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I OPTICALLY ACTIVE SULFOXIDES THE STEREOSPECIFICITY OF THE REACTION OF GRIGNARD REAGENTS WITH (-)-MENTHYL ARENESULFINATE ESTERS II ATTEMPT AT CONVERTING OPTICALLY ACTIVE DIARYL SULFOXIDES INTO OPTICALLY ACTIVE TRIARYLSULFONIUM SALTS

NICHOLAS E. PAPANIKOLAOU

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I. OPTICALLY ACTIVE SULFOXIDES. THE STEREO-
SPECIFICITY OF THE REACTION OF GRIGNARD RE-
AGENTS WITH (-)-MENTHYL ARENESULFINATE ESTERS.
II. ATTEMPT AT CONVERTING OPTICALLY ACTIVE
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INTO OPTICALLY ACTIVE TRIARYLSULFONIUM SALTS.

By

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B. A., St. Anselm's College, 1962

A THESIS

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In Partial Fulfillment of

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Department of Chemistry

December, 1966

This thesis has been examined and approved.

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December 15, 1966
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The author wishes to dedicate his thesis in memory of his parents Evangelos and Soultana, whose love and parental advice paved and lighted the way toward the achievement of this work.

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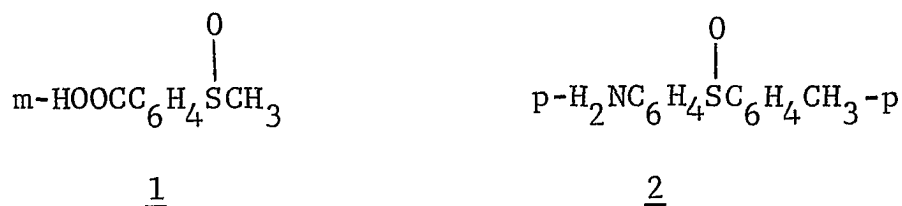
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PART I

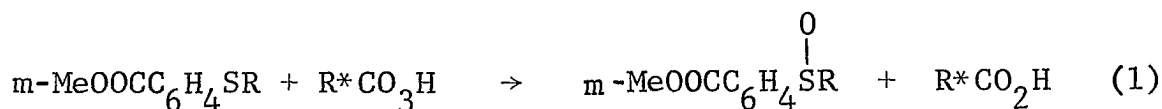
OPTICALLY ACTIVE SULFOXIDES. THE STEREOSPECIFICITY
OF THE REACTION OF GRIGNARD REAGENTS
WITH (-)-MENTHYL ARENESULFINATE ESTERS

INTRODUCTION

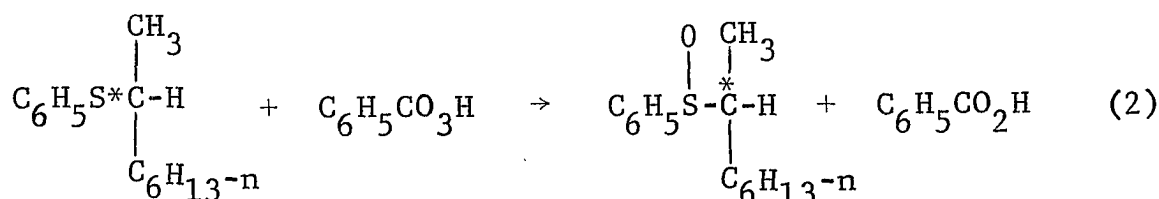
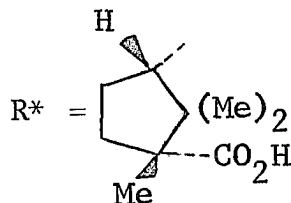
The successful resolution¹ of m-carboxyphenyl methyl sulfoxide (1) and p-aminophenyl p-tolyl sulfoxide (2) indicated that optical isomerism could exist in sulfoxides.

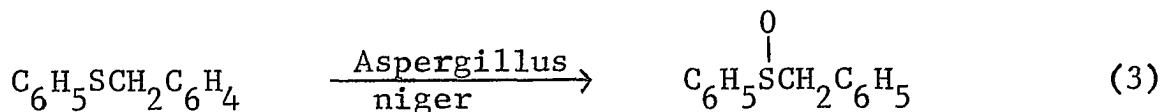


Resolution techniques, however, can only be applied to compounds that have certain functional groups present, and therefore, are limited in their scope. As a result, other methods were developed for the preparation of optically active sulfoxides. Such methods included asymmetric syntheses and fermentation processes. The first method involved oxidation of sulfides with^{2,3} (eq. 1), or without⁴ (eq. 2) optically active peracids, depending on the structure of sulfide, while the latter method involved microbial systems⁵ (eq. 3). These methods, however, produced sulfoxides of very low optical purity.^{6,7}

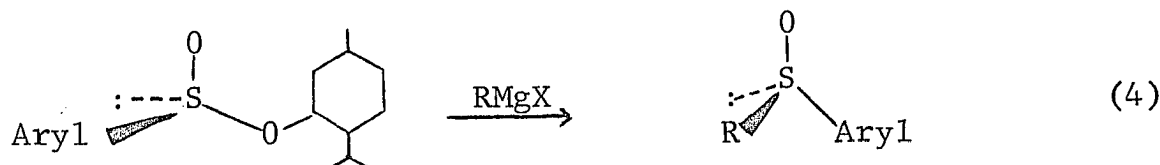


R=Me, Et, i-Pr, t-But

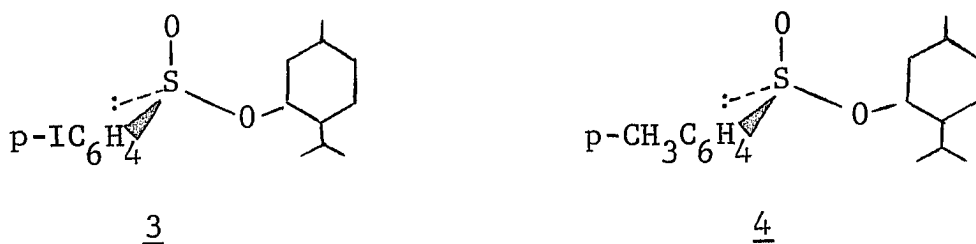




Recently, optically active sulfoxides were obtained from the reaction of Grignard reagents with optically active sulfinate esters.^{6,8} (eq. 4). This method produced high yields of sulfoxides of high optical purities.



Herbrandson and Cusano⁹ tentatively assigned the S-configuration to sulfur in (-)-menthyl (-)-p-iodobenzenesulfinate (3) on the basis of kinetic and thermodynamic data. Andersen⁶ assumed that (-)-menthyl (-)-p-toluenesulfinate ester (4) also had the S-configuration at the asymmetric sulfur center, since "para methyl and iodo groups would not be expected to change the sign of rotation of the powerfully rotating sulfinate ester group". Mislow and co-workers^{7,11} showed that both 3 and 4 had the S-configuration at sulfur.¹² The proof was based on x-ray analysis for the former, and chemical reactions for the latter.



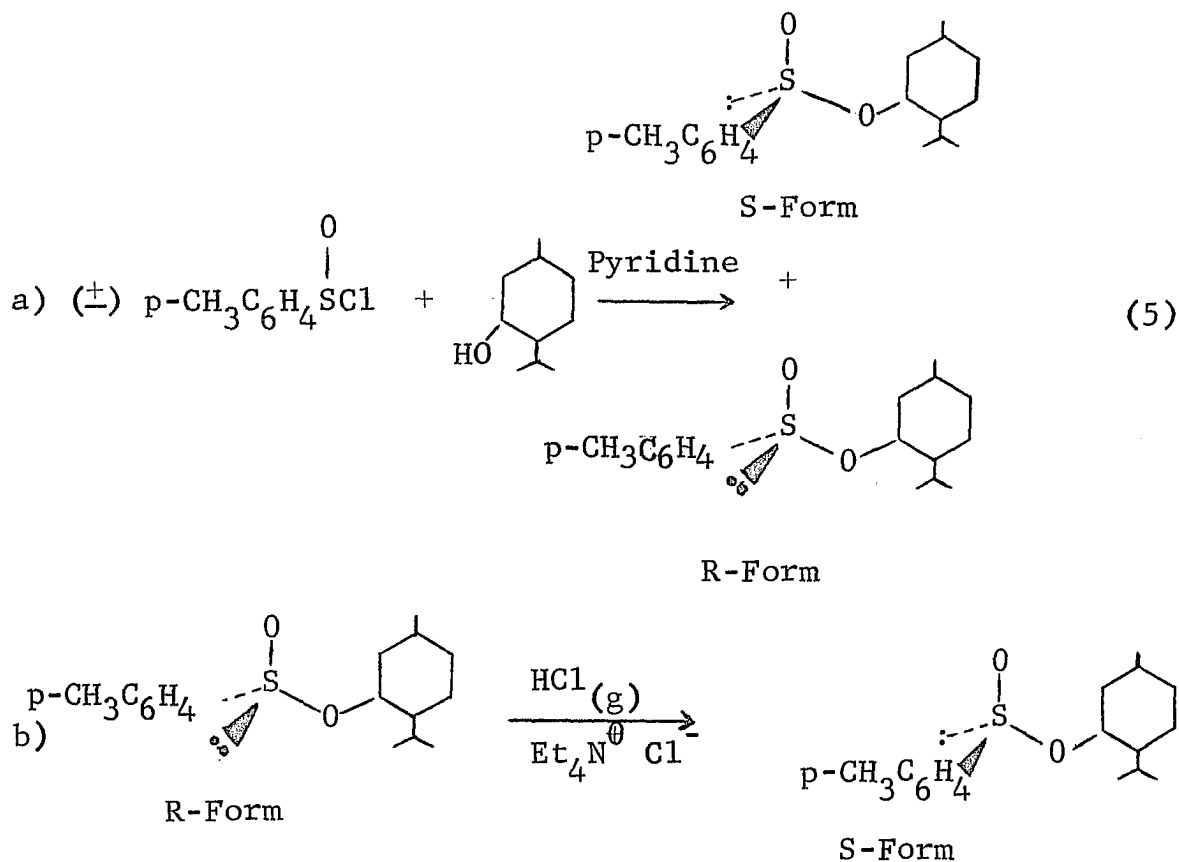
Andersen^{6,8} assumed that the reaction of Grignard reagents with optically active sulfinate esters goes with inversion of configuration at sulfur, on the basis of reported inversions at sulfur in the alcoholysis of optically

active alkyl p-toluenesulfinate esters¹⁴, and the basic hydrolysis of alkoxysulfonium salts¹⁵, ROSR_2^+ . In all three reactions, a nucleophilic attack on sulfur is involved. Based on this assumption, Andersen¹³ carried out chemical reactions, and correctly predicted the absolute configuration of naturally occurring levorotatory methyl isothiocyanate sulfoxides.¹⁷ Christensen and Kjaer¹⁸ confirmed Andersen's prediction by means of x-ray studies. Later, Mislow et al.⁷, unequivocally established the absolute configuration of optically active sulfinate esters and sulfoxides, and proved that the reaction of Grignard reagents with sulfinate esters proceeds with inversion.

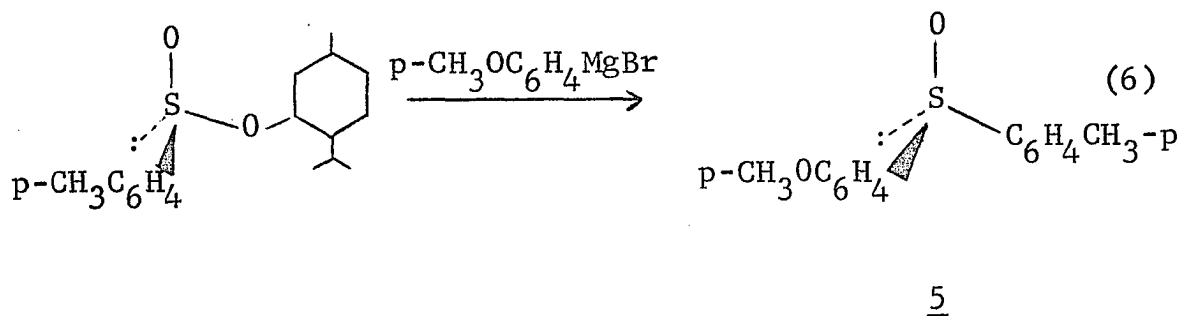
This part of the thesis deals with the problem of determining the stereospecificity of the reaction shown in eq. 4, i. e., whether the reaction proceeds with 100% inversion, or only partly so.

RESULTS AND DISCUSSION

The preparation of optically active sulfinate esters^{9,14,18} involves the reaction of racemic arenesulfinyl chlorides with (-)-menthol in ether-pyridine. The less soluble of the two epimers precipitates out and is removed by filtration. Addition of gaseous hydrogen chloride and a few crystals of tetraethylammonium chloride to the remaining ester catalyzes equilibration of the ester mixture. More of the less soluble epimer may thus be obtained. Repetition of this epimerization on the mother liquor permits high yields of one epimer to be isolated (70-90%). Both the reaction (a) and the epimerization (b) steps are exemplified in the case of (-)-menthyl p-toluenesulfinate (eq. 5).

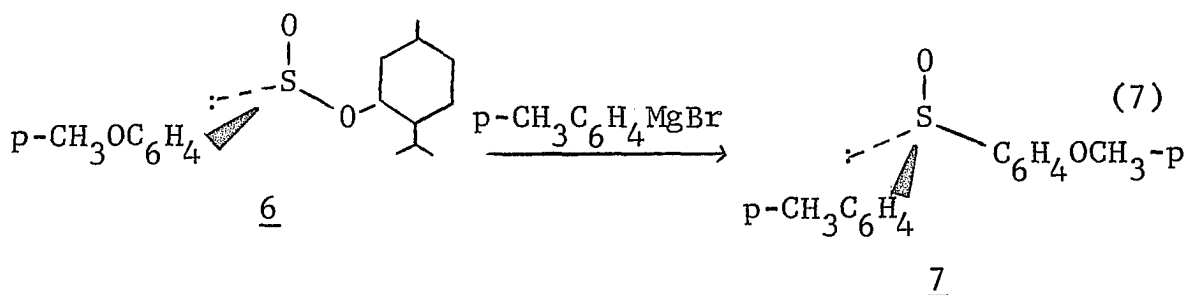


The reaction of p-methoxyphenylmagnesium bromide with (-)-menthyl (-)-p-toluenesulfinate (4) yielded (-)-p-anisyl p-tolyl sulfoxide (5) ($[\alpha]_D^{30} - 25^\circ$, c 1.99 in acetone) (eq. 6). Since the reaction proceeded with inversion⁷ of configuration the sulfoxide had the S-configuration.

