of the \(^1L_b\) bands of these systems. The other \(^1L_b\) transitions are also observable.

Due to the relatively small rotations of the sulfonium salts, the low wavelength primary band (\(^1L_a\)) was very difficult to record on the ORD and CD spectra of these compounds. It was possible in all cases to obtain the \(^1L_b\) bands of these systems and in one case, with a great deal of effort, to obtain the \(^1L_a\) transition. The Cotton Effects corresponding to the \(^1L_b\) transitions are optically active; the positive sign characterizes the "R" configuration and the negative sign the "S" configuration. The opposite appears true of the \(^1L_a\) bands, although more work is needed to substantiate this claim.
<table>
<thead>
<tr>
<th>Mode</th>
<th>Salt</th>
<th>Solvent</th>
<th>Concna</th>
<th>P</th>
<th>T</th>
<th>P</th>
<th>T</th>
<th>P</th>
<th>T</th>
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<td>260</td>
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<td>(400)</td>
<td>(200)</td>
<td>(815)</td>
<td>(800)</td>
<td>(1200)</td>
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<tr>
<td></td>
<td>(-)-64</td>
<td></td>
<td>0.006-</td>
<td>272</td>
<td>269</td>
<td>262</td>
<td>257.5</td>
<td>238</td>
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<td>(120)</td>
<td>(64)</td>
<td>(660)</td>
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<td>(+)-64</td>
<td>Ethanol</td>
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<td></td>
<td></td>
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<td>(1410)</td>
<td>(423)</td>
<td>(1434)</td>
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<td>0.045</td>
<td>273.5</td>
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<td>264</td>
<td>257</td>
<td>250</td>
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</tr>
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<td></td>
<td></td>
<td></td>
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<td>(-2200)</td>
<td>(-2900)</td>
<td>(-2750)</td>
<td>(-3600)</td>
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<tr>
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<td>(-)-64</td>
<td>Methanol</td>
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<td></td>
<td></td>
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<td>(-8600)</td>
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</table>
**TABLE VII.** (cont.)

| Mode<sup>a</sup> | Salt | Solvent | Concn<sup>b</sup> | P   | T   | P   | T   | P   | T   | P   | T   | P   | T   |
|------------------|------|---------|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| uv               | 64   | Ethanol | 0.0004-           | 274.5 | 272 | 266.5 | 262.5 | 255 | 253.5 | 230 | 215 |
|                  |      |         | 0.004             | (1800) | (1460) | (1900) | (1700) | (1720) | (1700) | (34000) | (22000) |
|                  | 80   | "       | 0.002-            | 274  | 272 | 266 | 257.5 | 254 | 251 | 229 | 218 |
|                  |      |         | 0.009             | (1375) | (1050) | (1615) | (1350) | (1375) | (1300) | (20000) | (11000) |
| "               | 79   | "       | 0.0046            | 275 | 273 | 266 | 263 | 254 | 253 | 230 |
|                  |      |         | (1100)            | (950) | (1350) | (1320) | (1650) | (1630) | (9000) |

<sup>a</sup>The following abbreviations were employed: P, peak; T, trough. The values in parentheses correspond to the observed molecular rotation (ORD), ellipticity (CD), or extinction coefficient (uv). The wavelengths are in nm.  

<sup>b</sup>Concn in g/100 ml of solvent.
Figure II. Ultraviolet spectra of methylethyl-\(p\)-tolylsulfonium bromide (80).
Figure III. Optical rotatory dispersion spectra of (+)-S- and (-)-R-methylethyl-p-tolylsulfonium bromide [(+)- and (-)-80].
Figure IV. Circular dichroism spectra of (+)-S- and (-)-R-methylethyl-p-tolylsulfonium bromide [(+)- and (-)-80].
Figure V. Ultraviolet spectra of methylethyl-\( p \)-tolylsulfonium tetrafluoroborate (64).
Figure VI. Optical rotatory dispersion spectra of (+)-S- and (-)-R-methylethyl-p-tolylsulfonium tetrafluoroborate [(+)- and (-)-64].
Figure VII. Circular dichroism spectra of (+)-S- and (-)-R-methylethyl-p-tolylsulfonium tetrafluoroborate [(+) and (-)64].
Figure VIII. Ultraviolet spectra of ethyl-n-butyl-p-tolylsulfonyl tetrafluoroborate (79).
Figure IX. Optical rotatory dispersion spectra of (+)-S-ethyl-\(n\)-butyl-\(p\)-tolylsulfonium tetrafluoroborate \([+79]\).
Figure X. Circular dichroism spectra of (+)-S-ethyl-n-butyl-p-tolylsulfonium tetrafluoroborate [(+)-79].
Figure XI. Circular dichroism spectra of (-)-R-methylethyl-p-tolylsulfonium tetrafluoroborate [(-)-64].
TABLE VIII
Nmr Parameters of Trialkyl-, Dialkylaryl-, Alkyldiaryl-, and Triarylsulfonium Salts<sup>a</sup>

<table>
<thead>
<tr>
<th>Sulfonium Salt</th>
<th>S&lt;sub&gt;H&lt;/sub&gt;</th>
<th>S&lt;sub&gt;H&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>S(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>S&lt;sub&gt;H&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>S&lt;sub&gt;H&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Ar&lt;sub&gt;H&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Ar</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>48&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.17t(6)</td>
<td>0.84t(6)</td>
<td>3.72m</td>
<td>1.44m</td>
<td>2.44s</td>
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<td>7.08m</td>
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<tr>
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<td>1.33m</td>
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<td>8.88s</td>
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<tr>
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<td>0.81t(5.5)</td>
<td>3.52m</td>
<td>1.37m</td>
<td>2.33s</td>
<td>7.5q(8)</td>
<td>6.8s</td>
<td></td>
</tr>
<tr>
<td>51&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.28s</td>
<td>1.24t(8)</td>
<td>3.64m</td>
<td></td>
<td>2.44s</td>
<td>7.8q(8.5)</td>
<td>7.04m</td>
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<tr>
<td>52&lt;sup&gt;b,e&lt;/sup&gt;</td>
<td>3.3s</td>
<td>1.19t(8)</td>
<td>3.64m</td>
<td></td>
<td>2.43s</td>
<td>7.8q(8)</td>
<td>8.9s</td>
<td></td>
</tr>
<tr>
<td>53&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>3.32s</td>
<td>0.86t(5.5)</td>
<td>3.68m</td>
<td>1.41m</td>
<td>2.44s</td>
<td>7.78q(8)</td>
<td>8.83s</td>
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<td>54&lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
<td></td>
<td></td>
<td>2.44s</td>
<td>7.7m</td>
<td>7.02m</td>
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<tr>
<td>55&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.24t(8)</td>
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<td></td>
<td>2.68s</td>
<td>7.52m</td>
<td></td>
</tr>
<tr>
<td>57&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.39t(8)</td>
<td>0.92t(6)</td>
<td>3.44m</td>
<td>1.64m</td>
<td></td>
<td></td>
<td>8.84s</td>
<td></td>
</tr>
<tr>
<td>58&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.76s</td>
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<td>2.42s</td>
<td>7.64q(8)</td>
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<sup>a</sup>Chemical shifts are given in ppm downfield from tetramethylsilane. Values in parenthesis are coupling constants in Hz. <sup>b</sup>DMSO-d<sub>6</sub>, internal TMS. <sup>c</sup>DMSO-d<sub>6</sub>, external TMS. <sup>d</sup>CH<sub>2</sub>Cl<sub>2</sub>, external TMS. <sup>e</sup>Reported by Dr. K. K. Andersen. <sup>f</sup>Reported by Mr. D. L. Ladd.
TABLE IX

Nmr Parameters of 2-Methyl-2,3-Dihydrobenzothiophenium Salts

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<th>Sulfonium Salt</th>
<th>SCH$_3$</th>
<th>SCHCH$_3$</th>
<th>SCH</th>
<th>ArCH$_2$</th>
<th>Ar</th>
<th>Anion</th>
<th>SOCH$_3$</th>
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<tr>
<td>68$^b$</td>
<td>2.88s</td>
<td>1.58d(8)</td>
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<td>3.06-4.2m</td>
<td>6.52-8.24m</td>
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<td>69$^b$</td>
<td>3.06s</td>
<td>1.47d(8)</td>
<td>4.46m</td>
<td>3.06-4.2m</td>
<td>6.52-8.24m</td>
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<td>70$^c$</td>
<td>1.46d(8)</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>7.46-8.32m</td>
<td>4.28s</td>
<td></td>
</tr>
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<td>71$^c$</td>
<td>1.40d(8)</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>7.46-8.32m</td>
<td>3.88s</td>
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TABLE X

Nmr Parameters of Adamantoxysulfonium Salts

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<th>SOAd,$\beta$</th>
<th>SOAd,$\lambda$</th>
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<th>Ar</th>
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</thead>
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<td>61$^e$</td>
<td>2.32m</td>
<td>2.1m</td>
<td>1.66m</td>
<td>3.55s</td>
<td>2.55s</td>
<td>7.48q(9)</td>
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<tr>
<td>62$^b$</td>
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<td>2.0m</td>
<td>1.62m</td>
<td>3.60s</td>
<td>2.46s</td>
<td>7.57q(8)</td>
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</table>

$^a$See footnote a, Table VII. $^b$See footnote b, Table VII. $^c$See footnote d, Table VII.
$^d$Absorptions were obscured by the solvent. $^e$CDCl$_3$, external TMS.
TABLE XI
Ir Parameters for Sulfonium Salts

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<td>2930 m (M)</td>
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<td>1025 s (M)</td>
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<tr>
<td></td>
<td></td>
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TABLE XI. (cont.)