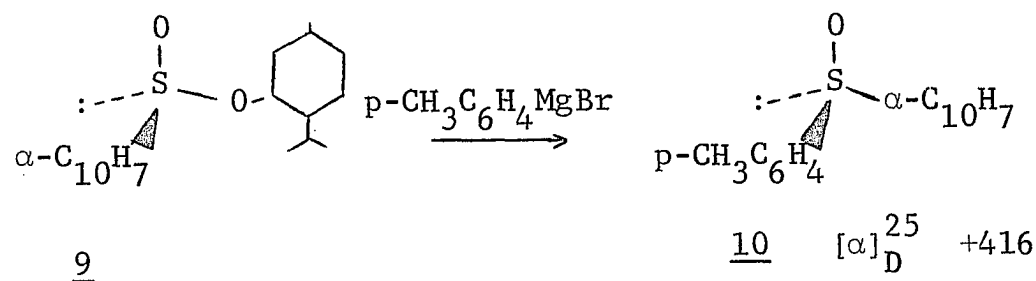
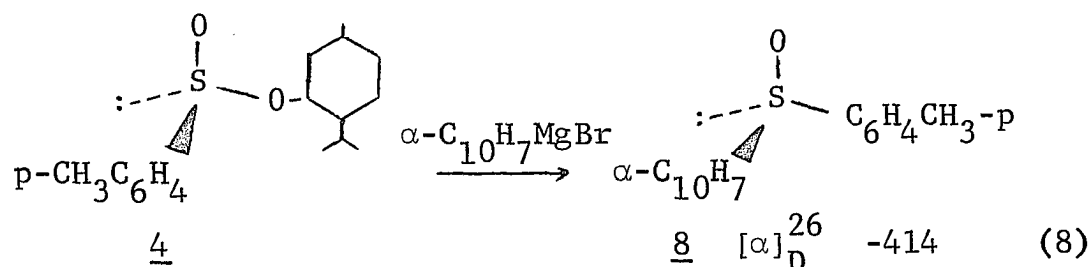


(-)-Menthyl (-)-p-methoxybenzenesulfinate¹⁸ (6) was prepared, in a similar fashion as (-)-menthyl (-)-p-toluenesulfinate (4), from p-methoxybenzenesulfinyl chloride and (-)-menthol in ether-pyridine. Both 4 and 6 were isolated as the least soluble epimers, and both have the S-configuration at sulfur as it is shown by eqs. 6 and 7 (see below), and the similar optical rotatory dispersion curves⁸ (fig. 1).

The reaction of S-(-)-menthyl (-)-p-methoxybenzenesulfinate (6) with p-tolylmagnesium bromide (eq. 7) yielded R-(+)-p-anisyl p-tolyl sulfoxide (7). Sulfoxide 7 had a rotation at the sodium D line ($[\alpha]_D^{20} + 24^\circ$, c 2.005 in acetone) equal in magnitude and opposite in sign to sulfoxide 5. In other words sulfoxides 5 and 6 are enantiomers.



A similar reaction, carried out by another investigator^{8,19} is shown in eq. 8. (-)-Menthyl (-)-p-toluenesulfinate (4) and 1-naphthylmagnesium bromide gave S-(-)- α -naphthyl p-tolyl sulfoxide (8) while (-)-menthyl (-)-1-naphthalenesulfinate (9) and p-tolylmagnesium bromide gave R-(+)- α -naphthyl p-tolyl sulfoxide (10).



$\alpha\text{-C}_{10}\text{H}_7 = \alpha\text{-naphthyl}$

The simplest immediate explanation of the results obtained from reactions (6), (7) and (8) is that the reactions are 100% stereospecific. In other words, optically pure sulfoxides are obtained when the general synthetic reaction (4) is employed.

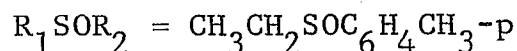
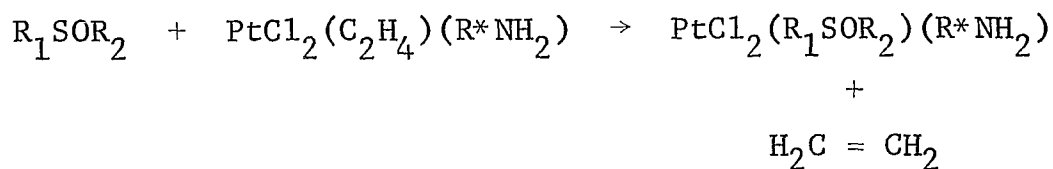
If the reaction is not completely stereospecific, then the observed equal rotation of the enantiomers (5 and 7) might have arisen from a) incompletely resolved sulfinate esters of the same optical purity, and b) incompletely resolved esters but of different optical purity. In the former case, these esters when treated with the different Grignard

reagents would have had to react either in completely stereospecific reactions or reactions with the same percentage of incomplete stereospecificity to yield sulfoxides of the same optical purity. In the latter case, the Grignard reactions would have had to proceed with different percentages of stereospecificity in order to yield enantiomeric sulfoxides fortuitously of the same optical purity. These situations seem most improbable.

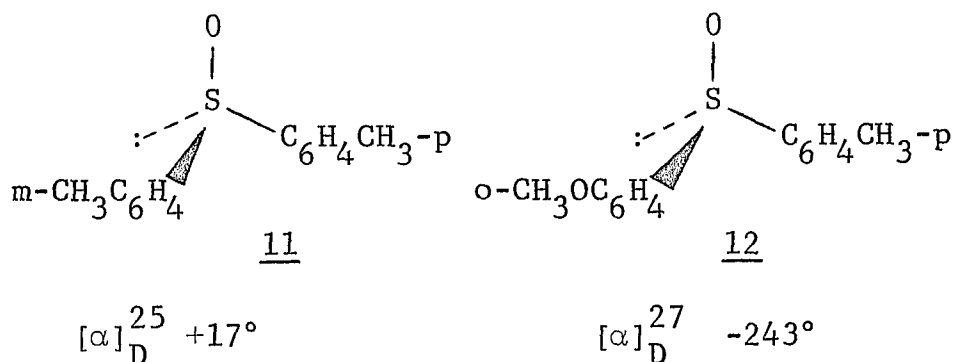
The only reasonable objection is that the sulfoxides were optically pure only because they were subjected to several recrystallizations. Any of the enantiomers formed by a competing reaction leading to retention of configuration might have been removed. This is possible, and it was demonstrated^{8,19} by mixing enantiomeric α -naphthyl p-tolyl sulfoxides (89 parts of levorotatory, and 11 parts of dextrorotatory) and recrystallizing once from acetone. The recovered sulfoxide had a rotation equal to that of the levorotatory enantiomer used to prepare the partially racemic mixture. However, since the pure sulfoxides are isolated in high yields, often over 80%, any reactions leading to racemization or retention must be minor.

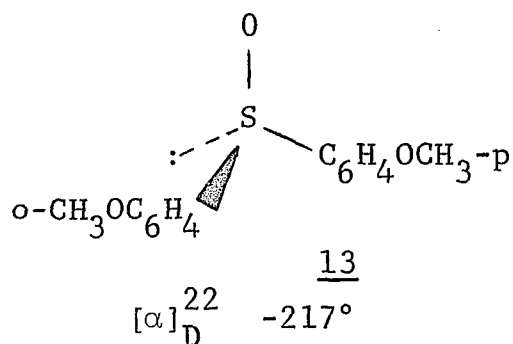
Evidence for the high optical yields of sulfoxides obtained by the general synthetic reaction (4) was provided by Cope and Caress.²⁰ Racemic ethyl p-tolyl sulfoxide was resolved via the complex (+ or -)-trans-dichloro(ethyl p-tolyl sulfoxide) (α -methylbenzylamine)platinum (II) (eq. 9). The diastereoisomers were separated by means of fractional crystallizations, and then decomposed with aqueous cyanide solution to give optically active sulfoxides ($[\alpha]_D^{25} +203$ and $[\alpha]_D^{25} -204$, c 0.93 in acetone). (+)-Ethyl p-tolyl sulfoxide prepared according to eq. (4), from (-)-menthyl

(-)-p-toluenesulfinate ester and ethylmagnesium bromide had $[\alpha]_D^{25} +186^\circ$ ⁸ and $[\alpha]_D^{25} +188^\circ$.⁷ Since the sulfoxide in the latter case was about 92% optically pure, the reaction went with 96% inversion and 4% retention. However, the retention in ethyl p-tolyl sulfoxide might be attributed to slightly impure starting materials such as (-)-menthol and (-)-menthyl (-)-p-toluenesulfinate ester, but that is only an assumption. It is possible that racemization occurred during distillation. The stereospecificity, therefore, is established beyond any shadow of a doubt, and if it is not 100%, it is very close to it.



In addition to sulfoxides S-5 and R-7, S-(+)-m-tolyl p-tolyl sulfoxide 11, and S-(-)-o-anisyl p-tolyl sulfoxide (12) were prepared from S-4, while S-(-)-o-anisyl p-anisyl sulfoxide (13) was prepared from S-6. The effect of the substituents on the optical rotation is clearly seen, but it will be discussed later with the optical rotatory dispersion studies.





The reaction of the aryl Grignard reagents with the arenesulfinate esters may be carried out at room temperature, since aryl sulfoxides react with aryl²¹ Grignard reagents only when at reflux in high boiling solvents (benzene or toluene). Therefore, this fact allowed the employment of two equivalents of the Grignard reagent in order to insure complete reaction of the arenesulfinate ester. Indeed, employment of excess Grignard reagent increases the yield of the diaryl sulfoxides considerably, than when one equivalent of the Grignard reagent is employed. The order of addition had no effect, and usually the ester was added to the Grignard solution. The crude product, after isolation, was always stirred with dilute aqueous sodium hydroxide solution in order to insure complete hydrolysis of any unreacted ester. The only exception, where no basic hydrolysis was employed, was in the preparation of (-)-p-anisyl p-tolyl sulfoxide (5). Although diaryl sulfoxides are racemized under certain acidic²² or thermal²³ conditions, they are unaffected in the aforementioned basic conditions.

Infrared Spectra. All sulfoxides and sulfinate esters show the characteristic sulfoxide and sulfinate S-O stretching band at about 1050 cm^{-1} and 1140 cm^{-1} , respectively.

Ultraviolet Spectra. The ultraviolet spectral data for the sulfinate esters and sulfoxides are listed in Table

1. The ultraviolet spectra of sulfinates esters^{7,8}, and sulfoxides^{7,8,24,25} have been previously discussed to some extent. Dialkyl sulfoxides absorb near 220 m μ ($\log \epsilon$ 3.2), presumably due to an $n \rightarrow \pi^*$ transition. The ultraviolet spectra of alkyl aryl sulfoxides and diaryl sulfoxides are complicated and more difficult to explain. The spectra of such compounds are considered as benzene spectra perturbed by resonance interaction between the aromatic π -system and the sulfinyl chromophore. Further perturbations are caused by additional substituents on the aromatic ring. There are usually two bands observed above 230 m μ for the compounds listed in Table 1. The short-wavelength, high intensity band has been designated the primary band, while the long-wavelength, lower-intensity band, has been designated as the secondary band. Any absorption below 230 m μ has been designated as a second primary band.²⁴

The position of the sulfoxide $n \rightarrow \pi^*$ transition in these aryl sulfinyl compounds is unclear. This transition presumably involves promotion of non-bonded electrons in sulfur to an unoccupied orbital of the aromatic ring, rather than to the sulfinyl group as postulated for dialkyl sulfoxides.^{7,24} The intense primary band is considered⁸ to arise from strong coupling between the local benzene $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations. The primary band for p-toluenesulfinates esters, as well as for alkyl aryl sulfoxides^{7,8,24}, is generally solvent dependent and blue shifted on going to polar solvents. Such bathochromic shifts are typical for $n \rightarrow \pi^*$ transitions. The fact that the absorption spectra of sulfinates (Table 1) parallel those of the alkyl aryl sulfoxides⁸ suggests that the electronic transition which is responsible for the primary band of both types of compounds is closely similar and comparable.

The interpretation of the absorption spectra of diaryl sulfoxides²⁴ is difficult, and the $n \rightarrow \pi^*$ transition is not readily identified, since many times no solvent effects are observed. Mislow, et al.⁷, report that m-tolyl p-tolyl sulfoxide (11) shows a red shift (longer wavelengths) on going from isooctane (233.5 m μ) to ethanol (238 m μ). Generally, simple diaryl sulfoxides have a very intense primary band ($\log \epsilon$ 4) at 230-250 m μ , and a somewhat less intense ($\log \epsilon$ 3.5) secondary band at 260-290 m μ . Figures 1 and 3 show the ultraviolet spectra of the aforementioned compounds.

Optical Rotatory Dispersion Curves. The optical rotatory dispersion and circular dichroism studies on optically active sulfoxides and sulfinate esters have previously been discussed.^{7,8} Both types of compounds have been classified^{8,26,27}, with the exception of para- and meta-substituted diaryl sulfoxides^{7,8}, as inherently dissymmetric chromophores. These have in common a dissymmetrically twisted π -system which essentially constitutes the entire chromophore. In inherently dissymmetric chromophores, the molecular amplitude of the optical rotatory dispersion curve and the maximum value of the circular dichroism curve are generally quite high.²⁸ The optical rotatory dispersion curves of the sulfinate esters and the sulfoxides are shown in Figures 2 and 4, while the molecular rotations at different wavelengths are listed in Table 3. The Cotton effect midpoints and amplitudes are listed in Table 2.

The arenesulfinate esters and diaryl sulfoxides seem to follow one of two patterns. The monoarylsulfinyl compounds 4, 6 have major Cotton effects, large in amplitude, which correlate well with their respective primary ultraviolet absorption bands (Table 1), and minor Cotton effects occurring as shoulders on the optical rotatory dispersion

curves which correlate with their secondary ultraviolet absorption bands. On the other hand, the diarylsulfinyl compounds 5, 7, 11 and 13, follow a different pattern. They have long wavelength Cotton effects well correlated with their secondary ultraviolet bands, but the short wavelength Cotton effects are not correlated with the primary ultraviolet bands; these Cotton effects occur at wavelengths shorter than the primary ultraviolet bands.²⁹

In sulfinate esters, as well as in alkyl aryl sulfoxides^{7,8}, a π -system, dissymmetric in all of its conformations, is produced which leads to high intensity Cotton effects (Fig. 2). However, the situation is different for diaryl sulfoxides. For diphenyl sulfoxide, a series of conformers may exist, some of which are dissymmetric. However, diphenyl sulfoxide is inactive since each conformer capable of showing optical activity has its mirror image present in equal number in the liquid state. The situation changes slightly when substituents are introduced. Two effects seem likely. The π -system would be asymmetrically perturbed and the conformations of a substituted ring vs. an unsubstituted ring relative to the sulfinyl group would be different. No longer would one dissymmetric conformation have an equal number of mirror image conformations present to cancel its contribution to the overall optical rotation of the sample. This latter reason would be expected to become more important as substituents began to sterically interfere with the sulfinyl oxygen; i. e., ortho substituents. This seems to be reflected in the amplitudes of the Cotton effects. In general, the ortho substituted diaryl sulfoxides have Cotton effects^{7,8} larger in amplitude than the meta and para substituted compounds (Table 2). Essentially, the diaryl sulfoxide chromo-

phore is symmetric when meta or para substituted. When ortho substituted, however, the molecule gives Cotton effects increased in amplitude. Its chromophore can then be classified as inherently dissymmetric.^{7,8}

The sign of the Cotton effect in a series of simple alkyl aryl sulfoxides^{7,8} is opposite and comparable to that of their parent ester, i. e., it is inverted. However, the sign of the Cotton effect in the diaryl sulfoxides depends on the substituents present. For example, both (-)-p-anisyl p-tolyl sulfoxide (5) and (+)-m-tolyl p-tolyl sulfoxide (11) have a p-toluenesulfinyl group of the same configuration in common since they were both synthesized from the same ester (4). Sulfoxide (5) has a negative Cotton effect, while sulfoxide 11 has a positive Cotton effect. The parent ester 4 has a negative Cotton effect.