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TABLE XI. (cont.)

Footnotes

aLetters in parenthesis are intensity abbreviations: VS, very strong, 0.70-1.0 A; S, strong, 0.40-0.70 A; M, medium, 0.10-0.40; W, weak, <0.10. The following abbreviations were used to describe the general shape of the peak: s, singlet; bs, broad singlet; vbs, very broad singlet; m, multiplet; ts, two singlets that are overlapped.

bKBr.

cCHCl₃.

dReported by Dr. K. K. Andersen.
EXPERIMENTAL

Instrumentation. Nmr spectra, obtained on a Varian A-60 or Jeolco HM-100 spectrometer, are in ppm downfield from TMS. Optical rotations, optical rotatory dispersion curves, and circular dichroism curves were obtained on a Cary 60 recording spectropolarimeter; optical rotations were also taken on a Carl Zeiss 0.005° photoelectric precision polarimeter. Uv spectra were recorded on a Cary Model 14 recording spectrophotometer. Ir spectra were obtained on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Melting points, determined on a Hoover capillary melting point apparatus, are uncorrected. Microanalysis were determined by Mrs. L. Heavner, Mrs. D. Cardin and Miss G. Lambert on a F&M Model 185 carbon, hydrogen, nitrogen analyzer. A Radiometer Model 25 pH meter was used in the acid-base titrations of the organometallics.

Materials. The following compounds are commercially available and are listed with the distributor and corresponding catalog number in parenthesis: ethyl n-propyl sulfide (K&K Laboratories, 15869), methyl fluorosulfonate (Aldrich Chemical Co., Inc., 16,048-2), methylmagnesium bromide (Alfa Inorganics, 87324), silver hexafluoroantimonate (Alfa Inorganics, 10100), silver perchlorate (Alfa Inorganics, 22125), sodium tetraphenylborate (Alfa Inorganics, 14171), trimethyloxonium tetrafluoroborate (Willow Brook Lab., Inc., 128).
A number of the compounds employed in the course of this research were prepared by other individuals and are listed along with the name of the person who prepared them: R-ethyl p-tolyl sulfoxide (Mr. D. L. Ladd), R-methyl p-tolyl sulfoxide (Dr. B. W. Christensen), R-(-)-methyl n-butyl sulfoxide (Dr. E. Olsen), (+)-n-butyl p-tolyl sulfoxide (Dr. K. K. Andersen), triethyloxonium tetrafluoroborate (Mr. D. L. Ladd), trimethyloxonium tetrafluoroborate (Mr. M. Buza), sodium 2,4,6-trinitrobenzenesulfonate (Dr. S. Yeager). The cis and trans isomers of (+)-2-methyl-2,3-dihydrobenzothiophene 1-oxide were prepared in conjunction with Dr. I. K. Nielsen.

Methylene chloride was distilled from phosphorous pentoxide and stored over oven-dried potassium carbonate. Nitromethane (spectral grade) was dried over molecular sieves (4Å).

The concentrations of the organometallics were determined by acid-base titration. Typically, 1 ml of the organometallic was hydrolyzed with an excess of 0.2 N hydrochloric acid and back titrated with 0.2 N sodium hydroxide. Two or three determinations were carried out on each sample.

Nmr and Ir Spectra. Nmr and ir spectra of the sulfonium salts prepared in the course of this research are described in Tables VIII - XI. The nmr and ir spectra of all other compounds are described within the experimental section.
Dialkyl- and Diaryl Cadmium Reagents. Distilled:
Magnesium (14.55 g, 0.6 mol) was placed in a 1000-ml, three-necked round-bottomed flask equipped with a mechanical stirrer, condenser with drying tube, and pipette inlet tube. The apparatus was flame-dried under nitrogen. A positive nitrogen pressure was maintained throughout the reaction by use of a mineral oil bubbler fitter with a "T"-bar inlet tube connected to the condenser through the calcium chloride drying tube. Anhydrous ether (ca. 500 ml) was introduced and methyl bromide was bubbled into the reaction through the pipette with stirring at room temperature. The addition of methyl bromide was continued until there was no longer any magnesium present.

The pipette was removed and a 125-ml Erlenmeyer flask containing oven dried cadmium chloride (65 g, 0.36 mol, 20% excess) was attached with Gooch tubing. The entire apparatus was immersed in an ice bath and the cadmium chloride was added in several small portions with stirring over a 1 hr period. The reaction was stirred for two additional hours at 0° and then overnight at room temperature.

The Erlenmeyer and Gooch tubing were removed and replaced with a nitrogen ebulator. A one-foot fractionating column, adapter, and 1000-ml round-bottomed flask were substituted in place of the condenser and drying tube. The round-bottomed collecting flask was immersed in a acetone-dry ice bath and ether was distilled from the reaction vessel by heating in an oil bath. A grey semi-solid product re-
mained after removal of the ether. An aspirator was attached and the dimethylcadmium was distilled. Heating was terminated when the oil bath reached a temperature of 120°: yield 75-100 ml of dimethylcadmium in ether (2.84 M).

Repetition of the reaction yielded 10-20 ml of dimethylcadmium (2.43 M) and a second 5-ml fraction found to be 2.08 M.

Diethylcadmium was prepared in the same way with the exception that the heating under aspirator pressure was terminated at 130°: yield 75-100 ml of diethylcadmium in ether (0.6 M).

NOTE: Dimethylcadmium (2.2 M) and diethylcadmium (2.75 M) were prepared and distilled by Dr. K. K. Andersen. Retitration of the latter compound, ca. one year later, showed the solution to be 2.4 M.

Undistilled: The following description of the preparation of dimethylcadmium will serve to illustrate the general procedure utilized in the preparation of undistilled dialkyl- and diarylcadmium reagents.

Oven dried cadmium chloride (1.1 g, 0.006 mol) was placed in a centrifuge tube which was fitted with a septum, wired, and flushed with nitrogen. Dry ether (ca. 15 ml) was introduced with a syringe and the flask was cooled to 0°. Ethereal methylmagnesium bromide (4 ml, 0.012 mol, 3 M) was slowly added. The reaction was allowed to stand an additional 30 min at 0° with periodic shaking. Following centrifuging, three layers were observed. The supernatant, consisting of
the top two layers was removed by use of a syringe and used immediately. The mixtures were not titrated but were assumed to have gone to 100% completion. The stoichiometry was based on a 20% excess of the cadmium reagent. The solutions exhibited a negative Gilman test.

Di-p-tolylcadmium and di-o-tolylcadmium were prepared in the same manner.

Alkyl and Aryl Grignard Reagents. The following preparation of ethylmagnesium bromide will serve to illustrate the general method utilized in the preparation of alkyl and aryl Grignard reagents.

Oven dried magnesium (8.8 g, 0.33 mol) was placed in ether in a 500-ml, three-necked round-bottomed flask equipped with an addition funnel, mechanical stirrer, and drying tube. Ethyl bromide (21.4 ml, 36.33 g, 0.33 mol), dissolved in 100 ml of ether, was added slowly dropwise over a 1 hr period at room temperature. The reaction was initiated through the addition of an iodine crystal. Refluxing was observed throughout the addition. Upon completion of addition, the mixture was allowed to stand an additional hour with refluxing maintained through the use of a heat gun. The ethylmagnesium bromide was decanted under a nitrogen atmosphere in a glove bag. The collection bottle was fitted with a septum and flushed with nitrogen. The solution was found to be 1.64 M by titration and was stored under refrigeration. The solution exhibited a positive Gilman test.
Other reagents prepared in this manner include: p-tolylmagnesium bromide (1.00 M) and o-tolylmagnesium bromide (2.71 M).

NOTE: Ethylmagnesium bromide (2.23 M) was prepared by D. L. Ladd. Diethylmagnesium (0.28 M) was prepared by R. Atkins. Phenylmagnesium bromide (1.58 M) was prepared by B. Kostyla.

Benzyl p-Tolyl Sulfide. p-Thiocresol (18.6 g, 17.38 ml, 0.15 mol) was dissolved in 200 ml of 3.5 M aqueous sodium hydroxide in a 500-ml round-bottomed flask equipped with a magnetic stirrer and addition funnel. Benzyl chloride (18.9 g, 17.2 ml, 0.15 mol) was added dropwise over a 1 hr period at room temperature. Upon completion of the addition, the mixture was stirred overnight at room temperature. The organic and aqueous layers were separated and the aqueous phase washed with several portions of ether. The organic layers were combined, dried over magnesium sulfate, and concentrated on the rotary evaporator to yield a yellow oil which crystallized on standing in the refrigerator overnight. Recrystallization from cyclohexane yielded 10.42 g (33%) of the desired product: mp 40-43° (lit. mp 40-41°). Nmr spectrum no. 15853 (CDCl₃): δ 6.82 (m,9,Ar), 3.73 (s,2, SCH₂), 1.95 (s,3,CH₃).

Methyl n-Butyl Sulfide. n-Butanethiol (36 g, 0.4 mol) was dissolved in 200 ml of aqueous sodium hydroxide (ca. 3.5 M) in a 500-ml, three-necked round-bottomed flask equipped with a mechanical stirrer and addition funnel.
Dimethyl sulfate (50.5 g, 0.4 mol, 24 ml) was added dropwise over a 1 hr period at room temperature with stirring. Upon completion of the addition, the mixture was allowed to stand for two additional hours at room temperature. The organic and aqueous layers were separated and the aqueous layer was extracted with five 25 ml portions of ether. The organic layers were combined, dried over anhydrous magnesium sulfate, and concentrated on the rotary evaporator. Distillation yielded 29.72 g (69%) of the desired product: bp 120-123° (760 mm) [lit.61 bp 122.5° (760 mm)]. Ir spectrum no. 20078 (neat): $\nu_{\text{max}}$ 2950, 2870, 1465, 1440, 1270, 1225, and 960 cm$^{-1}$.