TABLE 1

<u>Compound no.</u>	Ultraviolet spectra ^a		
	<u>Second primary band</u>	<u>Primary band</u>	<u>Secondary band</u>
<u>4</u>	225(4.06) 223(4.09) ^b	246(3.82) 256(3.66) ^b	273 ^s (3.05)
<u>6</u>		247(4.05)	281 ^s (2.94)
<u>5</u>		246(4.34)	
<u>7</u>		246(4.34)	
<u>11</u>		238(4.23)	268 ^s (3.83)
<u>13</u>		244(4.29)	278(3.84)

^a λ_{\max} in μ , log ϵ in parentheses; solvent, 95% ethanol unless specified otherwise. ^bIn isooctane. ^sShoulder.

TABLE 2

Compound no.	Cotton effects midpoints and amplitudes ^{a, e}		
	Second primary band	Primary band	Secondary band
<u>4</u>	(-) ^b	248(-73,000)	d
	(-) ^b	253(-61,000) ^c	d
<u>6</u>	(-) ^b	252(-97,000)	d
<u>5</u>	(-) ^b		270-261(-29,000) ^d
<u>7</u>	(+) ^b		270-261(+31,000) ^d
<u>11</u>	(+) ^b		260-256(+13,000) ^d
<u>13</u>		239(-90,000) ^c	281(-109,000)

^a λ_{\max} in m μ ; solvent, 95% ethanol unless specified otherwise. Midpoints calculated as halfway between the peak and trough of the o.r.d. curve. Where multiple peaks or troughs occur, a range is given. Amplitudes are apparent since multiple Cotton effects are often involved. ^b Apparent sign of a shorter wavelength c.e. Instrumental limitations preclude its measurement. These c.e. are not necessarily associated with the second primary ultraviolet band. ^c In isooctane. ^d One or more c.e. in this region apparent as shoulder on o.r.d. curve. ^e Amplitude is defined as $[\theta]_{\text{first extremum}} - [\theta]_{\text{second extremum}}$.

TABLE 3

<u>Compound no.</u>	<u>Optical Rotatory Dispersion^a</u>	<u>Concentration^b</u>
<u>4</u>	[\emptyset] ₃₅₀ -2670, [\emptyset] ₂₇₇ -15,500, [\emptyset] ₂₇₄ -14,200, [\emptyset] ₂₆₀ -19,800, [\emptyset] ₂₅₁ 0, [\emptyset] ₂₃₅ 53,300, [\emptyset] ₂₁₉ 0, [\emptyset] ₂₀₃ -44,000, [\emptyset] ₂₀₀ -41,900	0.116, 0.0116 E
<u>4</u>	[\emptyset] ₃₀₀ -6540, [\emptyset] ₂₇₇ -19,600, [\emptyset] ₂₇₄ -19,100, [\emptyset] ₂₇₂ -20,200, [\emptyset] ₂₅₈ 0, [\emptyset] ₂₃₃ 40,900, [\emptyset] ₂₁₉ 0, [\emptyset] ₂₁₂ -32,700, [\emptyset] ₂₁₅ -27,300	0.0054 I
<u>6</u>	[\emptyset] ₃₅₀ -2810, [\emptyset] ₂₆₃ -27,500, [\emptyset] ₂₅₅ 0, [\emptyset] ₂₄₁ 69,500, [\emptyset] ₂₂₈ 0, [\emptyset] ₂₂₂ -14,600, [\emptyset] ₂₂₀ -12,900, [\emptyset] ₂₁₅ -14,600	0.096, 0.0096 E
<u>5</u>	[\emptyset] ₃₅₀ -502, [\emptyset] ₂₈₉ -4330, [\emptyset] ₂₈₃ -2280, [\emptyset] ₂₇₈ -4100, [\emptyset] ₂₇₃ -1820, [\emptyset] ₂₇₁ -2280, [\emptyset] ₂₆₀ 0, [\emptyset] ₂₅₀ 25,100, [\emptyset] ₂₄₀ 0, [\emptyset] ₂₂₈ -31,900, [\emptyset] ₂₁₅ -9100	0.054, 0.0054 E 0.0011 E
<u>7</u>	[\emptyset] ₃₅₀ 384, [\emptyset] ₂₉₀ 6400, [\emptyset] ₂₈₃ 4430, [\emptyset] ₂₇₈ 6400,	0.005, 0.001 E

Table 3 (continued)

Compound no.	Optical Rotatory Dispersion ^a	Concentration ^b
	$[\phi]_{274}$ 2960, $[\phi]_{272}$ 3450, $[\phi]_{266}$ 0, $[\phi]_{250}$ -24,600, $[\phi]_{242}$ 0, $[\phi]_{227}$ 49,300, $[\phi]_{220}$ 22,200, $[\phi]_{215}$ 27,100	
<u>11^c</u>	$[\phi]_{350}$ 501, $[\phi]_{280}$ 3460, $[\phi]_{277}$ 1610, $[\phi]_{272}$ 2030, $[\phi]_{265}$ 0, $[\phi]_{240}$ -9700, $[\phi]_{226}$ 0, $[\phi]_{212}$ 37,000, $[\phi]_{210}$ 22,400	0.1930, 0.0193, E 0.0038
<u>13</u>	$[\phi]_{350}$ -4710, $[\phi]_{293}$ -46,500, $[\phi]_{283}$ 0, $[\phi]_{268}$ 62,000, $[\phi]_{251}$ 0, $[\phi]_{247}$ -16,100, $[\phi]_{242}$ 0, $[\phi]_{230}$ 73,900, $[\phi]_{220}$ 19,100, $[\phi]_{215}$ 35,800	0.044, 0.0044 E

^aAll curves plain from 589 m μ to first value listed. ^bG/100 ml. of solvent.
Solvents: E, 95% ethanol; I, isooctane. ^cMislow, et al.⁸, report, $[\phi]_{320}$ +570,
 $[\phi]_{281}$ +3400 (peak), $[\phi]_{275}$ +1120 (trough), $[\phi]_{273}$ +1920 (peak), $[\phi]_{268}$ 0,
 $[\phi]_{265}$ -1100 (shoulder), $[\phi]_{242}$ -11,800 (trough), $[\phi]_{228}$ 0, $[\phi]_{213}$ +51,000 (peak),
 $[\phi]_{207.5}$ +29,000, in absolute ethanol and concentrations. 0.0444-0.00056. In
isooctane and concentrations 0.00456-0.00114: $[\phi]_{281}$ +3000 (peak), $[\phi]_{276}$ +1200
(trough), $[\phi]_{273}$ +1600 (peak), $[\phi]_{269}$ 0, $[\phi]_{265.5}$ -1100 (trough), $[\phi]_{264}$ -900 (peak),
 $[\phi]_{238}$ -18,000 (trough), $[\phi]_{227}$ 0, $[\phi]_{215}$ +50,000 (peak), $[\phi]_{205}$ 0.

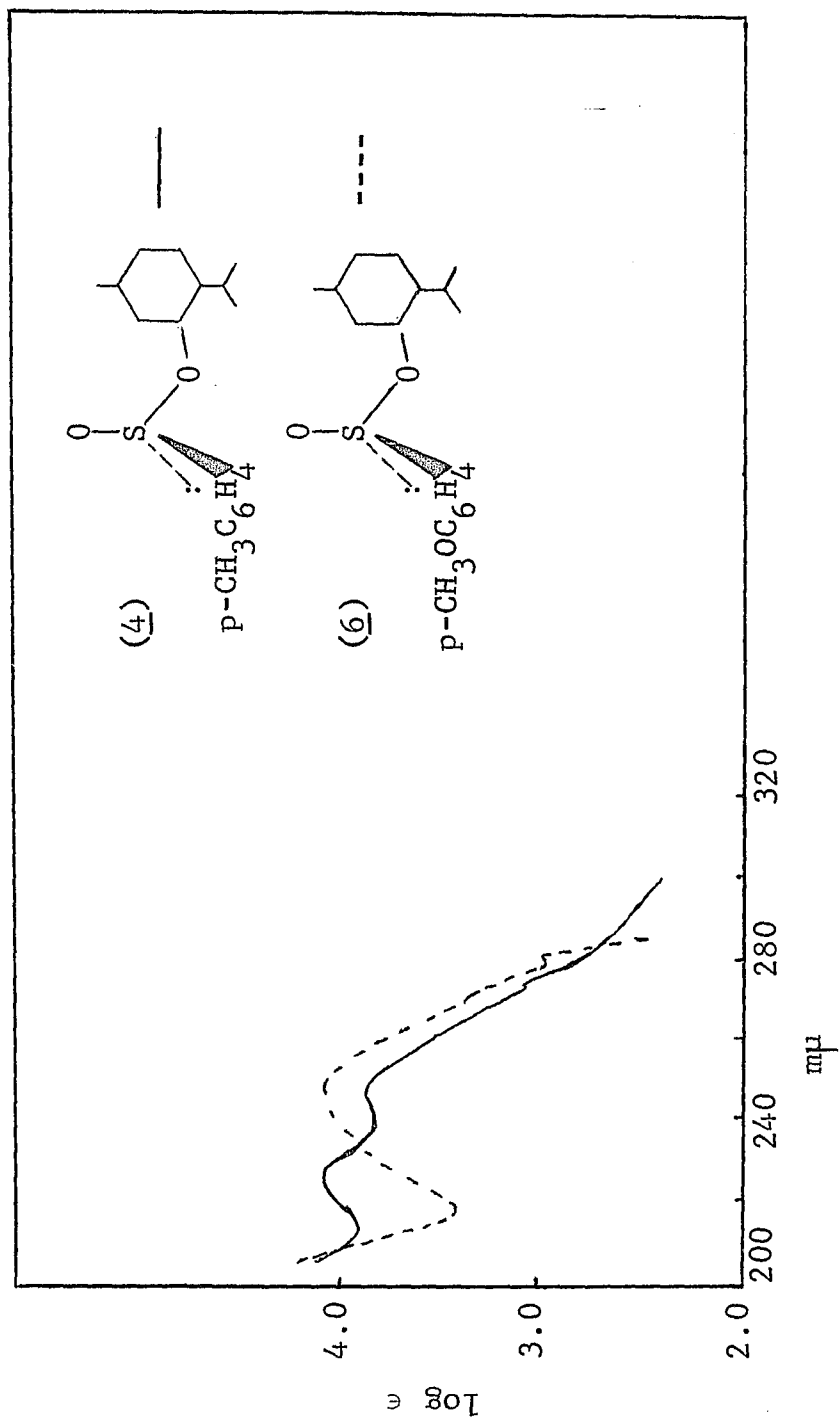


Fig. 1. - Ultraviolet spectra of 4 and 6 (see Table 1).

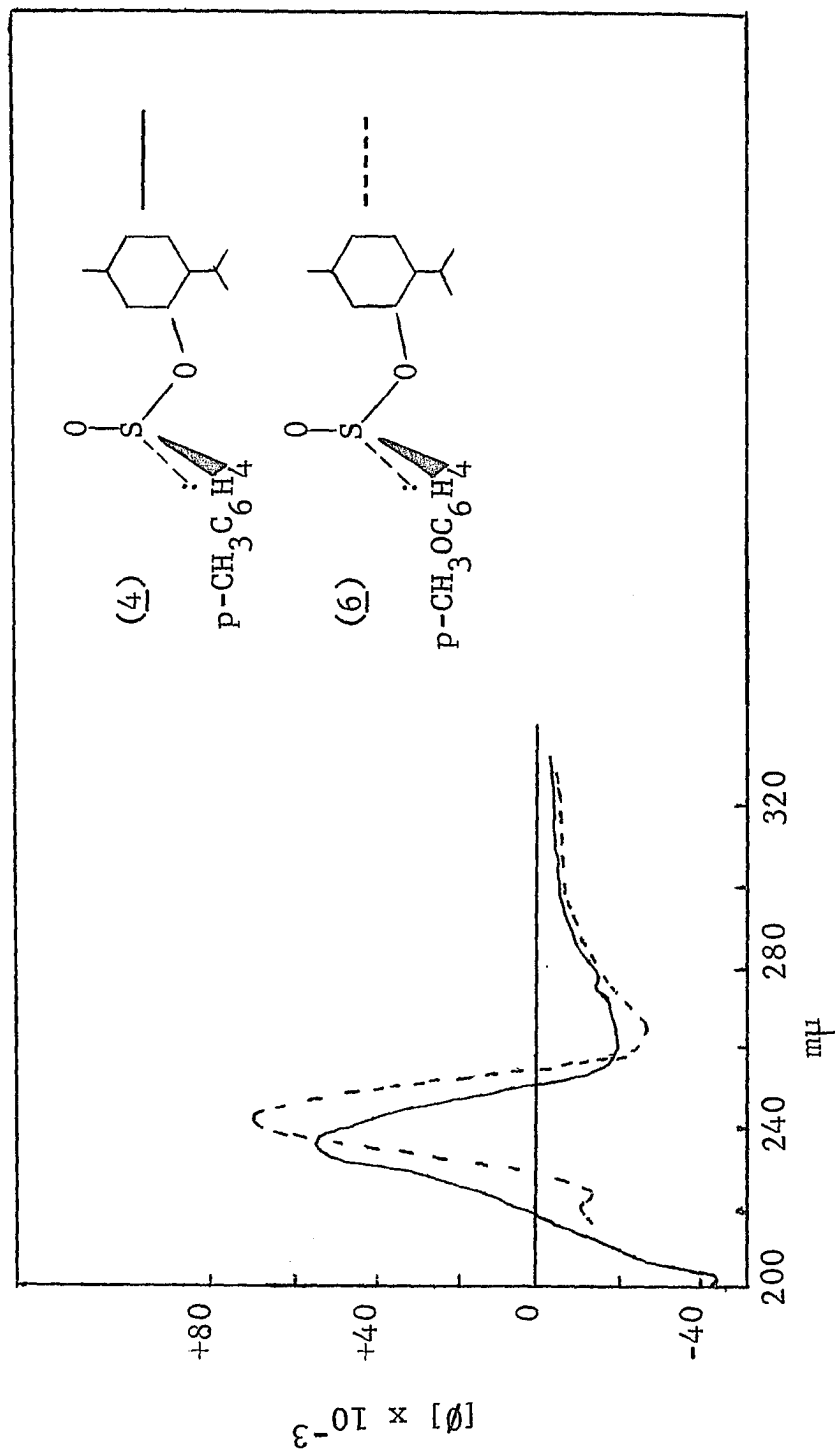


Fig. 2 - Optical rotatory dispersion curves of 4 and 6 (see Table 3).