_Di-n-butyl Sulfide._$^{58}$ _n-Butanethiol_ (30.06 g, 0.3 mol) was added to 200 ml of aqueous sodium hydroxide (3.5 M) in a 500-ml, one-necked round-bottomed flask equipped with a magnetic stirrer and addition funnel. _n-Butyl bromide_ (45.68 g, 0.3 mol) was added dropwise over a 1 hr period at room temperature. Upon completion of the addition the mixture was allowed to stand overnight. The aqueous and organic phases were separated and the aqueous phase extracted with five 25 ml portions of ethyl acetate. The organic fractions were combined, dried over magnesium sulfate, and concentrated on the rotary evaporator. Distillation yielded 27.47 g (58%) of the desired product: bp 182-189° (760 mm) [lit.61 bp 71° (14 mm)]. Ir spectrum no. 20114 (neat): $\nu_{\text{max}}$ 2960, 2880, 1470, 1268 and 1220 cm$^{-1}$. Nmr spectrum no. 14659 (neat): $\delta$ 2.32 (t, 4, $J = 6$Hz, SCH$_2$), 1.32 (m, 8, SCH$_2$CH$_2$CH$_2$), 0.83 (t, 6, $J = 5$Hz, CH$_3$).
Methyl p-Tolyl Sulfide. \textsuperscript{60} p-Thiocresol (55.1 g, 0.4 mol) was dissolved in 160 ml of aqueous sodium hydroxide (6.4 M) in a 500-ml three-necked round-bottomed flask equipped with a magnetic stirrer and addition funnel. Dimethyl sulfate (50.4 g, 24 ml, 0.4 mol) was added dropwise over a 1 hr period at room temperature with stirring. After being stirred for one more hour, the organic and aqueous layers were separated. The aqueous layer was extracted with two 50-ml portions of ether and the organic fractions were combined, dried over anhydrous magnesium sulfate, and concentrated on the rotary evaporator. Vacuum distillation yielded 35 g (63%) of the desired product: bp 100-102\(^\circ\) (20 mm) [lit.\textsuperscript{60} bp 62-63\(^\circ\) (0.25 mm)]. IR spectrum no. 17153 (neat): \(\nu_{\text{max}}\) 3080, 3030, 3020, 2990, 2920, 2870, 1500, 1445, 1085, 1020, 960, and 800 cm\(^{-1}\). NMR spectrum no. 1566 (DMSO-d\(_6\)): \(\delta\) 7.32 (q, 4, \(J = 3\text{Hz}, \text{Ar}\)), 2.44 (s, 3, SCH\(_3\)), 2.3 (s, 3, ArCH\(_3\)).

Phenyl p-Tolyl Sulfide. \textsuperscript{62} p-Tolylmagnesium bromide was prepared from p-bromotoluene (53.6 g, 0.34 mol) and magnesium (10.7 g, 0.44 mol, 30% excess) in anhydrous ether. The reaction was carried out in a 1-liter, three-necked round-bottomed flask equipped with a condenser, drying tube, and mechanical stirrer. Diphenyl disulfide (40 g, 0.18 mol) dissolved in 200 ml of ether was added slowly over a 1.5 hr period at room temperature. Upon completion of the addition, the mixture was stirred overnight. The reaction mixture was washed successively with a saturated ammonium chloride solu-
tion, sodium carbonate, and water. The ether layer was separated, dried over magnesium sulfate, and concentrated on the rotary evaporator yielding a crude yellow oil. Vacuum distillation yielded 11.28 g (33%) of the desired product: bp 139° (1 mm) [lit. bp 170-172° (15 mm)]. Nmr spectrum no. 12160 (CDCl₃): δ 7.2 (m, 9, Ar), 2.22 (s, 3, CH₃).

NOTE: Phenyl p-tolyl sulfide was also prepared by B. Mosher.

*p-Toluenesulfinyl Chloride.* Thionyl chloride (324 ml, 437 g, 4.5 mol) was placed in a 3-liter, three-necked round-bottomed flask equipped with a mechanical stirrer. Powdered sodium p-toluenesulfinate dihydrate (128.4 g, 0.6 mol) was added in several small portions over a 15 min period with stirring. Throughout the addition, rapid gas evolution was observed. When the evolution of gas slowed, a drying tube was attached and the mixture was allowed to stand at room temperature for 2 hr. The excess thionyl chloride was removed at aspirator pressure at 50°; the last traces were removed by the addition and removal of several small portions of dry ether. The resulting residue was treated with 100 ml of dry ether and filtered through a sintered glass filter. The collected solid was washed with two 50 ml portions of dry ether and the ether solutions were combined. Removal of ether on the rotary evaporator yielded 92.91 g (89%) of the sulfinyl chloride which was used undistilled. The ir spectrum (no. 17435, neat) exhibits a strong S=O band at 1150 cm⁻¹ and the characteristic 810
cm\(^{-1}\) band of 1,4-disubstituted benzenes. Strong bands also appear at 1600 and 1065 cm\(^{-1}\).

NOTE: Sodium \(p\)-toluenesulfinyl chloride\(^64\) was prepared at various times by B. Ackerman, E. Sherr, B. Kostyla and B. Mosher.

\((-\)-Menthyl \(p\)-Toluenesulfinyl.\) \(^65\) A 1-liter, three-necked round-bottomed flask was equipped with a magnetic stirrer, addition funnel, and drying tube. A solution of \(p\)-toluenesulfinyl chloride (92.91 g, 0.53 mol) in 300 ml of anhydrous ether was placed in the flask which was then immersed in an ice bath. A solution of \((-\)-menthol (82.8 g, 0.53 mol), pyridine (39.7 g, 0.53 mol), and 50 ml of dry ether was added at a moderate rate with stirring. Upon completion of the addition, the mixture was allowed to stand at 0° for an additional hour; then 125 ml of dry ether was added. The mixture was washed successively with 100 ml of water, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, and 100 ml of water. The ether layer was dried over anhydrous sodium sulfate and concentrated on the rotary evaporator yielding 138 g (95%) of crude material. The residue was filtered through a sintered glass funnel and the solid collected. The filtrate (oil) was equilibrated with catalytic amounts of dry HCl and tetraethylammonium chloride. After standing ca. 5 hr, the residue was again filtered and the solid collected. The process was repeated until no further solid was obtained on equilibration. The combined solids were recrystallized twice from aqueous
acetone (17:3) yielding 44.4 g (39%) of the pure ester:
mp 101-103° (lit. 66 mp 106-107°) and $[\alpha]_{D}^{25}$ -200.83° (c 1.20, acetone) [lit. 66 $[\alpha]_{D}^{25}$ -199.19° (c 2, acetone)].

The ir spectrum (no. 17490, CHCl$_3$) exhibits a strong S=O band at 1130 cm$^{-1}$ and the characteristic 810 cm$^{-1}$ band of 1,4-disubstituted benzenes. Strong bands also appear at 2940, 945, 920, 855, and 820 cm$^{-1}$. Nmr spectrum no. 11989 (CCl$_4$): δ 7.43 (q,4, $J = 12$ Hz, Ar), 3.88 (m,1,HCO), 2.4 (s,3,ArCH$_3$), the remainder of the protons appear as overlapped multiplets between 0.55 and 1.8 δ.

NOTE: Repetition of the reaction yielded 48% of the desired product: mp 102-104° and $[\alpha]_{D}^{25}$ -191.52° (c 1.38, acetone).

Preparation of Optically Active Alkyl Aryl Sulfoxides. 67 The following description of the preparation of R-ethyl p-tolyl sulfoxide will serve to illustrate the general method utilized in the preparation of optically active alkyl aryl sulfoxides.

Ethylmagnesium bromide (ca. 20% excess) was prepared from magnesium (8.22 g, 0.338 mol, 10% excess) and ethyl bromide (33.56 g, 0.308 mol) in anhydrous ether. The reaction was carried out in a 2-liter, three-necked round-bottomed flask equipped with a mechanical stirrer, Friedrich's condenser, drying tube, and addition funnel. The mixture was cooled to 0° and (-)-menthy l p-toluenesulfinate (70.08 g, 0.238 mol, $[\alpha]_{D}^{25}$ -196.31°), dissolved in ca. 500 ml of anhydrous ether, was added dropwise over a 1-hr period with
stirring. Upon completion of the addition, the mixture was allowed to stand 1 hr at 0° and 2 hr at room temperature with stirring, followed by hydrolysis with 3 N hydrochloric acid. The two layers were separated and the aqueous layer extracted with four 50 ml portions of ether. The organic layers were combined, washed successively with sodium carbonate and water, and concentrated on the rotary evaporator yielding a crude residue of solid and oil. The residue was steam distilled in the presence of 20% potassium hydroxide to remove any menthol. Following the distillation, the aqueous layer was extracted with four 250 ml portions of ether. The ether layer was dried over magnesium sulfate and concentrated on the rotary evaporator. Vacuum distillation yielded 5.64 g (15%) of the desired product: bp 108-110° (1-1.2 mm) [lit.\textsuperscript{68} bp 94° (0.4 mm)], and [α]\textsubscript{D}\textsuperscript{25} 185.55° (c 1.8, acetone) [lit.\textsuperscript{69} [α]\textsubscript{D}\textsuperscript{25} 187.5° (acetone)].