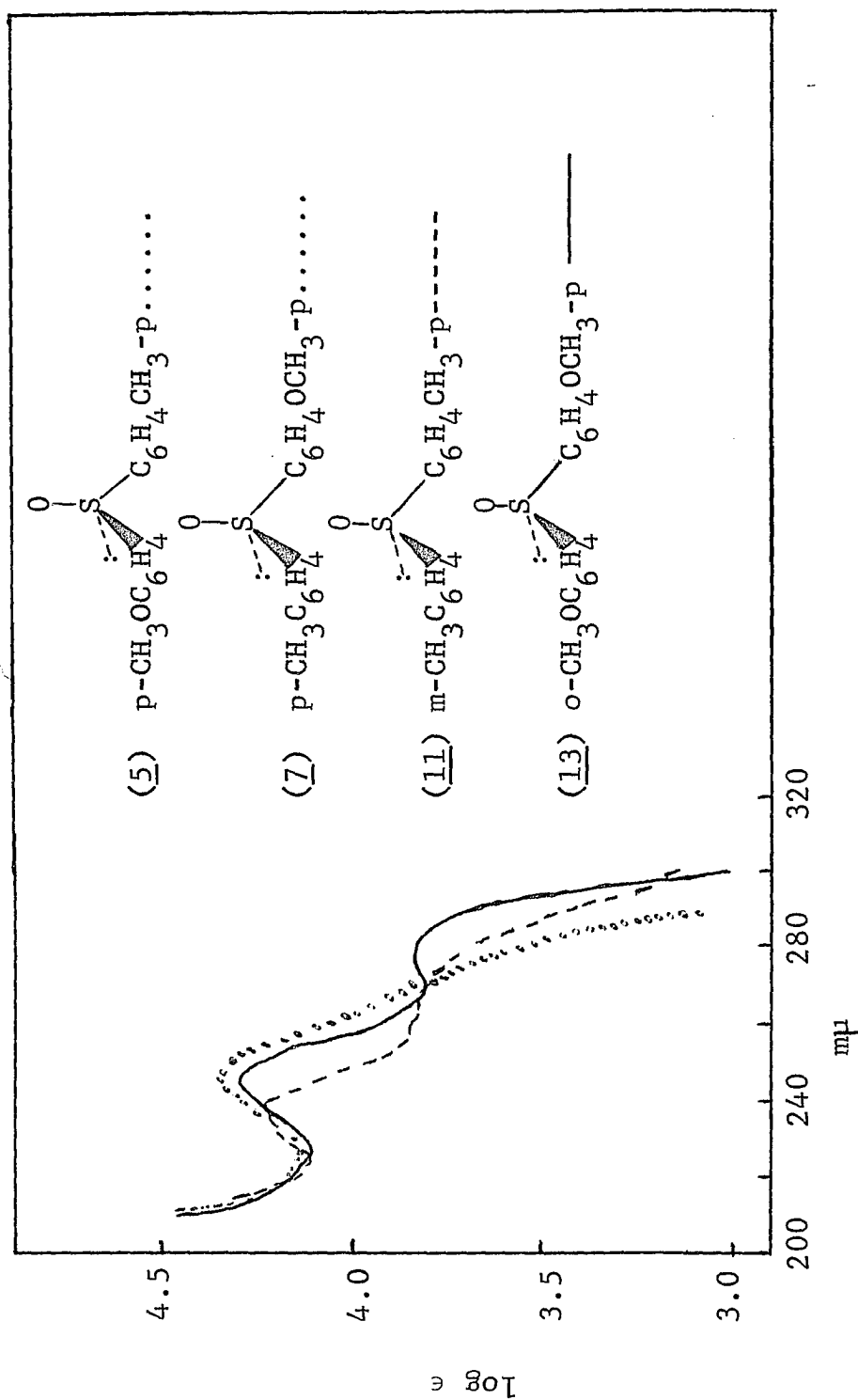


Fig. 3 - Ultraviolet spectra of 5, 7, 11, and 13 (see Table 1).

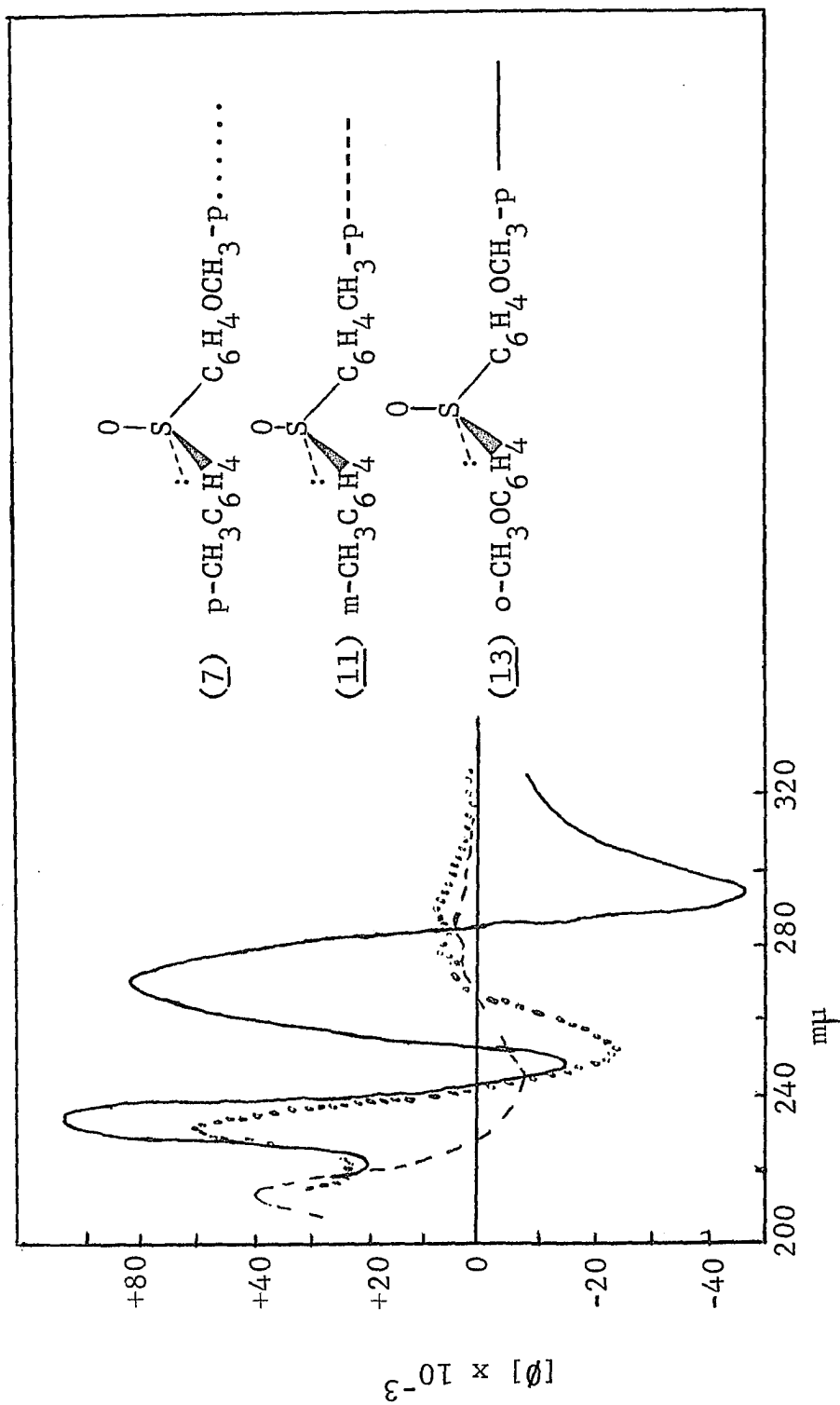


Fig. 4 - Optical rotatory dispersion curves of 7, 11, and 13
(see Table 3).

DESCRIPTION OF EXPERIMENTS

The infrared absorption spectra were determined with a Perkin-Elmer Model 21 infrared spectrophotometer, or a Perkin-Elmer Model 337 grating infrared spectrophotometer. The nuclear magnetic resonance spectra were determined with a Varian Model A-60 nuclear magnetic resonance spectrometer. The ultraviolet absorption spectra were measured with a Model 4000 spectracord, or a Cary Model 14.

The optical rotations at the sodium D line were determined with a Franz Schmidt and Haensch polarimeter. The optical rotatory dispersions were determined on a Cary Model 60 recording spectropolarimeter, or a Rudolph Model 260/655/850/810-614 recording spectropolarimeter.

Microanalyses were determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The boiling points and melting points are in degrees centigrade and are uncorrected.

Sodium p-Toluenesulfinate.³⁰ - p-Toluenesulfonyl chloride (190.7 g., 1.000 mole) was ground in a mortar to break up all lumps. Distilled water (1.8 l.) was placed in a 4-l. beaker provided with a mechanical stirrer and rubber tubing for passing steam directly into the water. Steam was passed into the water until the temperature reached 70°. The steam was shut off and zinc dust (260 g., 2.00 g. atoms) was added. The sulfonyl chloride was then added in small portions by means of a porcelain spoon over a 10-min. period. Stirring was continued for ten minutes after the last of the sulfonyl chloride had been added. Steam was then passed into the mixture until the temperature reached 90°. The steam was then shut off, and 12 N aqueous sodium hydroxide solution (200 ml.) was added. Then powdered sodium carbonate (100 g., 0.945 mole) was added carefully to avoid frothing. The mixture was filtered by suction. The cake of unchanged zinc dust and zinc compounds was transferred back to the beaker and distilled water (600 ml.) was added. The stirrer was started and steam was passed in until the mixture started to froth violently. The steam was then shut off, but the stirring was continued for ten minutes. The mixture was filtered and the filtrate was added to the main solution in a large evaporating dish. The solution was concentrated to 300 ml. by means of a Bunsen burner, cooled to room temperature and then to ice temperature. The mixture was filtered and the white crystals were air-dried. The product according to the literature³⁰ is the dihydrate salt. Yield: 214 g. (1.00 mole, 100% yield).

Toluenesulfinyl Chloride.³¹ - Powdered sodium p-toluenesulfinate salt dihydrate (150 g., 0.701 mole) was added in portions into a round bottomed flask containing thionyl chloride (500 ml., 755 g., 6.35 mole) at room temperature over a 20-min. period. The temperature rose at first but soon it dropped to 0°C as the addition proceeded. The reaction mixture, a yellow liquid containing a white solid, was protected from moisture by means of a calcium chloride drying tube, and was set aside at room temperature for 3 hrs. The excess thionyl chloride was distilled off at aspirator pressure at 30-50°. The last traces of thionyl chloride were removed by addition, followed by removal using the aspirator, of small portions of anhydrous ether. The crude p-toluenesulfinyl chloride was dissolved in anhydrous ether, and filtered by suction under a nitrogen atmosphere. The inorganic solid was washed with several portions of anhydrous ether, and ether solution was concentrated until a heavy oil was obtained. Yield: 74 g. (0.42 mole, 61% yield).

(-)-Menthyl (-)-p-Toluenesulfinate.¹⁸ - p-Toluenesulfinyl chloride (74 g., 0.42 mole) was diluted with anhydrous ether (100 ml) and added to a 300-ml. three-neck, round bottomed flask provided with a mechanical stirrer, an addition funnel, and a reflux condenser with a calcium chloride drying tube. A solution of (-)-menthol (64 g., 0.41 mole) and anhydrous pyridine (37 g., 0.47 mole) in anhydrous ether (20 ml.) was added dropwise at -5° to 0° over a 50-min. period. The reaction mixture was allowed to come to room temperature and then 5% aqueous hydrochloric acid (50 ml.) was added dropwise over a 20-min. period. After separation of the layers, the organic layer was washed

twice with 5% hydrochloric acid (50 ml.), once with aqueous sodium carbonate (50 ml.), twice with distilled water (50 ml.), and finally dried over anhydrous magnesium sulfate. After filtering, the ether solution was concentrated (200 ml.) and cooled in a Dry Ice acetone bath. Tetraethylammonium chloride (0.05-0.1 g.) was added, and hydrogen chloride gas was bubbled in slowly for about five minutes. Crystals were obtained. After filtering, the solution was concentrated to smaller and smaller volumes, and treated as above with tetraethylammonium chloride, and hydrogen chloride gas. When the solution was 50 ml., no more crystals could be obtained. Yield: 80 g. (0.26 mole, 68% yield). The crude ester was recrystallized five times from 3.5-1 (by weight) acetone-water, air-dried, and finally placed in an evacuated desiccator over anhydrous calcium chloride. The specific rotation ($[\alpha]_D^{25.5} -199^\circ$, c 1.950, acetone) agreed with that given in the literature³² ($[\alpha]_D^{25} -199.19^\circ$, c 2, acetone).

p-Bromoanisole.³³ - p-Bromophenol (67.7 g., 0.391 mole) was dissolved in an aqueous sodium hydroxide solution (16 g., 0.40 mole). Dimethyl sulfate (54 g., 0.43 mole) was added dropwise with stirring. The basic solution was stirred for one hour. The yellow oil that appeared was taken up in ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and concentrated until a yellow oil (73.6 g.) was obtained. Distillation at aspirator pressure gave a colorless liquid (62 g., 0.32 mole, 85% yield).

(-)-p-Anisyl p-Tolyl Sulfoxide.^{6,8} - A solution of (-)-menthyl (-)-p-toluenesulfinate (20.2 g., 0.069 mole) in anhydrous ethyl ether (250 ml.) was placed into a 3-neck round bottomed flask equipped with a stirrer, an addition funnel and a condenser with a calcium chloride drying tube. A solution of p-anisyl magnesium bromide (0.075 mole), prepared from p-bromoanisole (14 g., 0.075 mole) and magnesium (3.0 g., 0.13 g. atom) in anhydrous ethyl ether, was added dropwise with stirring at 0°. After hydrolysis with saturated aqueous ammonium chloride, the layers were separated and the ether solution was dried over anhydrous sodium sulfate. After filtration and concentration of the solvent, cooling gave white crystals (5.79 g.) which were recrystallized several times from petroleum ether. Odorless white, cotton-like crystals (0.6586 g., 0.003 mole, 4.1% yield, $[\alpha]_D^{29.5}$ -24.7°, c 1.990, acetone) were obtained, m.p. 79.5-80.5°. Infrared spectrum no. 4857.

p-Methoxybenzenesulfonyl Chloride.³⁴ - Chlorosulfonic acid (327 g., 2.80 mole) was added dropwise with stirring to a solution of anisole (150 g., 1.40 mole) in chloroform (600 ml.) at -5° to 0° over a 35-min. period. The reaction mixture changed from colorless to yellow, and then to orange as the reaction proceeded. The reaction mixture was allowed to come to 20° with stirring, and then it was poured carefully onto crushed ice. The product was extracted with chloroform, dried over anhydrous magnesium sulfate, filtered, and concentrated at aspirator pressure. A white solid was obtained (188.5 g.) which was distilled at aspirator pressure (160 g., 0.777 mole, 55.5% yield). M.p. 40-41°, lit.³⁴, 41-42°. Infrared spectrum no. 190.

Sodium p-Methoxybenzenesulfinate. - The procedure was the same as in the case of sodium p-toluenesulfinate. Sodium p-methoxybenzenesulfinate dihydrate (126 g., 0.550 mole, 71% yield) was prepared from p-methoxybenzenesulfonyl chloride (160 g., 0.777 mole), and zinc powder (130 g., 2.00 g. atom).

p-Methoxybenzenesulfinyl Chloride. - The procedure was the same as in the case of p-toluenesulfinyl chloride. p-Methoxybenzenesulfinyl chloride (77 g., 0.44 mole, 74% yield) was prepared from sodium p-methoxybenzenesulfinate dihydrate (126 g., 0.550 mole) and thionyl chloride (476 ml., about 4 moles).

(-)-Menthyl (-)-p-Methoxybenzenesulfinate. - The procedure was the same as in the case of (-)-menthyl (-)-p-toluenesulfinate except that most of the ester precipitated out of the ether solution as soon as it was formed. The ether solution was treated with tetraethylammonium chloride, and hydrogen chloride gas to obtain more of the desired ester. (-)-Menthyl (-)-p-methoxybenzenesulfinate (92 g., 0.30 mole) was prepared from a solution of methoxybenzenesulfinyl chloride (77 g., 0.44 mole) in anhydrous ethyl ether (50 ml.), and a solution of (-)-menthol (60 g., 0.39 mole) in pyridine (40 g., 0.50 mole) and anhydrous ethyl ether (50 ml.) The ester was recrystallized four times from acetone water solution (3.5-1 by weight) and the pure ester (35 g., 0.11 mole, 28% yield) was dried in an evacuated desiccator over anhydrous calcium chloride. M.p. 101-104°, lit., 116-117.5°, $[\alpha]_D^{23.5} -189.2^\circ \pm 3$ (c 1.20, acetone), lit.¹⁸, $[\alpha]_D^{25} -190.3^\circ$ (c 1.2, acetone). Infrared spectrum no. 15.

(+)-p-Anisyl p-Tolyl Sulfoxide. - p-Tolyl magnesium bromide (0.064 mole) was prepared from magnesium (2 g., 0.08 g. atom) and p-tolyl bromide (11 g., 0.064 mole) in anhydrous ethyl ether (100 ml.) in a 3-neck round bottomed flask, provided with a magnetic stirrer, an addition funnel, and a reflux condenser with a calcium chloride drying tube. A solution of (-)-menthyl (-)-p-methoxybenzenesulfinic acid ester (10 g., 0.032 mole) in anhydrous tetrahydrofuran (50 ml.) was added dropwise over a 2³/₄ hr. period with stirring and cooling in an ice bath. After stirring for an additional one hour at room temperature, saturated aqueous ammonium chloride was added at 0°, filtered and the layers were separated. The aqueous layer was washed three times with tetrahydrofuran (40 ml.), which was combined with the main organic layer. After drying over anhydrous magnesium sulfate, the solution was filtered, concentrated (40 ml.) and cooled in an ice bath. The solid obtained was dissolved in ether and stirred for eight hours with 10% aqueous sodium hydroxide solution (25 ml.). After separation of the layers, the ether solution was washed with distilled water, and then concentrated. Cooling gave crystals which were recrystallized several times from ligroin (b.p. 60-75°), and finally once from ethyl ether. Yield: 1.19 g. (0.00500 mole, 15% yield). M.p. 81-81.5°; $[\alpha]_D^{20} +24.4 \pm 1^\circ$ (c 2.005, acetone). Infrared spectrum no. 259.

Analysis. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.21; H, 5.85.

p-Anisyl p-Tolyl Sulfone. - a) Impure (+)-p-anisyl p-tolyl sulfoxide (1 g.) was dissolved in glacial acetic acid (20 ml.). The solution was boiled on a hot plate, and 8 drops of 30% hydrogen peroxide were added. After 5 min. of boiling, 8 more drops were added, and the solution was concentrated almost to dryness. Addition of cold distilled water gave crystals, which were recrystallized once from benzene and once from benzene-ethanol (1:1 by volume). M.p. 103-104° (uncor.), lit.³⁵, 104-105°. b) Similarly, (-)-p-anisyl p-tolyl sulfoxide was oxidized to p-anisyl p-tolyl sulfone, m.p. 104-106°, lit.³⁵, 104-105°.

(-)-o-Anisyl p-Anisyl Sulfoxide. - The set up for the reaction was essentially the same as in the case of the preparation of (-)-o-anisyl p-tolyl sulfoxide. A solution of (-)-menthyl (-)-p-methoxybenzenesulfinate ester (9.0 g., 0.029 mole) in anhydrous tetrahydrofuran (60 ml.) was added at room temperature over a 3-hour period with stirring to a solution of o-anisyl magnesium bromide (0.059 mole) in anhydrous ethyl ether (100 ml.). The Grignard reagent had been prepared from p-bromoanisole (11 g., 0.059 mole) and magnesium (2 g., 0.080 g. atom). After stirring for an additional three hours, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride. After separation of the layers, the organic solution was dried over anhydrous magnesium sulfate, filtered, and concentrated (20 ml.). Cooling in an ice-bath gave crystals (4.0 g., 0.058 mole, 53% yield). The sulfoxide was redissolved in ether, and it was stirred overnight in the presence of 10% aqueous sodium hydroxide solution (30 ml.). After separation of the layers, the organic solution was dried over anhydrous magnesium sulfate, filtered and concentrated. Cooling in an ice-bath gave crystals, which were recrystallized three times from

ether. M.p. 114.5-115.5°, $[\alpha]_D^{22} -217.4 \pm 1^\circ$ (c 2.010, acetone). Infrared spectrum no. 297. Oxidation of the sulfoxide with 30% hydrogen peroxide in glacial acetic acid gave o-anisyl p-anisyl sulfone, m.p. 121-122°, lit.³⁶, m.p. 124-125°.

Analysis. Calcd. for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 64.37; H, 5.28.

(+)-m-Tolyl p-Tolyl Sulfoxide. - The procedure was the same as in the case of the preparation of (-)-o-anisyl p-anisyl sulfoxide. A solution of (-)-menthyl (-)-p-toluene-sulfinate (4.0 g., 0.013 mole) in anhydrous ethyl ether (50 ml.) was reacted with a solution of m-toluene magnesium bromide (0.0412 mole), prepared from m-bromotoluene (7.0 g., 0.041 mole) and magnesium (2 g., 0.08 g. atom), in anhydrous ethyl ether (100 ml.). Four recrystallizations from ligroin (b.p. 60-75°) gave pure sulfoxide (1.150 g., 0.0050 mole, 38% yield), m.p. 61-63°, $[\alpha]_D^{25} +16.9 \pm 0.5^\circ$ (c 2.015, acetone). Infrared spectrum no. 453.

Analysis. Calcd. for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.19; H, 6.13.

(-)-o-Anisyl p-Tolyl Sulfoxide. - (-)-o-Anisyl p-tolyl sulfoxide was prepared in 84% yield from one equivalent of (-)-menthyl (-)-p-tolylsulfinate ester and two equivalents of o-anisyl magnesium bromide in ethyl ether. M.p. 83.5-84.5°, $[\alpha]_D^{27} -243.1 \pm 1^\circ$ (c 2.065, acetone). Infrared spectrum no. 2848.

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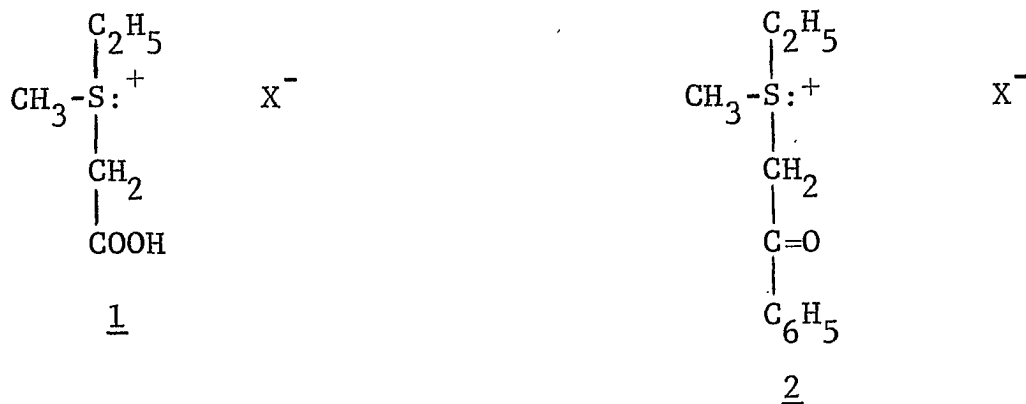
PART II
ATTEMPT AT CONVERTING OPTICALLY ACTIVE DIARYL SULFOXIDES
INTO OPTICALLY ACTIVE TRIARYLSULFONIUM SALTS

SULFONIUM SALTS

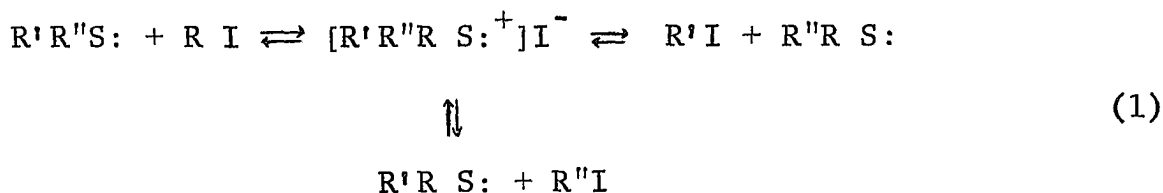
Introduction

This part of the thesis deals with the attempt of synthesizing optically active triaryl sulfonium salts directly from optically active diaryl sulfoxides.¹

Pope and Peachey² first resolved the d- and l-forms of methylethylcarboxymethylsulfonium salt (1), followed by Smiles³, who separated the two forms of methylethylphenacylsulfonium salt (2).



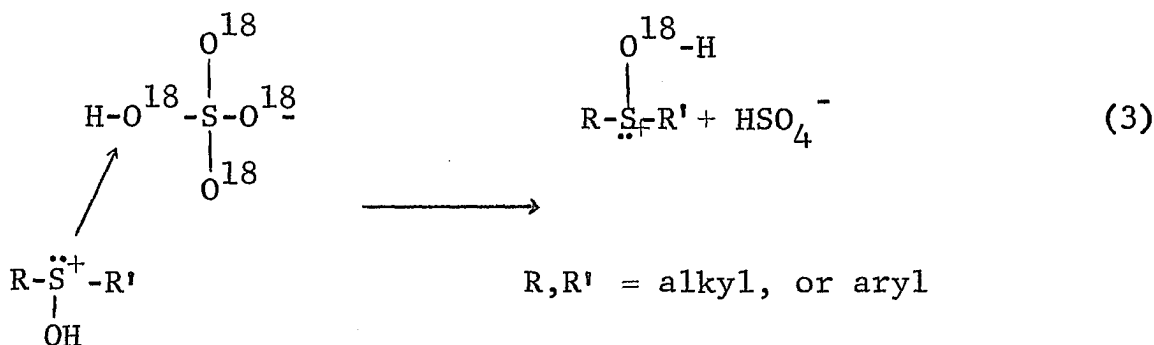
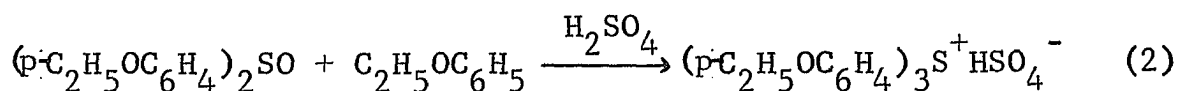
Balfe, et al.⁴, repeated Smiles' work and reported that the sulfonium (2) picrate, mercurytriiodide and α -bromocamphorsulfonate in solution, were optically active after six months, with only a slight but definite loss of optical activity. It was observed, however, that addition of iodide ions, racemized the sulfonium salts rapidly. The iodide ion, a strong nucleophile, displaced the alkyl groups, resulting in decomposition of the sulfonium salt^{4,5} into dialkyl sulfides and alkyl iodides. A reasonable mechanism is shown in eq. 1.



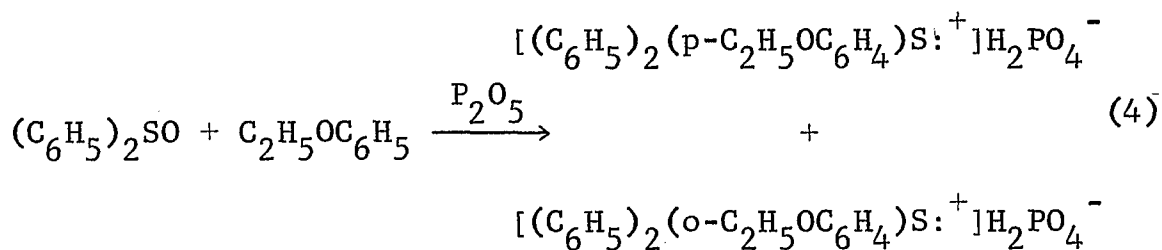
Literature survey showed that there had not been reported any attempts of preparing optically active triarylsulfonium salts, either through resolution or by other means. Perhaps, the biggest confrontation of the problem through resolution lay in the difficulty of obtaining crystalline asymmetric triarylsulfonium salts.

Andersen's¹ method of preparing optically active diaryl sulfoxides in high yields seemed to offer an excellent route to optically active sulfonium salts by asymmetric synthesis, in as much as there were several ways that diaryl sulfoxides might be converted into triarylsulfonium salts (a-f).

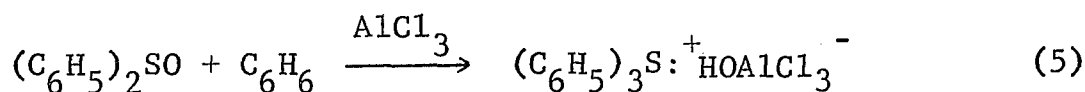
a) Smiles and Rossignol⁶ condensed di-(4-ethoxyphenyl) sulfoxide with ethoxybenzene in the presence of concentrated sulfuric acid (eq. 2). However, this method could not be used because it was reported^{7,8} that sulfoxides readily exchanged oxygen (eq. 3) and that optically active d-4-amino-diphenyl sulfoxide racemized in concentrated sulfuric acid at 0°.



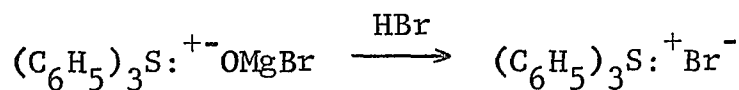
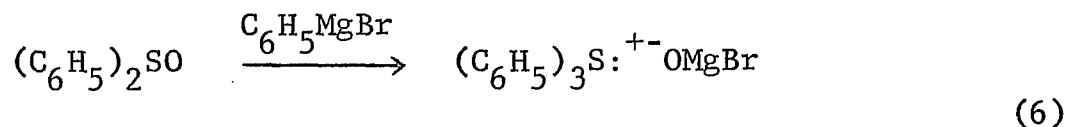
b) Smiles and Rossignol⁶ condensed diphenyl sulfoxide with ethoxybenzene in the presence of phosphorus pentoxide (eq. 4) at water-bath temperatures.



c) Courtot and Tung⁹ condensed diaryl sulfoxides with aromatic compounds, such as benzene, toluene and xylene in the presence of anhydrous aluminum chloride at 40° (eq. 5).