The ir spectrum (no. 21087, neat) exhibits a strong S=O band at 1050 cm\textsuperscript{-1} and the strong 812 cm\textsuperscript{-1} band of 1,4-disubstitutedbenzenes. Strong bands also appear at 3050, 2990, 2940, 2880, 1500, 1480, 1090, and 1010 cm\textsuperscript{-1}. Nmr spectrum no. 1082 (CDCl\textsubscript{3}): δ 7.8 (q\textsuperscript{A}, J = 2.2 Hz, Ar), 3.08 (m,2,SCH\textsubscript{2}), 2.7 (s,3,ArCH\textsubscript{3}), 1.46 (t,3, J = 2 Hz, CH\textsubscript{2}CH\textsubscript{3}).

In some instances, inverse addition of the Grignard reagent to the (-)-menthyl p-toluenesulfinate was employed. The mode of addition had no effect on the yields which were in the range of 10-30%. 
The following sulfoxides were prepared as described above:

1. **R-methyl p-tolyl sulfoxide (29%)**: mp 72-73° (lit. mp 73-74°), bp 116-119° (1.6-1.8 mm), and \([\alpha]D^{25}_{D} 140.95°\) (c 0.56, acetone) [lit. \([\alpha]D^{25}_{D} 145.5°\) (acetone)]. Nmr spectrum no. 1083 (CDCl₃): \(\delta 7.48\) (q,4, \(J = 2\) Hz, Ar), 2.68 (s,3,\(\text{SCH}_3\)), 2.42 (s,3,\(\text{ArCH}_3\)).

2. **R-methyl p-tolyl sulfoxide (15%)**: mp 74-76°, and \([\alpha]D^{25}_{D} 141.9°\) (c 0.89, acetone), Nmr spectrum no. 1126.

3. **R-n-butyl p-tolyl sulfoxide (7%)**: bp 119-122° (0.12 mm) [lit. bp 100° (0.07 mm)], and \([\alpha]D^{25}_{D} 186.7°\) (c 1.6, acetone) [lit. \([\alpha]D^{25}_{D} 187°\) (acetone)]. Ir spectrum no. 21186 (neat): \(\nu_{\text{max}}\) 3050, 2980, 2950, 2890, 1500, 1480, 1410, 1145, 1085, 1035, 1015, and 810 cm⁻¹.

**NOTE**: (-)-Menthyl p-toluenesulfinate was also prepared by D. Bernstein.

**(+)-Ethyl n-Propyl Sulfoxide.** Sodium metaperiodate (10.69 g, 0.05 mol, 5% excess) was dissolved in 100 ml of water in a 250-ml Erlenmeyer flask equipped with a magnetic stirrer. The flask was immersed in an ice bath and ethyl n-propyl sulfide (5 g, 0.047 mol) was introduced. The flask was stoppered and stirred at 0° for 24 hr. The solution was saturated with sodium chloride and extracted with four 25 ml portions of chloroform. The chloroform was dried over magnesium sulfate and concentrated on the rotary evaporator. Vacuum distillation yielded 4 g (78%) of the desired product: bp 65.5-67° (1.1 mm).
The IR spectrum (no. 18933, neat) exhibits a very strong S=O band at 1045 cm\(^{-1}\). Strong bands also appear at 2970, 2940, 2880, 1460, 1420, 1380, and 973 cm\(^{-1}\). NMR spectrum no. 12340 (CDCl\(_3\)): \(\delta\) 2.63 (m, 4, SCH\(_2\)), 1.77 (m, 2, SCH\(_2\)CH\(_2\)), 1.27 (t, 3, \(J = 7.1\) Hz, SCH\(_2\)CH\(_3\)), 1.06 (t, 3, \(J = 6.5\) Hz, SCH\(_2\)CH\(_2\)CH\(_3\)).

**S-Methyl n-Butyl Sulfoxide.**

n-Butylmagnesium bromide was prepared from magnesium (3.2 g, 0.133 mol, 10% excess) and n-butyl bromide (16.62 g, 13.1 ml, 0.1209 mol) in anhydrous ether. After completion of the reaction, which was carried out in a 500-ml, three-necked round-bottomed flask equipped with a mechanical stirrer, condenser with drying tube, and addition funnel, (-)-menthyl methylsulfinate (19.4 g, 0.093 mol), dissolved in 50 ml of ether, was added slowly over a 1.5 hr period at room temperature. The mixture was allowed to stand an additional hour. Excess Grignard was hydrolyzed with a saturated ammonium chloride solution and the ether layer was separated and washed with water. The aqueous layers were combined, saturated with sodium chloride, and extracted with five 25 ml portions of methylene chloride. The organic fractions were combined, dried over magnesium sulfate, concentrated on the rotary evaporator, and vacuum distilled yielding 4.76 g (43%) of the desired product: bp 81° (2.5 mm) [lit.\(^{71}\) bp 36-38° (0.1 mm)], and \([\alpha]_D^{25}\) 13.54° (c 1.2, isooctane) [lit.\(^{68}\) \([\alpha]_D^{25}\) 42.0° (c 0.91, isooctane)].
The ir spectrum (no. 20431, neat) exhibits a very strong S=O band centered at 1028 cm\(^{-1}\). Strong bands are also present at 2970, 2940, 2880, 1460, 1420, and 950 cm\(^{-1}\).

NOTE: (-)-Menthyl methylsulfininate\(^{68}\) was prepared by D. L. Ladd.

\textit{R-Phenyl p-Tolyl Sulfoxide.\(^{67}\)} (-)-Menthyl p-toluenesulfininate (22.3 g, 0.0738 mol, \([\alpha]_{25}^{546} -200.83^\circ\)), dissolved in 350 ml of anhydrous ether, was placed in a flame-dried 1-liter, three-necked round-bottomed flask equipped with a condenser, drying tube, mechanical stirrer, and addition funnel. Phenylmagnesium bromide (35 ml, 0.094 mol, 2.67 N) was added dropwise over a 1 hr period at room temperature with stirring. After completion of the addition, the mixture was allowed to stand an additional 1.5 hr followed by hydrolysis with a saturated ammonium chloride solution. The two layers were separated and the aqueous layer extracted with two 100 ml portions of ether. The ether layers were combined, dried over sodium sulfate, and concentrated on the rotary evaporator yielding the crude product as a yellow oil. The oil was dissolved in ligroin (65-70\(^\circ\)), filtered hot, and cooled in ice. Crystals of \textit{R-phenyl p-tolyl sulfoxide} precipitated and were removed by filtration. A second recrystallization yielded 3.9 g (25\%) of the desired product: mp 91.92\(^\circ\) (lit.\(^{72}\) mp 92-93\(^\circ\)), and \([\alpha]_{25}^D 21.05^\circ\) (c 2.61, acetone) [lit.\(^{72}\) \([\alpha]_{25}^D 22^\circ\) (c 2, acetone)].

The ir spectrum (no. 17500, neat) exhibits a strong S=O band at 1054 cm\(^{-1}\) and the 820 cm\(^{-1}\) band characteristic
of 1,4-disubstitutedbenzenes.

(+)-Phenyl p-Tolyl Sulfoxide. Phenyl p-tolyl sulfide (6.61 g, 0.035 mol) was dissolved in 20 ml of acetic acid (96%) in an Erlenmeyer flask equipped with a magnetic stirrer. The flask was immersed in an ice bath and an equimolar amount of hydrogen peroxide was added in small aliquots over a 1 hr period. After standing for an additional hour, the reaction mixture was poured onto crushed ice and neutralized with 20% sodium hydroxide. The solution was saturated with sodium chloride and extracted with five 50 ml portions of ethyl acetate. The extracts were dried over anhydrous magnesium sulfate and concentrated on the rotary evaporator yielding a crude yellow oil. White crystals were obtained by dissolving the oil in ligroin (65-70°C) and allowing the solution to stand in an ice bath for a few hours. Recrystallization from ligroin (65-70°C) yielded 1.3 g (20%) of the desired product: mp 71-72°C (lit. mp 71-72°C).

The ir spectrum (no. 20255, neat) exhibits a strong S=O band at 1054 cm⁻¹ and the 820 cm⁻¹ band characteristic of 1,4-disubstitutedbenzenes. Strong bands also appear at 3090-3000 (2 peaks), 1590, 1500, 1480, 1450, 1100, 760 and 700 cm⁻¹.

This reaction was first attempted with sodium metaperiodate and then with hydrogen peroxide in 30% acetic acid. Both attempts gave only partial oxidation and account for the small yield finally obtained.
Tetramethylene Sulfoxide. Tetrahydrothiophene (29.39 g, 0.33 mol) was added to ca. 40 ml of acetic acid (96%) in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer. The flask was immersed in an ice bath and an equimolar amount of hydrogen peroxide was added in small aliquots over a period of 1 hr. After standing for an additional hour, the reaction mixture was poured onto crushed ice and neutralized with 20% sodium hydroxide. Excess peroxide was destroyed by the addition of small amounts of potassium iodide. The iodine formed by this process was subsequently destroyed by sodium bisulfite. This process was continued until the addition of potassium iodide no longer caused the appearance of the brown iodine color. The solution was saturated with sodium chloride and extracted with five 50 ml portions of ethyl acetate. The extracts were dried over magnesium sulfate and concentrated on the rotary evaporator. Vacuum distillation yielded 13.53 g (39%) of the desired product: bp 85-86° (0.9 mm) [lit.74 bp 107-108° (13 mm)].

The ir spectrum (no. 20053, neat) exhibits a strong S=O band at 1025 cm⁻¹. Strong bands also appear at 2950, 2870, 1460, 1420, and 1090 cm⁻¹. Nmr spectrum no 958 (acetone-d₆): δ 2.92 (m,4,SCH₂), 2.2 (m,4,SCH₂CH₂).

The sulfoxide was stored under refrigeration due to its short shelf life at room temperature.75

Dialkylarylsulfonium Salts. Several procedures were employed in the synthesis of both optically active and racemic dialkylarylsulfonium salts. One example, typical of each method, is described below. The following scheme
summarizes the general breakdown of these procedures.

A. The alkylation of sulfides by trialkyloxonium salts.

B. The alkylation of sulfides by methyl fluorosulfonate ("Magic Methyl").

C. The alkylation of sulfides by alkyl halides.

D. The reaction of O-methylated sulfoxides with dialkylcadmium reagents.

E. The reaction of O-methylated sulfoxides with alkylmagnesium halides.

F. The reaction of O-ethylated sulfoxides with alkylmagnesium halides.

G. The reaction of adamantoxyalkylarylsulphonium salts with dialkylcadmium reagents.

A. (+)-Methylbenzyl-p-tolylsulphonium Tetraphenylborate. Trimethyloxonium tetrafluoroborate (0.94 g, 6.9 mmol, 10% excess) was dissolved in ca. 20 ml of nitromethane in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Benzyl p-tolyl sulfide (1.36 g, 6.3 mmol), dissolved in nitromethane, was introduced by means of a syringe and the reaction was stirred for 1.5 hr at room temperature. The nitromethane was removed on the rotary evaporator yielding 1.99 g (ca. 100%) of the crude tetrafluoroborate salt as a thick yellow oil.
Sodium tetraphenylborate (2.17 g, 6.3 mmol) was dissolved in a minimum amount of acetone in a Erlenmeyer flask. The crude sulfonium salt (prepared above) was dissolved in a second flask in the same manner and the two solutions were combined. The desired product was obtained by precipitation from the acetone by adding an excess of ether. The product obtained was purified by dissolution in acetone and precipitation with ether several times followed by several washings with ether yielding 2.6 g (75%) of the desired product: mp 130.5-133.5° (EtOH) (reported mp 133-134°, see section C). Nmr spectrum no. 15863.

The 2,4,6-trinitrobenzenesulfonate salts were prepared in the same way by use of sodium 2,4,6-trinitrobenzenesulfonate in the final step. Methylene chloride was the solvent employed in the reactions with triethyloxonium tetrafluoroborate.

The following salts were prepared according to this procedure:


(2) (+)-ethyl-n-butyl-p-tolylsulfonium 2,4,6-trinitrobenzenesulfonate (50%): mp 150-152° (acetone:ether). Nmr spectrum no. 14993. Anal. Calcd for C_{19}H_{23}N_{3}O_{9}S_{2}: C, 45.5; H, 4.61; N, 8.37. Found: C, 45.8; H, 4.61; N, 8.37.
B. (+)-1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetraphenylborate. (+)-2-Methyl-2,3-dihydrobenzothiophene (1 g, 6.66 mmol) was converted to the title compound by alkylation with methyl fluorosulfonate (0.835 g, 7.33 mmol, ca. 10% excess). The reaction was carried out in methylene chloride according to the conditions and isolation procedure outlined in procedure A above. The salt was isolated in 55% yield (1.62 g) and consisted of a 13:27/trans:cis mixture: mp 167-169° (EtOH). Ir spectrum no. 20692. Nmr spectrum nos. 389-391.

Anal. Calcd for C$_{34}$H$_{33}$BS: C, 84.28; H, 6.90. Found: C, 84.01; H, 6.81.

C. (+)-Methylbenzyl-$p$-tolylsulfonium Tetraphenylborate. Methyl $p$-tolyl sulfide (2 g, 14.5 mmol) was dissolved in ca. 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with septum, and flushed with nitrogen. The flask was immersed in an ice bath and $\alpha$-chlorobenzene (1.78 g, 14.5 mmol) was added by means of a syringe. The mixture was stirred for 1.5 hr at 0°. Following completion of the reaction, the methylene chloride was removed on the rotary evaporator yielding the crude sulfonium chloride as a thick yellow oil.

The chloride salt was converted to the tetraphenylborate in the normal way (procedure A above) yielding 0.19 g (15%) of the desired product: mp 133-134° (acetone:ether). Nmr spectrum no. 15781. Ir spectrum no. 20556.
Anal. Calcd for C_{39}H_{37}BS: C, 85.38; H, 6.80.
Found: C, 85.59; H, 6.87.

D. S-(+)-Methylethyl-\(p\)-tolylsulfonium Tetraphenylborate. Trimethyloxonium tetrafluoroborate (0.96 g, 6.5 mmol, 10% excess) was dissolved in ca. 20 ml of nitromethane in a 50-ml round-bottomed flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. \(R\)-Ethyl \(p\)-tolyl sulfoxide (1 g, 5.9 mmol, \([\alpha]_{D}^{25} 186.6^\circ\), dissolved in nitromethane, was introduced by means of a syringe and the mixture was stirred for 2 hr at room temperature. Following completion of the reaction, the solution was concentrated on the rotary evaporator and the \(R\)-methoxyethyl-\(p\)-tolylsulfonium tetrafluoroborate was precipitated by the addition of an excess of ether. The salt was purified by dissolution in methylene chloride and precipitation with ether several times, followed by several washings with ether yielding 1.27 g (80%) of the salt as a thick yellow oil.

The oil was dissolved in methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Dimethylcadmium (3 ml, 6.18 mmol, 30% excess, 2.08 M) was introduced by means of a syringe with rapid stirring. The stirring was terminated and the mixture was allowed to stand for 20 min at room temperature. Following completion of the reaction, excess cadmium reagent was hydrolyzed with 5% sulfuric acid. The entire mixture was extracted with two 100 ml
portions of ether. The combined ether layers were extracted with two 25 ml portions of water and the aqueous layers were combined. The aqueous layer was saturated with ca. 20 g of sodium tetrafluorobororate and extracted with five 25 ml portions of methylene chloride. The methylene chloride was dried over magnesium sulfate and concentrated on the rotary evaporator. The tetrafluorobororate was obtained as a thick yellow oil which was purified by dissolution in methylene chloride and precipitation with ether several times followed by several washings with ether. The oil was dried under vacuum yielding 0.88 g (73%) of $\text{S}_-^-(+)-$methylethyl-$p$-tolyl-sulfonium tetrafluorobororate: $[\alpha]_D^{25} 21.7^\circ$ (c 0.4, ethanol). Nmr spectrum no. 1816.

The tetrafluorobororate (0.2 g, 0.79 mmol) was converted to the tetraphenylborate in the normal way (procedure A above) yielding 0.33 g (90%) of the desired product: mp 168-170° (EtOH) (reported mp 168-170° of the racemic material, see section A), and $[\alpha]_D^{25} 9.04^\circ$ (c 0.61, acetone). Nmr spectrum no. 1869.

The following salts were prepared according to this procedure:

1. $R_--(-)-$methylethyl-$p$-tolylsulfonium tetraphenylborate (75%): mp 168-170° (EtOH) (reported mp 168-170° of the racemic material, see section A), and $[\alpha]_D^{25} -10.46^\circ$ (c 1.3 acetone). Nmr spectrum no. 1944. The $R_--(-)-$methylethyl-$p$-tolylsulfonium tetrafluorobororate precursor was obtained in 56% yield: $[\alpha]_D^{25} -15.84^\circ$ (c 0.6, ethanol). Nmr spectrum no.
1900. The R-methoxymethyl-p-tolylsulfonium tetrafluoroborate intermediate was obtained in 92% yield. Nmr spectrum no. 1886.

(2) S-(+)-ethyl-n-butyl-p-tolylsulfonium tetraphenylborate (ca. 100%): mp 140-142° (EtOH) (reported mp 141-142° of the racemic material, see section F), and [α]D 25 10.18° (c 1.6, acetone). Nmr spectrum no. 2075. The S-(+)-ethyl-n-butyl-p-tolylsulfonium tetrafluoroborate precursor was obtained in 64% yield: [α]D 25 8.70° (c 0.46, EtOH). The S-methoxy-n-butyl-p-tolylsulfonium tetrafluoroborate intermediate was obtained in 79% yield.

(3) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (85%): mp 176-178° (EtOH) (reported mp 167-169° of the 73:27/trans:cis mixture, see section B). The tetrafluoroborate precursor was obtained in 32% yield. Nmr spectrum nos. 1487 and 1488. The salt was obtained as a 15:85 mixture (trans:cis). The O-methylated sulfoxide was obtained in 62% yield. Nmr spectrum no. 1481. The latter salt was isolated as a 85:15 mixture (trans:cis).

(4) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (90%): mp 176-178° (EtOH). The tetrafluoroborate precursor was obtained in 31% yield. Nmr spectrum no. 1501. The salt was obtained as a 92:8 mixture (trans:cis). The O-methylated sulfoxide was obtained in 77% yield. Nmr spectrum no. 1500. The latter salt was isolated as a 5:95 mixture (trans:cis).
(5) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (70%): mp 177-178° (EtOH). The tetrafluoroborate precursor was obtained in 45% yield. Nmr spectrum no. 1508. The salt was obtained as a 15:85 mixture (trans:cis). The O-methylated sulfoxide was obtained in ca. 100% yield. Nmr spectrum no. 1507. The latter salt was isolated as the pure trans isomer.