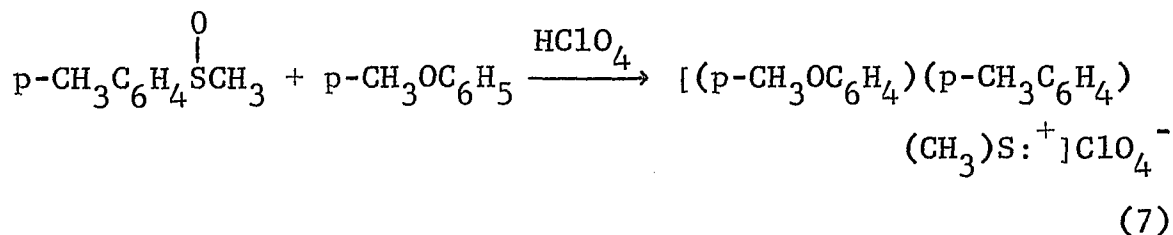


d) Wildi, et al.¹⁰, succeeded in obtaining triaryl-sulfonium salts by refluxing in benzene diaryl sulfoxides with excess Grignard reagents (eq. 6). When an aryllithium was employed a negligible yield of the sulfonium salt was obtained. It has been shown that aryllithium reagents reduce diaryl sulfoxides to diaryl sulfides¹¹ and that they usually exchange aryl groups with triarylsulfonium salts.¹²

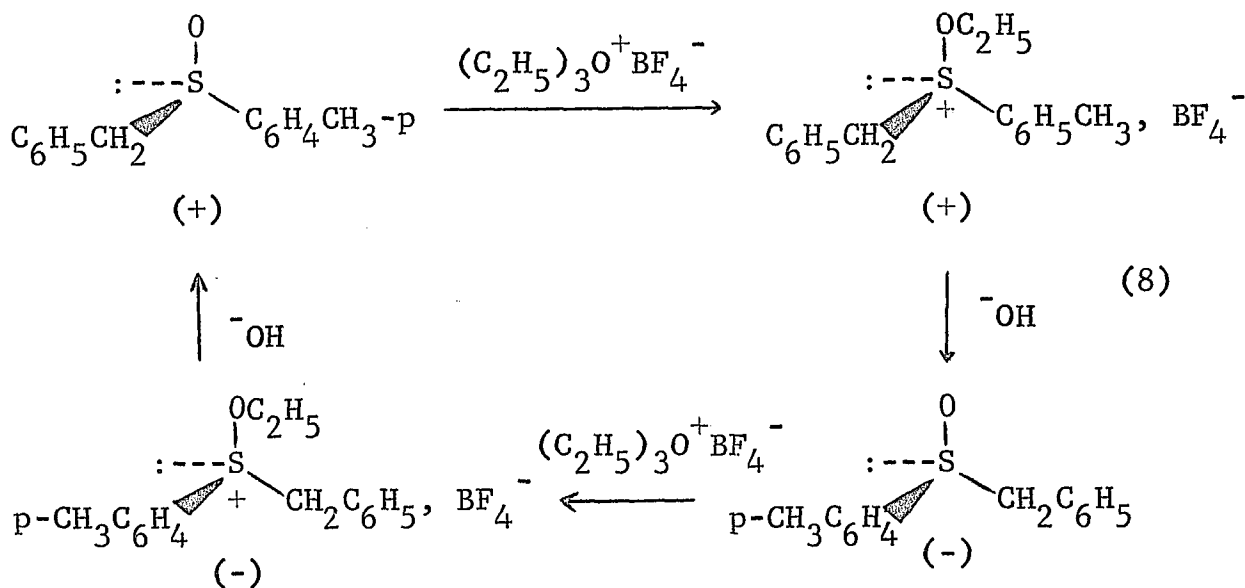


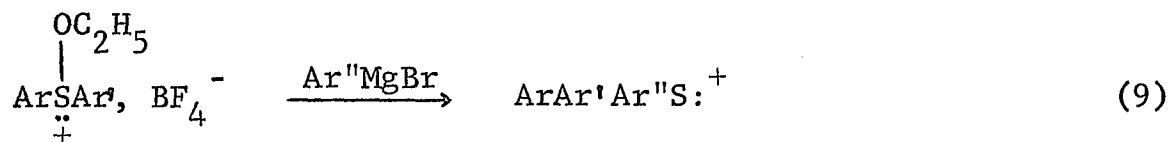
e) Hirose, et al.¹³, condensed racemic alkyl aryl sulfoxides with phenol derivatives in 70% perchloric acid and obtained high yields of sulfonium salts (eq. 7). It was logical to try to condense an optically active alkyl aryl sulfoxide with a phenol derivative and test the resulting

sulfonium salt as to its optical activity. The reaction of diaryl sulfoxides with such derivatives was not mentioned.



f) Johnson and Sapp¹⁴ demonstrated the stereospecific Walden inversion of optically active sulfoxide groupings. For example, R-(+)-benzyl p-tolyl sulfoxide^{1,15} has been converted to (+)-benzyl-p-tolyloethoxysulfonium tetrafluoroborate with triethyloxonium tetrafluoroborate. Basic hydrolysis of this ethoxysulfonium salt yielded S-(-)-benzyl p-tolyl sulfoxide (eq. 8). It was, therefore, thought that reaction of optically active diarylethoxysulfonium salts with aryl Grignard reagents might prove to be an excellent route to optically active sulfonium salts (eq. 9).





RESULTS

The Reaction of Aryl Grignard Reagents with Diaryl Sulfoxides. Aryl Grignard reagents were found to react with diaryl sulfoxides when refluxed for long periods of time in benzene, or di-n-butyl ether¹⁰ (eq. 6). The reaction of diphenyl sulfoxide with excess phenylmagnesium bromide, yielded, after hydrolysis with hydrobromic acid, triphenylsulfonium bromide. The yields ranged from 12-40%. However, the reaction of substituted phenylmagnesium reagents, such as 2,4-xyllylmagnesium bromide, with diphenyl sulfoxide yielded sulfonium salts always in low yields (10%). All of the sulfonium salts gave a blue precipitate in aqueous solution when treated with cobaltous¹⁶ ammonium thiocyanate complex. This reaction was employed as a qualitative test for water soluble sulfonium salts. This test along with the orange precipitate that water soluble sulfonium salts give when reacted with bismuth in the presence of iodide ions¹⁶, were also employed in the present work.

The poor yields of sulfonium salts is a limitation to the above Grignard reaction, and the high temperatures and long periods of refluxing offer an unpromising route to optically active sulfonium salts. Indeed, when o-anisylmagnesium bromide was refluxed with (+)-p-anisyl p-tolyl sulfoxide¹⁷ ($[\alpha]_D^{20} +24^\circ$) in benzene for 21 hours (eq. 6), a negligible amount of an oil was obtained which was inactive at the sodium D-line. The presence of the sulfonium salt was

indicated by the blue precipitate obtained when treated with cobaltous ammonium thiocyanate complex.¹⁶

The Reaction of Diarylethoxysulfonium Salts with Grignard Reagents. Optically active diarylethoxysulfonium salts were prepared by stirring a solution of an optically active diaryl sulfoxide with triethyloxonium tetrafluoroborate salt in anhydrous methylene chloride¹⁴ (eq. 8). Although dialkyl and alkylarylethoxysulfonium salts may be precipitated as crystalline compounds^{14,18} by the addition of excess anhydrous ether to the methylene chloride solution, diarylethoxysulfonium salts were precipitated, generally, as semisolid compounds, and therefore they were never isolated. However, evidence for the formation of these salts was established several times. For example, (+)-phenyl p-tolyl sulfoxide ($[\alpha]_D^{22} +16^\circ$) was reacted with triethyloxonium tetrafluoroborate in methylene chloride. Hydrolysis of the reaction mixture with dilute aqueous sodium hydroxide yielded (-)-phenyl p-tolyl sulfoxide^{14,18} ($[\alpha]_D^{22} -15^\circ$) (eq. 8).

The optically active diaryl sulfoxides employed in this part of the thesis were prepared¹⁷ as described in part I of this thesis. The reaction of the diarylethoxysulfonium salts with different Grignard reagents and the results obtained are summarized below (for details see experimental).

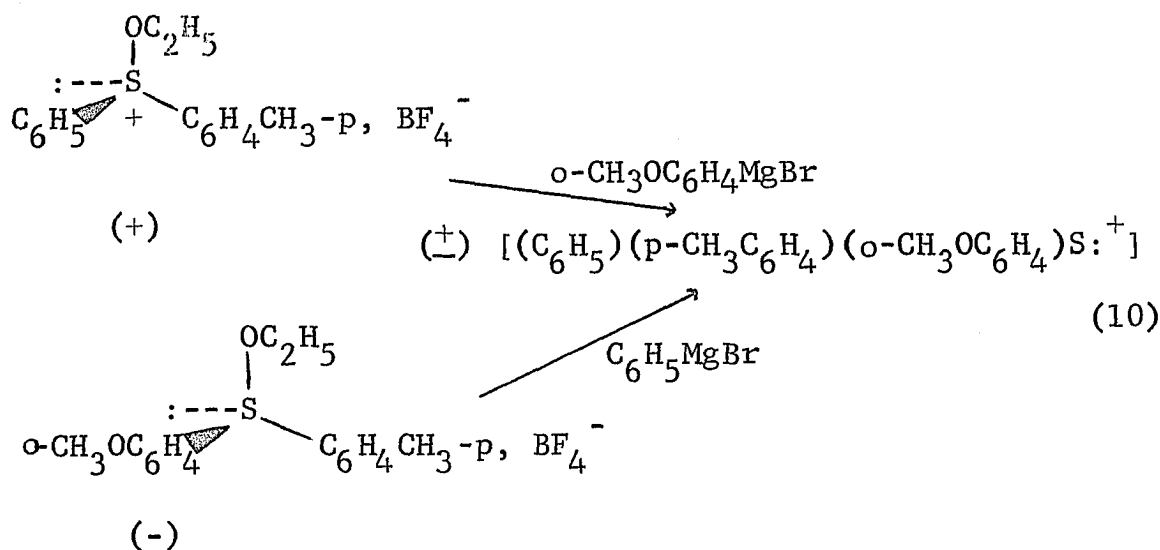
a). Phenyl-m-tolyl-p-tolylsulfonium salt. (+)-m-Tolyl-p-tolylethoxysulfonium tetrafluoroborate (0.012 mole) in anhydrous tetrahydrofuran was added at 0° to a solution of phenylmagnesium bromide (0.0625 mole) in tetrahydrofuran. After hydrolysis with 20% hydrobromic acid, the sulfonium salt was removed with chloroform.¹⁹ Evaporation of the solvent gave a thick oil, which gave the cobalt and bismuth

tests.¹⁶ The oil was converted to its crystalline sulfonium perchlorate, whose rotation at the sodium D line was zero.

b) Phenyl-p-tolyl-o-anisylsulfonium salt (eq. 10). i. A solution of o-anisylmagnesium bromide (0.0320 mole) in anhydrous tetrahydrofuran was added at 0° to (+)-phenyl-p-tolylolethoxysulfonium tetrafluoroborate in anhydrous tetrahydrofuran. After hydrolysis with saturated aqueous ammonium chloride, the sulfonium salt was removed with chloroform.¹⁹ Evaporation of the solvent gave an oil, which was converted to its crystalline sulfonium perchlorate. The optical rotatory dispersion curve from 600 m μ to 300 m μ gave no evidence of optical activity of this compound.

ii. A solution of phenylmagnesium bromide (0.01 mole) in anhydrous ethyl ether was added at -10° to -20° to a solution of (-)-p-tolyl-o-anisylethoxysulfonium tetrafluoroborate (0.0041 mole) in anhydrous dimethoxyethane. After hydrolysis with saturated aqueous ammonium chloride, the sulfonium salt was removed with chloroform.¹⁹ A fraction of the sulfonium salt was converted to its water-insoluble tetraphenylborate²⁰, whose optical rotation at the sodium D line was zero. The rest of the sulfonium salt was converted to its crystalline perchlorate salt.¹⁹

The sulfonium salts obtained from the two routes had similar infrared spectra, melting points, and elemental analyses.



iii. A solution of *o*-anisylmagnesium bromide (0.0081 mole) in anhydrous ethyl ether was added at 0° to a mixture of (+)-phenyl-*p*-tolylethoxysulfonium tetrafluoroborate (0.007 mole) and sodium tetraphenylboron (0.004 mole) in dimethoxyethane-ethyl ether. The sulfonium tetraphenylborate, thus obtained, did not show any activity at the sodium D line. The optical rotatory dispersion from 600 m μ to 320 m μ did not show any optical activity for this compound.

iv. A solution of (-)-*p*-tolyl-*o*-anisylethoxysulfonium tetrafluoroborate (0.0090 mole) and sodium tetraphenylboron (0.0080 mole) in dimethoxyethane was added at 0° to a filtered solution of phenylmagnesium bromide (0.027 mole) in dimethoxyethane-ethyl ether. The optical rotatory dispersion of the sulfonium tetraphenylborate obtained gave zero rotation up to 320 m μ .

v. A solution of *o*-anisylmagnesium bromide (0.0161 mole) in tetrahydrofuran was added at 0° to a solution of (+)-phenyl-*p*-tolylethoxysulfonium tetrafluoroborate (0.0158 mole) in tetrahydrofuran. After hydrolysis with 10% aqueous nitric acid, the sulfonium salt was removed with chloroform. Evaporation of the solvent gave a white semisolid, which did

not rotate light at the sodium D line. The sulfonium salt was converted to its crystalline tetraphenylborate salt for identification purposes.

Sulfonium Salts by Means of Phosphorus Pentoxide.

(+)-Phenyl p-tolyl sulfoxide was condensed with anisole at 85° in the presence of phosphorus pentoxide⁶ (eq. 4) to yield an oil which was inactive at the sodium D line. However, it was found that phosphorus pentoxide racemized sulfoxides. For example, (-)-o-anisyl p-tolyl sulfoxide ($[\alpha]_D^{23} -248^\circ$) and 1,3-dimethoxybenzene were reacted in the presence of lesser amounts of phosphorus pentoxide. The reaction was interrupted long before the recommended⁶ time, and the unreacted sulfoxide isolated showed considerable racemization ($[\alpha]_D^{23} -110^\circ$, 55% optically pure).

Sulfonium Salts by Means of Aluminum Chloride.

a) Phenyl-p-tolyl-o-anisylsulfonium salt. (-)-o-Anisyl p-tolyl sulfoxide was condensed at 40° with benzene in the presence of anhydrous aluminum chloride.⁹ The sulfonium salt was converted to its crystalline perchlorate salt, whose rotation at the sodium D line was zero.

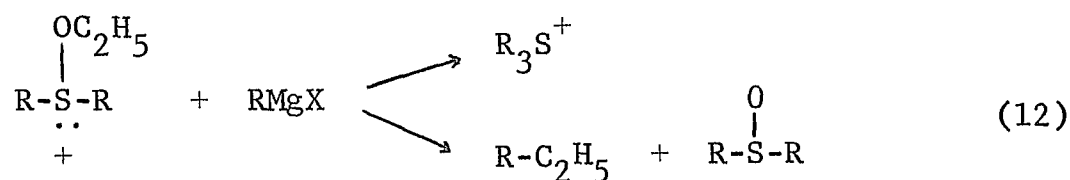
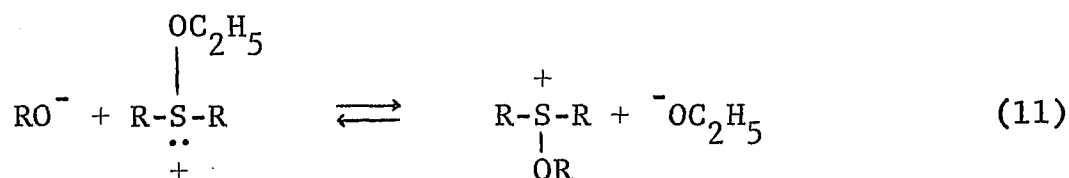
b) Phenyl-p-tolyl-2,5-dimethylphenylsulfonium salt. (+)-Phenyl p-tolyl sulfoxide and p-xylene were reacted at 40° in the presence of anhydrous aluminum chloride. The sulfonium salt was converted into its crystalline tetraphenylborate, whose optical rotatory dispersion curve from 600 m μ to 320 m μ did not show any optical activity. The recovered sulfoxide indicated that it did not racemize under the conditions employed.