E. (+)-Methyl-n-butyl-p-tolylsulfonium Tetraphenylborate. The title compound was prepared according to procedure D with the following modifications: (1) methylmagnesium bromide was used in place of the dialkylcadmium reagents and (2) the reaction of the organometallic and the alkylated sulfoxide was carried out over a 1 hr period at -78°. (+)-Methyl-n-butyl-p-tolylsulfonium tetrafluoroborate was isolated as a thick yellow oil in a yield of 56% (0.48 g): Nmr spectrum nos. 1207 and 1288. The tetrafluoroborate was converted to the tetraphenylborate in the normal way (procedure A above) with an 80% recovery: mp 119-121° (reported mp 119-121° of the (-)-isomer, see section F). The O-methylated sulfoxide intermediate was obtained in 60% yield.

The following salts were prepared according to this procedure:

(1) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (40%): mp 178-180° (EtOH) (reported mp 167-169° of the 73:27/trans:cis mixture, see section B).
Nmr spectrum nos. 848 and 913. Ir spectrum no. 21239.
The tetrafluoroborate precursor was obtained in 40% yield.
Nmr spectrum no. 823. The salt was obtained as a 50:50 mixture (trans:cis). The O-methylated sulfoxide was obtained in 81% yield. Nmr spectrum no. 824. The latter salt was isolated as the pure trans isomer.

(2) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (100%): mp 175-178° (EtOH). The tetrafluoroborate precursor was obtained in 30% yield. Nmr spectrum no. 1307. The salt was obtained as a 35:65 mixture (trans:cis). The O-methylated sulfoxide was obtained in 79% yield. Nmr spectrum no. 1300. The latter salt was isolated as the pure trans isomer.

(3) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (20%): mp 172-175° (EtOH). The tetrafluoroborate precursor was obtained in 50% yield. Nmr spectrum no. 1318. The salt was obtained as a 95:5 mixture (trans:cis). The O-methylated sulfoxide was obtained in 79% yield. Nmr spectrum no. 1319. The latter salt was isolated as the pure cis isomer.

(4) (+)-1,2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (98%): mp 172-174° (EtOH). Nmr spectrum nos. 796, 802, and 890. Ir spectrum no. 21007. The tetrafluoroborate precursor was obtained in 45% yield. Nmr spectrum no. 795. The salt was obtained as 90:10 mixture (trans:cis). The O-methylated sulfoxide was obtained in 75% yield. The latter salt was isolated as the pure cis isomer.
Anal. Calcd for C$_{33}$H$_{33}$SB: C, 84.28; H, 6.87.

Found: C, 84.71; H, 6.78.

(5) (+)-methylethyl-p-tolylsulfonium tetraphenylborate (88%): mp 170-172° (acetone:ether) (reported mp 168-170°, see section A). The tetrafluoroborate precursor was obtained in 57% yield. Nmr spectrum no. 1659. This reaction was run for a fifteen hour period at room temperature.

F. S-(+) -Methylethyl-p-tolylsulfonium Tetraphenylborate. Triethyloxonium tetrafluoroborate (1.32 g, 6.6 mmol, 10% excess) was dissolved in ca. 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer fitted with a septum, and flushed with nitrogen. R-Ethyl p-tolyl sulfoxide (1.0 g, 5.90 mmol, [α]$_D^{25}$ 185.7°), dissolved in methylene chloride was introduced by means of a syringe and the mixture was allowed to stand with stirring for 1 hr at room temperature. The flask was then immersed in an acetone-dry ice bath and methylmagnesium bromide (2.0 ml, 6 mmol, 3.0 M) was added slowly. The mixture was stirred for 1 hr at -78° followed by hydrolysis of any unreacted Grignard reagent with 5% sulfuric acid. The entire mixture was extracted with an equal volume of ether and the two layers were separated. The ether layer was washed with two 25 ml portions of water and the aqueous layers combined. The aqueous layer was saturated with sodium bromide (ca. 35 g) and extracted with four 40 ml portions of chloroform. The chloroform was
dried over magnesium sulfate and concentrated on the rotary evaporator yielding 0.52 g (40%) of the crude sulfonium bromide as a yellow oil.

The bromide was converted to the tetraphenylborate in the normal way (procedure A above) yielding 0.04 g (22% from bromide) of the desired product: mp 165-166° (reported mp 168-170° of the racemic material, see section A), and \([\alpha]_D^{25} 7.84° (c 0.4, \text{acetone})\). Ir spectrum no. 17410. Nmr spectrum no. 14973.

The following salts were prepared according to this procedure:

1. \(\mp\)-ethyl-n-butyl-p-tolylsulfonium tetraphenylborate (11%): mp 141-142° (acetone:ether). Nmr spectrum no. 11924. Ir spectrum no. 17459. This compound was prepared from optically active sulfoxide which yielded racemic material.

**Anal.** Calcd for C\(_{37}\)H\(_{41}\)BS: C, 84.07; H, 7.81. Found: C, 84.28; H, 7.82.

2. \(\mp\)-ethyl-n-butyl-p-tolylsulfonium tetraphenylborate (3%): mp 142-144° (acetone:ether) (reported mp 141-142°, see above). Nmr spectrum no. 18382. Ir spectrum no. 17397.

3. \(\mp\)-(+)methyl-n-butyl-p-tolylsulfonium tetraphenylborate (11%): mp 119-121° (acetone:ether), and \([\alpha]_D^{25} -17.48° (c 0.49, \text{acetone})\). Nmr spectrum no. 11944. Ir spectrum no. 17479.
(4) $\text{R-ethyl-n-butyl-p-tolylsulfonium 2,4,6-trinitrobenzenesulfonate (5\%)}$: mp 148-150° (acetone:ether) (reported mp 150-152°, of the racemic material, see section A), and $[\alpha]_D^{25} = 6.18°$ (c 0.18, acetone). Nmr spectrum no. 11925. Ir spectrum no. 17463.

G. (+)-Methylethyl-p-tolylsulfonium Tetraphenylborate. (+)-Adamantoxyethyl-p-tolylsulfonium hexafluorodantimonate (0.45 g, 0.856 mmol) was dissolved in 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Diethylcadmium (0.32 ml, 0.856 mmol, 2.75 M) was introduced by means of a syringe with rapid stirring. The stirring was terminated, and the mixture was allowed to stand for ca. 24 hr at room temperature followed by workup according to procedure D above. (+)-Methylethyl-p-tolylsulfonium tetrafluoroborate was isolated as a thick yellow oil: yield 0.22 g (100%). Nmr spectrum no. 1569. The tetrafluoroborate was converted to the tetraphenylborate in the normal way (procedure A above) with a 70% recovery: mp 169-171° (EtOH) (reported mp 168-170°, see section A). Nmr spectrum no. 1582.

The following salts were prepared according to this procedure:
(1) \( \text{R}-(\text{-})-\text{methylethyl-}p\text{-tolylsulfonium tetrafluoroborate (54\%)} \): Nmr spectrum nos. 1781 and 1810. The material contained very slight amounts of impurities which could not be removed even after repeated recrystallizations. No further work was performed on the compound.

_Attempted Preparation of Optically Active Phenyl-o-tolyl-p-tolylsulfonium Tetraphenylborate._ Triethylxoxonium tetrafluoroborate (1.25 g, 6.6 mmol, 10\% excess) was dissolved in ca. 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. \( \text{R} \)-Phenyl \( p \)-tolylsulfoxide (1.325 g, 6.02 mmol, \( [\alpha]_D^{25} \) 21.05°), dissolved in methylene chloride, was introduced by means of a syringe and the mixture was allowed to stand for 36 hr at 0°. Di-o-tolylcadmium (6.02 mmol) was introduced slowly and the mixture was stirred for 1.5 hr at 0° followed by hydrolysis of any unreacted cadmium reagent with 5\% sulfuric acid. The reaction mixture was extracted with two equal portions of ether. The ether layers were combined and washed with two 25 ml portions of water. The aqueous layers were combined, saturated with sodium bromide (ca. 30 g), and extracted with four 40 ml portions of chloroform. The chloroform extracts were dried over magnesium sulfate and concentrated on the rotary evaporator yielding 2.6 g (ca. 100\%) of the crude sulfonium bromide as a thick yellow oil.

The bromide (oil) was converted to the tetraphenylborate (solid) in the normal way (procedure A for the prep-
aration of dialkylarylsulfonium salts, see above) yielding 0.5 g (20%) of the desired product: mp 171-174° (acetone: ether) (reported mp 172.5-174°; see below), and $[\alpha]_{D}^{25}$ 0°. Nmr spectrum nos. 15156 and 15143.

Repetition of the reaction gave the same results.

(+)−Phenyl−o−tolyl−p−tolylsulfonium Tetraphenylborate.
The title compound was prepared from (+)-phenyl p-tolyl-sulfoxide (1.3 g, 6.02 mmol) which was alkylated with triethylxomonium tetrafluoroborate (1.25 g, 6.6 mmol, 10% excess) in methylene chloride and then treated with o-tolyl-magnesium bromide (2.22 ml, 6 mmol, 2.7 M) according to procedure outlined for the attempted preparation of optically active phenyl-o-tolyl-p-tolylsulfonium tetraphenylborate (see above) with the following modification: the organometallic and alkylated sulfoxide were reacted at -78° for one hour. (+)-Phenyl-o-tolyl-p-tolylsulfonium tetraphenylborate was isolated in 46% yield (1.42 g): mp 172.5-174° (acetone: ether). Nmr spectrum no. 15081.

Anal. Calcd for C_{44}H_{39}BS: C, 86.54; H, 6.43.
Found: C, 86.25; H, 6.35.

Attempted Preparation of Optically Active Ethyl−phenyl−p−tolylsulfonium Tetraphenylborate. Trimethyloxonium tetrafluoroborate (0.47 g, 3.18 mmol, 10% excess) was dissolved in ca. 20 ml of nitromethane in a 50-ml round-bottomed flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. R−Phenyl p-tolylsulfoxide (0.63 g, 2.87 mmol, $[\alpha]_{D}^{25}$ 15.24°), dissolved in nitromethane, was
introduced by means of a syringe and the reaction was stirred for 20 min at room temperature. Then, the solution was concentrated on the rotary evaporator, and the R-methoxyphenyl-p-tolylsulfonium tetrafluoroborate was precipitated by the addition of a large excess of ether. The salt was purified by dissolution in methylene chloride and precipitation with ether several times followed by several washings with ether yielding 0.55 g (60%) of the desired product as a thick yellow oil.

The oil was dissolved in methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Distilled diethylcadmium (4.32 ml, 2.6 mmol, 0.6 M, 50% excess) was introduced by means of a syringe with rapid stirring. The stirring was terminated, and the mixture was allowed to stand for 20 min at room temperature. Then, excess cadmium reagent was hydrolyzed with 5% sulfuric acid. The entire mixture was extracted with two 100 ml portions of ether. The combined ether layers were extracted with two 25 ml portions of water and the aqueous layers were combined. The aqueous layer was saturated with ca. 20 g of sodium tetrafluoroborate and extracted with five 25 ml portions of methylene chloride. The methylene chloride extracts were dried over magnesium sulfate, and concentrated on the rotary evaporator. The tetrafluoroborate was obtained as a thick yellow oil which was purified by dissolution in methylene chloride and precipitation with ether several times, followed
by several washings with ether. The oil was dried under vacuum yielding 0.4 g (73%) of (+)-ethylphenyl-p-tolylsulfonyl tetrafluoroborate.

The tetrafluoroborate (oil) was converted to the tetraphenylborate (solid) in the normal way (procedure A for the preparation of dialkylarylsulfonium salts, see above) yielding 0.7 g (80%) of the desired product: mp 139.5-141° (methylene chloride:ether), and \([\alpha]_{D}^{25} 0°\). Nmr spectrum no. 2136.

**Anal.** Calcd for C_{39}H_{37}SB: C, 85.38; H, 6.80. Found: C, 85.87; H, 6.54.

**Ethyl-di-n-butylsulfonium 2,4,6-Trinitrobenzenesulfonate.** Trimethyloxonium tetrafluoroborate (2.09 g, 11 mmol, 10% excess) was dissolved in ca. 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Di-n-butyl sulfide (1.46 g, 10 mmol), dissolved in methylene chloride, was introduced by means of a syringe and the mixture was stirred at room temperature for two hours. The solution was concentrated on the rotary evaporator yielding 2.58 g (ca. 100%) of the crude tetrafluoroborate as a thick yellow oil.

The tetrafluoroborate (oil) was converted to the 2,4,6-trinitrobenzenesulfonate in the usual way (procedure A for the preparation of dialkylarylsulfonium salts, see above) yielding 1 g (43%) of the desired product: mp 120-122°. Nmr spectrum nos. 14729 and 67.
Anal. Calcd for C₁₆H₂₅N₃O₉S₂: C, 41.11; H, 5.39; N, 8.99. Found: C, 41.05; H, 5.44; N, 8.82.

Other salts prepared in this way include:

(1) S-methyltetramethylenesulfonium tetrafluoroborate (80%): mp 244-246° (lit. mp 250-251°). Nmr spectrum no. 14522.

**Attempted Preparation of Racemic and Optically Active Trialkylsulfonium Salts from O-alkylated Sulfoxides.**

The reaction of O-alkylated dialkyl sulfoxides (racemic or optically active) with Grignard reagents at -78° for 1 hr or dialkylcadmium reagents for 20 min at room temperature (procedures D, E, and F for the preparation of dialkylaryl sulfonium salts, see above) failed to yield the desired trialkylsulfonium salts. The products isolated include starting sulfoxide (partially racemized in the case of optically active sulfoxide), the corresponding sulfide, and some unidentified products (tlc, nmr).

The sulfoxides were often isolated as a 1:1 complex with 2,4,6-trinitrobenzenesulfonic acid, the anion which was used in the attempted isolation of the sulfonium salt. The preparation and characterization of these complexes is described below.

A number of variations in the reaction conditions were attempted. They include: 1) temperature, 2) reaction time, 3) organometallic, 4) leaving group, and 5) anion. The same results were obtained in all cases.
(+)-Methyl n-Butyl Sulfoxide 2,4,6-Trinitrobenzene-
sulfonic Acid Complex. (+)-Methyl n-butyl sulfoxide (1.2 g, 0.01 mol) was dissolved in a minimum amount of acetone in an Erlenmeyer flask. Sodium 2,4,6-trinitrobenzenesulfonate was dissolved in a second flask in the same manner. The two solutions were mixed and allowed to stand for 5 min. An excess of anhydrous ether was added to the mixture causing the immediate precipitation of a yellow oil. The ether was decanted off and the oil redissolved in acetone and precipitated with ether. A yellow semi-solid appeared. After standing several hours under ether, the semi-solid completely crystallized. The solid was filtered and washed twice with ether yielding 1.02 g (50%) of the desired product: mp 111-112°. Nmr spectrum no. 14555 (DMSO-d₆): δ 10.66 (s, 1, SO₃H), 8.6 (s, 2, Ar), 2.46 (m, SCH₂), 2.32 (s, SCH₃), 1.26 (m, SCH₂CH₂CH₃), and 0.64 (t, J = 6 Hz, SCH₂CH₂CH₃); the latter four resonances signals integrate for a total of 12 protons.


Attempted Resolution of Dialkyl Sulfoxides; (+)-Methyl n-Butyl Sulfoxide d-10-Camphorsulfonic Acid Complex. Methyl n-butyl sulfoxide (2 g, 0.016 mol) was dissolved in a minimum amount of acetone in an Erlenmeyer flask. d-10-Camphorsulfonic acid (3.72 g, 0.016 mol) was dissolved in a second flask in the same manner. The two solutions were combined, allowed to stand for a few minutes, and concentrated on the
rotary evaporator. The complex was precipitated as an oil by the addition of excess ether. The oil was allowed to stand for several days under ether, but crystallization never occurred. A drop of concentrated hydrochloric acid was added, the solution was shaken, and allowed to stand several more days. A small amount of yellow needles crystallized. The crystals were collected, dissolved in 10% sodium hydroxide, diluted with water, saturated with sodium chloride and extracted with five 25 ml portions of ethyl acetate. The ethyl acetate extracts were washed with a saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated on the rotary evaporator yielding 0.5 g (25%) of methyl n-butyl sulfoxide: $\left[\alpha\right]_D^{25} 0^\circ\text{.}$

Several repetitions of the reaction yielded the same results.

**Optical Stability of O-Alkylated Sulfoxides.** Tri-ethyloxonium tetrafluoroborate (1.76 g, 8.8 mmol, 10% excess) was dissolved in 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. $\text{R-}\text{Methyl n-butyl sulfoxide (0.968 g, 8.8 mmol, }\left[\alpha\right]_D^{25} -37^\circ\text{)}$, dissolved in methylene chloride, was introduced by means of a syringe and the reaction was allowed to stand 1 hr at room temperature. Following completion of the reaction, an aliquot of the reaction mixture was transferred to a polarimeter cell and the optical rotations at 578 and 546 nm were recorded at
various intervals over a 24 hr period: \([\alpha]_{D,\text{initial}}^{25} -33.7^\circ (c\ 4.8, \text{CH}_2\text{Cl}_2)\) and \([\alpha]_{D,\text{final}}^{25} -33.7^\circ (c\ 4.8, \text{CH}_2\text{Cl}_2)\). The solution was removed from the polarimeter cell and the methylene chloride removed on the rotary evaporator yielding a thick yellow oil. The oil was dissolved in water, a few drops of phenolphthalein added, and the solution titrated to neutrality with 1% sodium hydroxide. The solution was saturated with sodium chloride and extracted with three 50 ml portions of methylene chloride. The methylene chloride was dried over magnesium sulfate and concentrated on the rotary evaporator yielding 0.71 g (75%) of the sulfoxide of inverted configuration: \([\alpha]_{D}^{25} 33.1^\circ (c\ 1, \text{hexane})\) [lit.\(^7\) \([\alpha]_{D}^{25} 42.0^\circ (c\ 0.91, \text{isooctane})\)]. IR spectrum no. 20330.

The study was repeated with R-methyl p-tolyl sulfoxide yielding analogous results.

NOTE: R-Methyl n-butyl sulfoxide\(^7\) was prepared by Dr. E. Olsen.

Hydrolysis of O-Alkylated Sulfoxides. Triethyl-oxonium tetrafluoroborate (ca. 6 mmol) was dissolved in 20 ml of methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Optically active sulfoxide (ca. 6 mmol), dissolved in methylene chloride, was introduced by means of a syringe and the mixture was stirred for 1 hr. Diethylcadmium was added and the mixture was stirred for an additional 20 min. The reaction mixture was hydrolyzed by the addition of a large excess (ca. 70 ml) of water or
sodium hydroxide (1%). The aqueous solution was added with rapid stirring and the mixture was stirred for an additional 30 min at room temperature. The solutions were saturated with sodium bromide and extracted with five 25 ml portions of ether. The ether extracts were dried over magnesium sulfate and concentrated on the rotary evaporator yielding the desired product. After drying under vacuum, the sulfoxide was dissolved in the appropriate solvent and the optical rotation measured. Optical purity was determined from the following equation: \( \frac{\alpha_{\text{obsd}}}{\alpha_{\text{max}}} \times 100 = \text{optical purity} \). The results are summarized in Table III.