Sulfonium Salts by Means of Perchloric Acid. (+)-Methyl p-tolyl sulfoxide ($[\alpha]_D +139^\circ$) was condensed with anisole in the presence of 70% perchloric acid¹³ (eq. 7) to yield a semisolid, whose optical rotatory dispersion curve

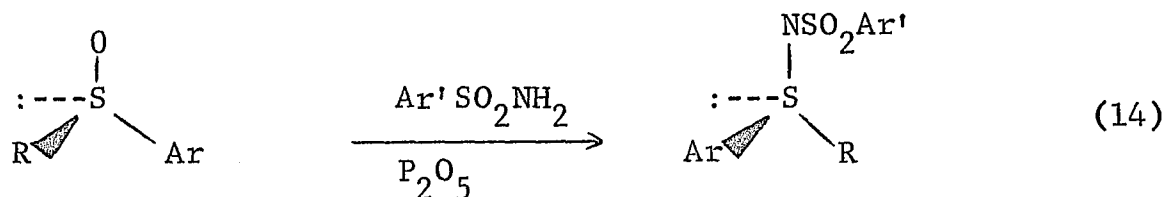
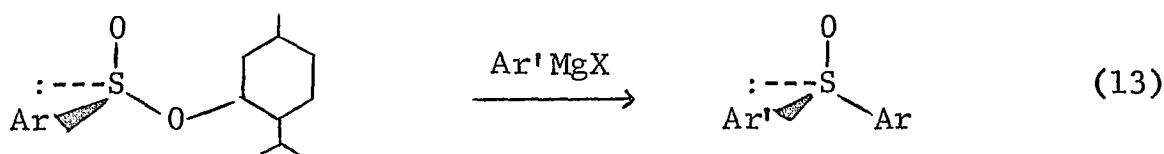
from 600 m μ to 320 m μ did not indicate any optical activity. It was found, however, that 70% perchloric acid racemized optically active sulfoxides. For example, the observed rotation of (-)-o-anisyl p-tolyl sulfoxide in 70% perchloric acid, changed from 179.10° to 179.49° after 5 hours.

DISCUSSION

The reaction of optically active diarylethoxysulfonium salts with Grignard reagents was carried out under different conditions. Very often low temperatures and short periods of time were employed to avoid reaction of the generated ethoxide ions with unreacted diarylethoxysulfonium salts. It was found^{18,21} that alkyl- and alkylarylalkoxy-sulfonium salts rapidly interchanged alkoxy groups in the presence of alkoxides (eq. 11). The yields of the sulfonium salts many times were not recorded because the interest was centered on obtaining optically active sulfonium salts by changing one, or more conditions. However, the recorded yields ranged between 30% and 40%, with the exception of triphenylsulfonium salt which was obtained in 60% yield. The fact that the yields were rather low are attributed to competition reactions¹⁸ (eq. 12).



The lack of optical activity²² is surprising in view of the analogy between the reaction of diarylethoxysulfonium salts (eq. 9) and the stereospecific syntheses of sulfoxides¹⁷ (eq. 13) and sulfilimines²³ (eq. 14), and the stereospecific basic hydrolysis of ethoxysulfonium salts^{14,18} (eq. 8).



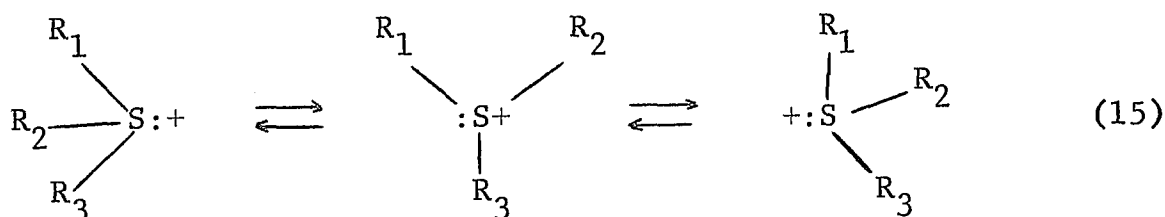
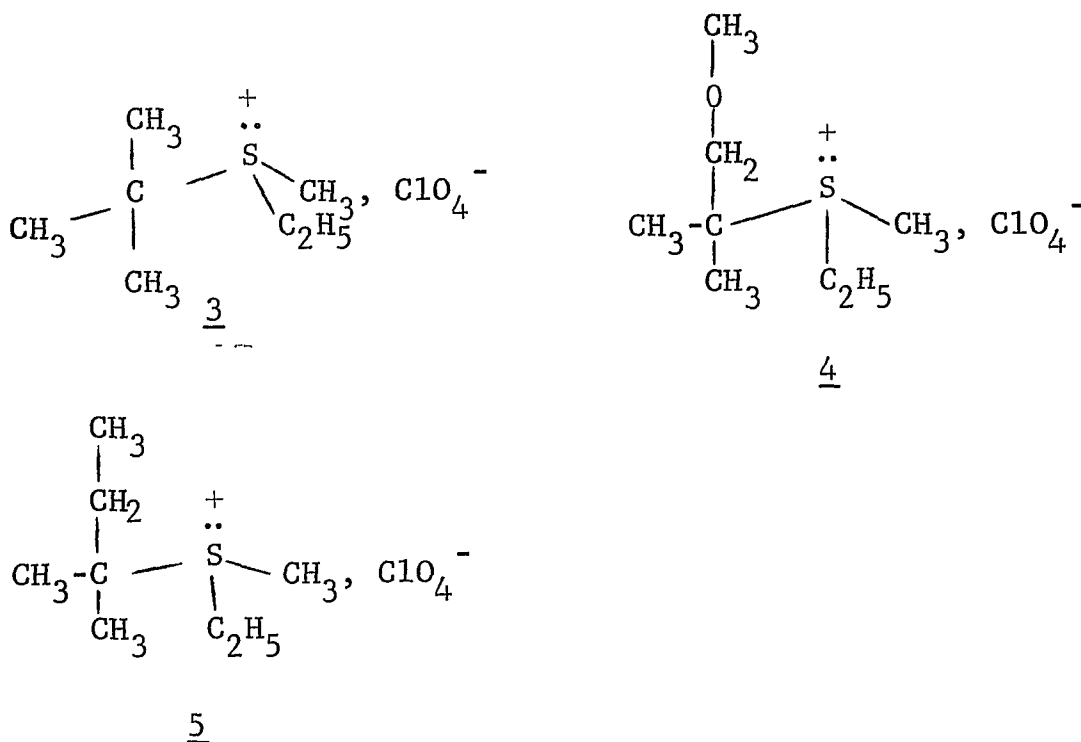
Either the reaction proceeds through a symmetrical intermediate or transition state, or the triarylsulfonium salts, presumably pyramidal about sulfur as are the trialkylsulfonium salts, have a low barrier for enantiomer interconversion analogous to the amines.

The possibility of symmetrical intermediate is unlikely in view of eqs. 8, 13, and 14. Exchange of aryl groups of the sulfonium salt with the aryl groups of the Grignard, a process which takes place with triarylsulfonium salts and aryllithium compounds¹² and which might lead to racemization, apparently does not take place since phenyl-p-tolyl-o-anisylsulfonium perchlorate can be prepared from two routes (eq. 10).

The possibility of a low barrier to enantiomer interconversion seems the more likely explanation especially since sulfoxides can be racemized thermally.²⁴ A steric factor has been shown to be operative here; i.e., the sulfoxides with bulky R groups racemize the most easily. By analogy, triarylsulfonium salts would be expected to have lower energy barriers for racemization than the trialkylsulfonium salts.^{2,3}

Recently, Darwish and Tourigny^{25a,b} studied the solvolysis and the relative rates of racemization of optically active sulfonium salts 3, 4, and 5. The rates of racemization

of 3, 4 and 5 were 1:1.8:4.2 respectively; i.e., the bulkier the groups on the sulfonium salts the easier the racemization. It was suggested that the most probable pathway for racemization was a "flip" of the sulfonium ion (eq. 15) analogous to the inversion of ammonia.

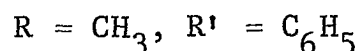
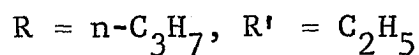
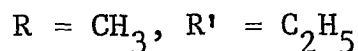
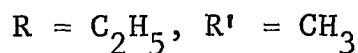
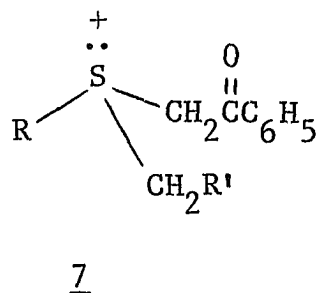
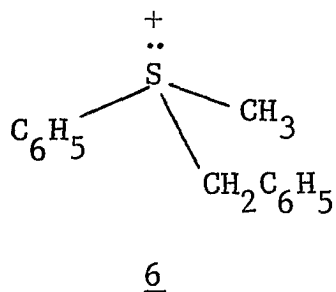


Transition State

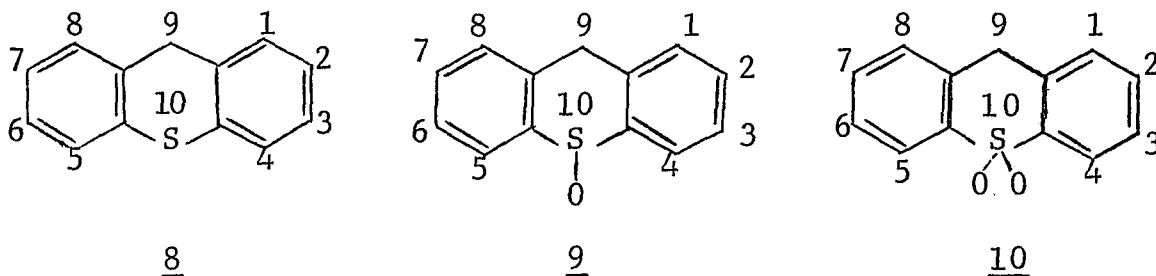
If a pyramidal inversion occurs, as it has been suggested^{24,25}, then the racemization of the bulkier sulfonium salts and sulfoxides can be understood. With increasing bulk²⁴ of the groups attached to sulfur, non-bonded repulsion will be increasingly relieved by a spreading of the bond angles in

the ground state. This will bring the geometry of the molecule in the ground state closer to that of the transition state, and thus lessen the energy gap between the ground and the transition states (eq. 15). Sulfonium salts might utilize their d-orbitals to conjugate with aromatic rings; however, due to the non-directional character of the 3d orbitals it is not known whether such a conjugation would further lower the energy gap between the ground and transition states. At least in the thermal racemization of diaryl sulfoxides²⁴, the rates of racemization, while sensitive to steric factors, were relatively insensitive to electronic effects.

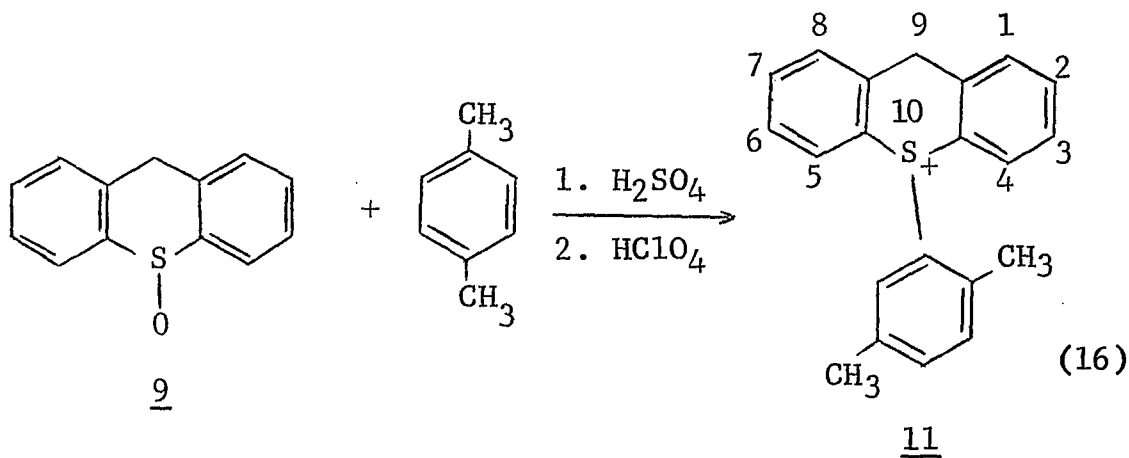
Nuclear Magnetic Resonance Studies. It is well known that the protons removed by one or more bonds from a center of molecular asymmetry may be magnetically nonequivalent and display AB-type nuclear magnetic resonance spectra.^{26a,b,c} It was thought that it would be worthwhile to study sulfonium salts that have a methylene group attached to the sulfur atom. If nonequivalence were observed, then rates of racemization would be studied. The nuclear magnetic resonance spectrum of methylphenylbenzylsulfonium perchlorate (6) revealed only a singlet for the methylene protons even at -50°. A similar observation was made by Ratts²⁷ for a series of sulfonium salts (7). A singlet for the methylene group of R'¹CH₂- was obtained in all cases. However, other investigators²⁸ indicated that isopropylphenyl- α -naphthylsulfonium tetrafluoroborate exhibited the two doublets expected of diastereomeric methyl groups. Although a kinetic study of this system could be of value, it was decided to investigate a system that would provide some definite clues about the racemization of triarylsulfonium salts.



Thioxanthene (8) was chosen as the starting point of this investigation. A singlet was observed for the protons of C_9 at 6.18τ in deuteriochloroform.²⁹ The aromatic region occurred as a multiplet with the highest peak at 2.80τ . Oxidation of 8 with 30% hydrogen peroxide yielded thioxanthene 10-oxide³⁰ (9). The nuclear magnetic resonance spectrum of 9 in deuteriochloroform revealed a quartet for the protons of C_9 with peaks at 5.70τ , 5.98τ , 6.17τ , 6.45τ , and a coupling constant $J_{\text{AB}} \approx 17$ cps. The aromatic region exhibited a multiplet, centered at about 2.17τ , and a doublet with peaks at 2.62τ , and 2.67τ . Oxidation of 8 with excess 30% hydrogen peroxide yielded thioxanthene 10,10-dioxide³⁰ (10). The nuclear magnetic resonance spectrum of 10 in deuteriochloroform exhibited a singlet at 5.77τ for the protons of C_9 . The aromatic region occurred as a multiplet, centered at 1.98τ , and as a doublet with peaks at 2.53τ , and 2.58τ .

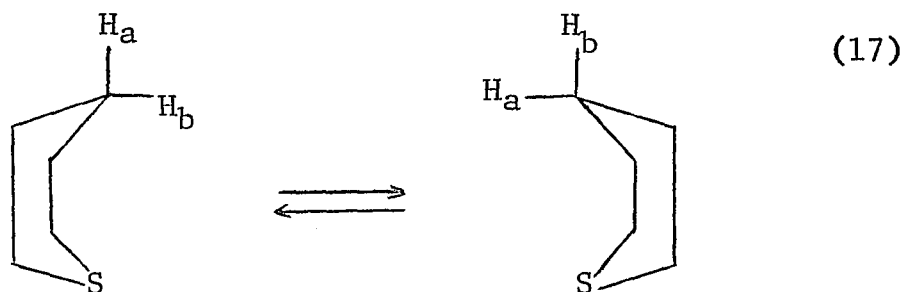
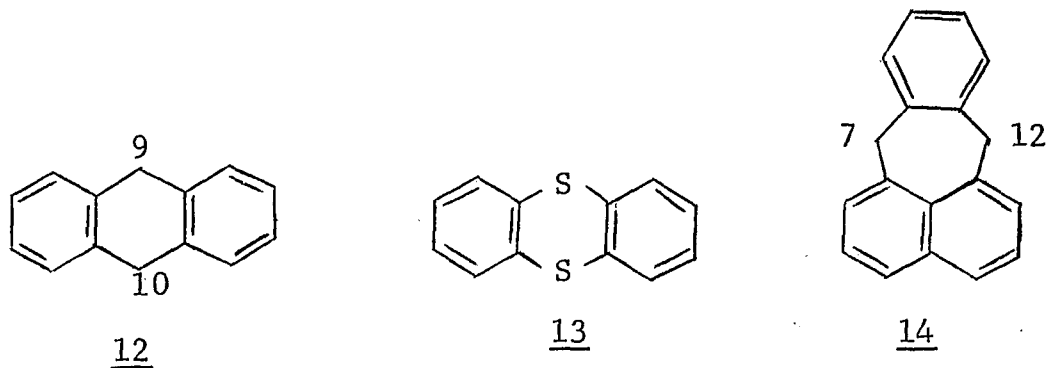


The reaction of thioxanthene 10-oxide (9) with p-xylene in concentrated sulfuric acid⁶ yielded 9,10-dihydro-10-(2,5-dimethylphenyl)thioxanthylum salt, which was converted to its crystalline perchlorate salt (11) (eq. 16). The nuclear magnetic resonance spectrum of 11 in deuteriochloroform revealed only a singlet for the methylene hydrogens of C₉ at 5.52 τ . The methyl substituents of the benzene ring occurred at 7.28 τ , and 7.72 τ , while the aromatic region occurred as a multiplet, centered at 2.08 τ , and as two singlets with peaks at 2.55 τ , and 3.20 τ .