**Attempted Preparation of Racemic Sulfonium Salts from N-Methylated Sulfilimines.** N-Tosyl methyl phenyl sulfilimine (1 g, 3.4 mmol) was dissolved in methylene chloride in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Methyl fluorosulfonate (0.52 g, 3.4 mmol) was introduced by means of a syringe and the reaction was stirred for 24 hr at room temperature. The flask was immersed in an acetone-dry ice bath and n-butylmagnesium bromide (1.45 ml, 3.4 mmol, 2.4 M) was added. The mixture was allowed to proceed for an additional hour at -78° followed by hydrolysis of any unreacted Grignard reagent with an excess of 5% sulfuric acid. The reaction mixture was washed with two 50 ml portions of ether which were combined and washed with an equal portion of water. The aqueous layers were combined, saturated with sodium bromide (ca. 25 g) and extracted with five 25 ml portions of chloroform.
The chloroform was dried over magnesium sulfate and concentrated on the rotary evaporator yielding a crude yellow oil which consisted of N-tosyl methyl phenyl sulfilimine, N-methyl p-toluenesulfonamide, and methyl phenyl sulfoxide (tlc, nmr). None of the desired product was obtained.

Repetition of the reaction with N-tosyl phenyl ethyl sulfilimine and diethylcadmium yielded analogous results.

Adamantoxy sulfonium Salts; Dialkyl- and Alkylaryl-. The procedure outlined for the preparation of (+)-adamantoxy-methyl-p-tolylsulfonium perchlorate will serve to illustrate the general method employed in the synthesis of the title compounds.

Silver perchlorate (1.44 g, 7 mmol) was placed in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. (+)-Methyl p-tolyl sulfoxide (1.08 g, 7 mmol) dissolved in ca. 20 ml of methylene chloride was introduced by means of a syringe. The flask was covered with aluminum foil and stirring was initiated. Adamantyl bromide (1.5 g, 7 mmol), dissolved in methylene chloride, was added in several small aliquots over a 15 min period. Following completion of the addition, the mixture was allowed to stand an additional hour at room temperature. The silver bromide produced was removed by filtration through a sintered glass funnel. (+)-Methyl-p-tolyladamantoxy sulfonium perchlorate (1.42 g, 53%) was obtained as a fluffy white solid by precipitation from the methylene chloride by an excess of ether: mp 153-155°d
The hexafluoroantimonate salts were prepared and purified in an analogous way by use of silver hexafluoroantimonate.

Other salts prepared according to this procedure include:

(1) (+)-adamantoxymethyl-$p$-tolylsulfonium hexafluoroantimonate (53%): mp 124-126° (ethylene chloride: ether), and $[\alpha]_D^{25} 68.37°$ (c 1, acetone). Nmr spectrum no. 1567.

**Anal.** Calcd for $C_{18}H_{25}SSbF_6$: C, 41.16; H, 4.80.

Found: C, 41.12; H, 4.80.

(2) (+)-adamantoxymethyl-$n$-propylsulfonium hexafluoroantimonate (20%): mp 110-112° (ethylene chloride: ether).

**Anal.** Calcd for $C_{14}H_{25}SSbF_6$: C, 35.24; H, 5.28.

Found: C, 35.17; H, 5.11.

(3) (+)-adamantoxymethyl-$p$-tolylsulfonium hexafluoroantimonate (50%): mp 110-112° (methylene chloride: ether) (reported mp 124-126° for the (+)-isomer, see above). Nmr spectrum no. 16358.

**Attempted Preparation of Racemic Trialkylsulfonium Salts from Adamantoxydialkylsulfonium Salts.** The reaction of dialkyladamantoxydium salts with dialkylcadmium reagents at room temperature for ca. 20 hr (procedure G for
the preparation of dialkylarylsulfonium salts, see above) failed to yield the desired trialkylsulfonium salts. The products isolated include the starting sulfoxide, adamantanol, and several unidentified by-products (tlc, nmr).

The sulfoxides were often isolated as a 1:1 complex with 2,4,6-trinitrobenzenesulfonic acid, the anion used in the attempted isolation of the sulfonium salt. The preparation and characterization of these complexes is described above.

The reaction was also attempted for a 20 min period at room temperature several times. The same result was obtained in all cases.

(+)-2-Methyl-2,3-dihydrobenzothiophene 1-Dioxide. A mixture of (+)-2-methyl-2,3-dihydrobenzothiophene (24.4 g, 0.16 mol), 2,3-dihydrobenzothiane (7.06 g, 0.05 mol), and p-thiocresol (5.04 g, 0.045 mol) was slurried in ca. 100 ml of water in a 500-ml Erlenmeyer flask equipped with a magnetic stirrer. Potassium permanganate (40.29 g, 0.255 mol, dissolved in ca. 200 ml of water) was added at a moderate rate with stirring. An ice bath was used to cool the mixture as needed. The addition of permanganate was terminated when its purple color persisted in the reaction mixture. The solution was stirred for an additional 15 min and diluted with an equal portion of water. Sodium bisulfite was added until the solution was colorless. The mixture was filtered through a sintered glass funnel and the resulting residue washed with water. The desired product was collected by
washing the residue with methylene chloride and collecting the filtrate. The methylene chloride was dried over magnesium sulfate and concentrated on the rotary evaporator yielding a crude semi-solid. Recrystallization from cyclohexane yielded 15.42 g (52%) of the desired product: mp 113-114° (lit. mp 115.5-116.5°).

The ir spectrum (no. 20613, KBr) exhibits two strong \( \text{SO}_2 \) bands at 1380 and 1150 cm\(^{-1}\). Strong bands also appear at 3055, 2980, 2930, 1590, 1460, 1440, 1295, 1250, 1245, 1190, 1130, 1105, 1060, 1000, 760, and 730 cm\(^{-1}\). Nmr spectrum no. 361 (CDCl\(_3\)): 7.64 (m,4,Ar), 3.44 (m,2,ArCH\(_2\)), 2.9 (m,1,SO\(_2\)CH), 1.5 (d,3, \( \gamma = 4 \) Hz, CH\(_3\)).

The oxidation was first attempted with 30% hydrogen peroxide in acetic acid (96%) which yielded a mixture of sulfide, sulfoxide, and sulfone. The low yield may be partially attributed to mechanical losses in the recovery of material from this initial reaction.

NOTE: The sulfide, \( \sigma \)-thiocresol mixture used in this reaction was provided by Dr. I. K. Nielsen.

**Reaction of \( R \)-Methoxymethyl-\( \sigma \)-tolylsulfonium Tetrafluoroborate with Magnesium Bromide and Magnesium Methoxide.**

Anhydrous magnesium bromide (0.52 g, 2.8 mmol) was placed in a 125-ml Erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Methylene chloride was introduced and stirring was initiated. \( R \)-Methoxymethyl-\( \sigma \)-tolylsulfonium tetrafluoroborate (0.72 g, 2.8 mmol, \([\alpha]_{D}^{23} \ 186°\)), prepared from \( R \)-methyl \( \sigma \)-tolyl sul-
foxide (1 g, 6.48 mmol, $[\alpha]^23_D 140.9^\circ$) and trimethyloxonium tetrafluoroborate, dissolved in 10 ml of methylene chloride, was added and the mixture was stirred at room temperature for 1.5 hr. The magnesium bromide was filtered off and the filtrate hydrolyzed with ca. 50 ml of 1% sodium hydroxide. The two layers were separated and the aqueous layer was saturated with ca. 20 g of sodium bromide and extracted with four 25 ml portions of methylene chloride. The methylene chloride was dried over magnesium sulfate, concentrated on the rotary evaporator, and dried under vacuum yielding 0.18 g (46%) of methyl $\beta$-tolyl sulfide and 0.15 g (33%) of $R$-methyl $\beta$-tolyl sulfoxide; $[\alpha]^{22}_D 25.3^\circ$ (c 1, acetone), 18% optically pure.

Also, $R$-methoxymethyl-$\beta$-tolylsulfonium tetrafluoroborate was treated with magnesium methoxide. Following the reaction conditions and work-up as above, $S$-methyl $\beta$-tolyl sulfoxide (0.43 g, 100%) was isolated; $[\alpha]^{23}_D -24.2^\circ$ (c 1, acetone), 17.2% optically pure.

NOTE: Magnesium methoxide was prepared by Dr. I. K. Nielsen.

Thermal Equilibration of 1,2-Dimethyl-2,3-dihydrobenzo thiophenium Tetrafluoroborate. A 93% trans and 7% cis mixture of 1,2-dimethyl-2,3-dihydrobenzo thiophenium tetrafluoroborate (0.04 g) was dissolved in 96% acetic acid (0.5 ml) in nmr tube. The isomers were equilibrated in a bath of refluxing toluene (bp 110°). The apparatus consisted of a 250-ml round-bottomed flask equipped with a 2-necked
adapter, thermometer, and pipette inlet adapter in which the nmr tube was placed. The nmr tube was removed at periodic intervals over a nine day period and its nmr spectrum recorded. The cis:trans ratio of the two isomers was determined from the S-methyl singlets which were clearly resolved in all spectra. Very little decomposition of the starting material was observed: \( k = 2.18 \times 10^{-2} \text{ hr}^{-1} \), \( k' = 3.42 \times 10^{-2} \text{ hr}^{-1} \) (trans \( \frac{k}{k'} \) cis) and \( t_{1/2} = 20.39 \text{ hr} \).

NOTE: 1,2-Dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate (93% trans:7% cis) was prepared by Dr. I. K. Nielsen.
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