The conformation of thioxanthene (8) is expected to be similar to the conformations exhibited by 9,10-dihydroanthracene^{31a,b} (12), thianthrene³² (13), and 7,12-dihydropleiadene³³ (14). All three compounds (12, 13, 14) are not planar, but bent, producing a "butterfly" shaped structure^{31a}, whose central ring exists in a boat conformation. Compounds

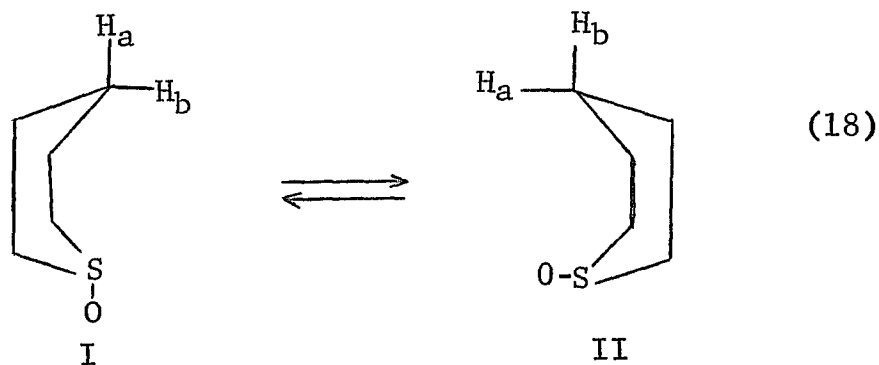
12, 13, and 14, rapidly interconvert between two boat conformations, and in an analogous manner thioxanthene (8), is expected to behave in a similar fashion (eq. 17).

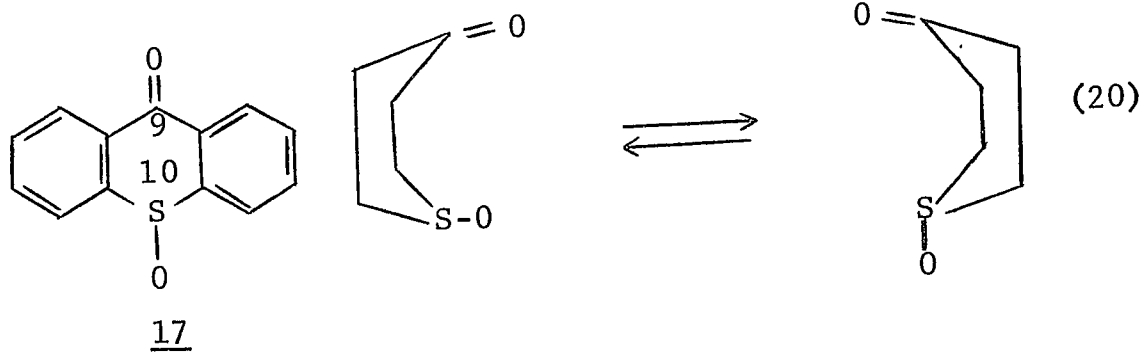
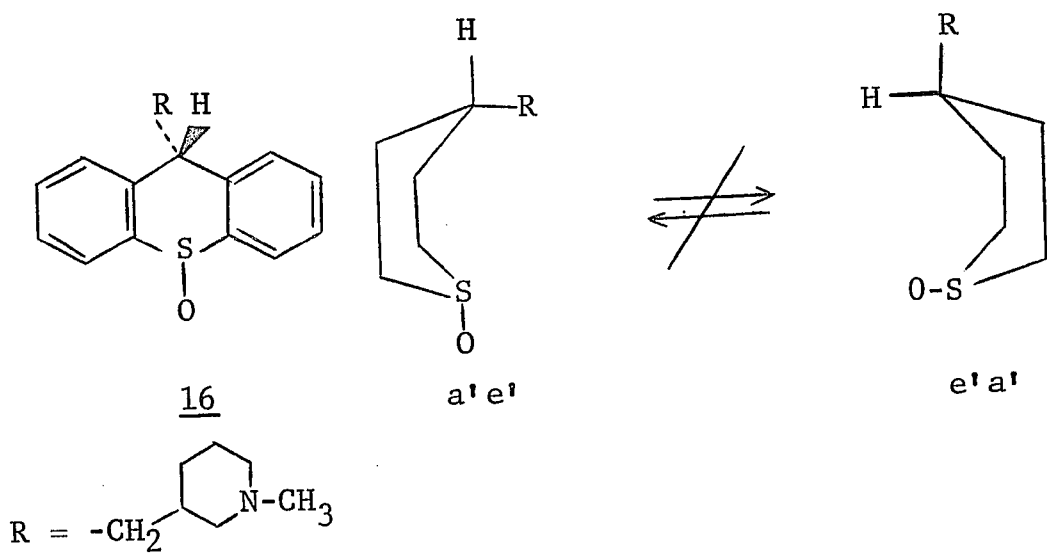
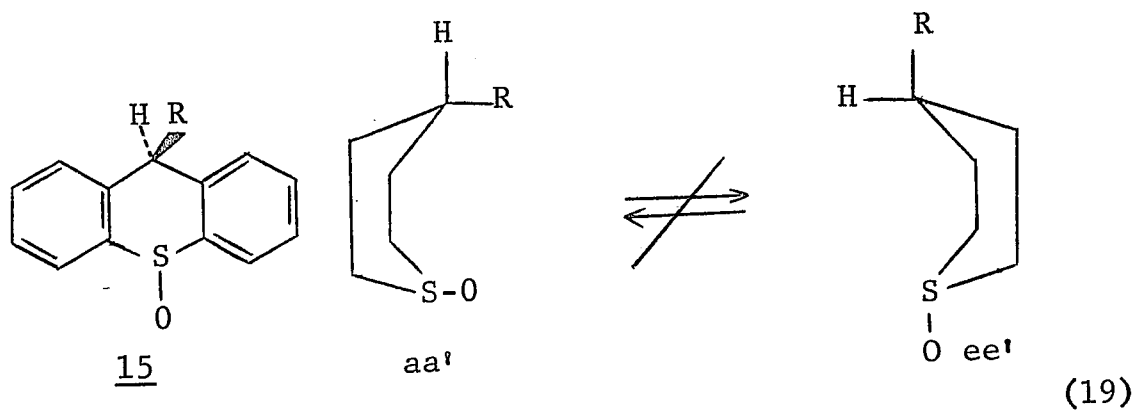


Thioxanthene (8) in its boat conformation has two different carbon-hydrogen bonds in 9-position. One of the bonds is oriented in a direction opposite to which the molecule is folded and almost at right angles to the line joining positions 9 and 10. This bond is called axial.³³ The other bond is directed away from the center of the molecule along the 9:10 axis and is called equatorial. In eq. 17, protons H_a and H_b of the left boat conformation are designated as equatorial and axial respectively, while their designation is reversed in the right boat conformation.

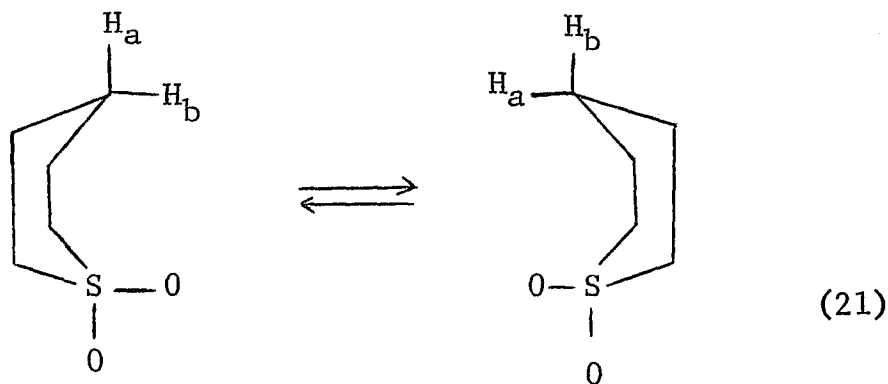
Since protons H_a and H_b are different, nuclear magnetic resonance would reveal an AB-type spectrum, i.e., a quartet. However, because the interconversion is very rapid, protons H_a and H_b experience the same environment, and therefore they become equivalent, as it was indicated by the observed singlet.

Thioxanthene 10-oxide (9), in analogous manner to thioxanthene (8), must also rapidly interconvert between I and II (eq. 18), although it is possible to obtain non-converting sulfoxides, if certain requirements are met. For example, Michaelis et al.³⁴, isolated sulfoxides 15 and 16, which exist as aa' (axial axial) and a'e' (axial equatorial) respectively. (eq. 19). The large R group prefers the axial position because of interaction with aromatic hydrogens at 1- and 8-positions in the equatorial position. Castrillon and Szmant³⁵ also reported that thioxanthen-9-one 10-oxide (17) had a boat conformation and that the energy barrier of the folded structure for inversion was too low to allow the isolation of one isomer at room temperature (eq. 20). As in the case of thioxanthene (8), protons H_a and H_b of sulfoxide 9 (eq. 18) are different; however, fast interconversion between I and II never cause the two protons to experience the same environment, and therefore they do not become equivalent as they do in (8). It is felt, that the observed quartet for 9 is a time-average quartet of conformations I and II.





In analogous manner, sulfone 10 must rapidly interconvert between two boat conformations (eq. 21) in agreement with the observed singlet for protons H_a and H_b of C_9 .



Sulfonium salt 11 is a more complicated system than either 8, 9, or 10, in as much as it can have both ring interconversion and sulfur inversion (eq. 22). The analyses of the different possibilities are summarized below (1-5).

1. No Ring Interconversion, No Sulfur Inversion.

If there is no ring interconversion, or sulfur inversion, and only one isomer is present (III or IV), then protons H_a and H_b are nonequivalent, and an AB-type spectrum would result. If both isomers III and IV are present in appreciable amounts, then two AB-type spectra might result.

2. Slow Ring Interconversion, Rapid Sulfur Inversion.

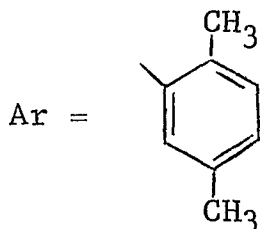
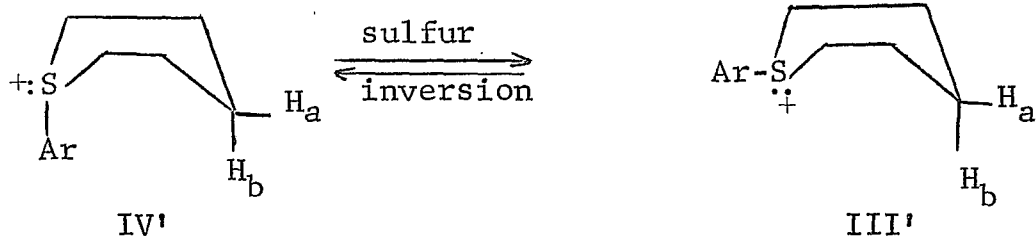
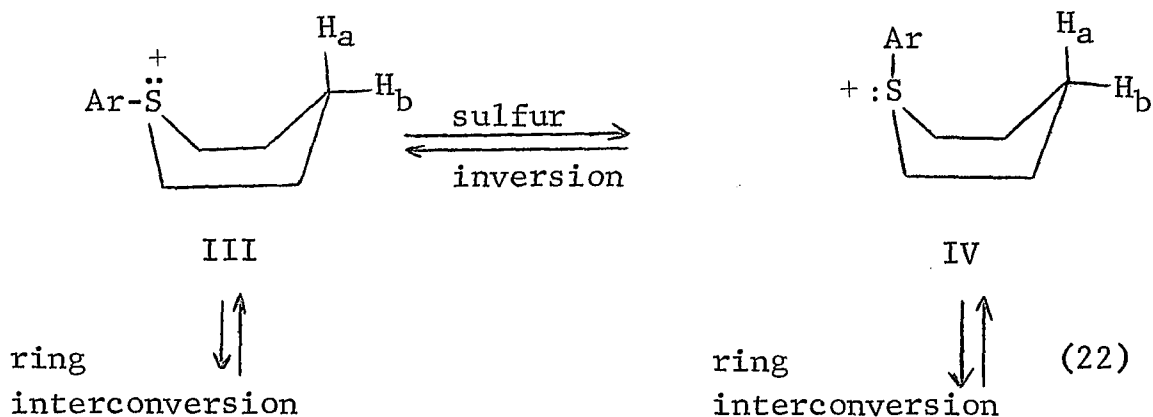
If there is slow ring interconversion, but rapid sulfur inversion, then protons H_a and H_b are nonequivalent, and an AB-type spectrum would result.

3. Rapid Ring Interconversion, Slow Sulfur Inversion.

If there is rapid ring interconversion, and slow sulfur inversion, protons H_a and H_b go rapidly between axial and equatorial positions, but they are still different, and as a result an AB-type spectrum would result.

4. Rapid Ring Interconversion, Rapid Sulfur Inversion. If there are both rapid ring interconversion and sulfur inversion, then protons H_a and H_b experience the same environment, and they become equivalent. As a result an A_2 -type spectrum (singlet) would result.

5. Slow Ring Interconversion, Slow Sulfur Inversion. If there are both slow ring interconversion, and sulfur inversion, then the same situation as in 1 exists.



The spectrum of 11 indicated that, at room temperature, it consisted of a singlet for the protons of C₉. This fact would make one conclude that there were both rapid ring interconversion, and sulfur inversion. It was noticed, however, that the peak due to the protons of C₉ was somewhat broad (half-width 5.5 cps) in comparison with the peaks of 8 (half-width 2 cps), and 10 (half-width 2.5 cps). Because the chemical shift difference is many times affected by the type of solvent used^{26, 27}, and because there are instances where AB-type spectra are revealed in some solvents, but not others, the nuclear magnetic resonance spectra of 11 were obtained in dimethylformamide, 1,1,2,2-tetrachloroethane, chloroform, and deuteriochloroform. A singlet was obtained in all cases.

The fact that the peak due to the protons of C₉ was broad prompted a high temperature study of 11 at 60 Mc. The objective was to observe whether the singlet due to the protons at C₉ would get sharper at higher temperatures, i.e., whether inversion at sulfur would become faster. It was decided to compare the half-width of the peak due to the protons at C₉ with the half-widths of the peaks due to the methyl substituents present in 11. It was expected that the half-widths of the methyl groups would not be affected by the higher temperatures. Any change in the half-widths due to the loss of tuning of the instrument would be reflected in both types of peaks compared. As a result the ratio of the half-widths would be more meaningful. The results of such a study are shown in Table 1. The ratio of the half-widths shows a decreasing trend, and that is a good indication of a fast inversion.

TABLE I

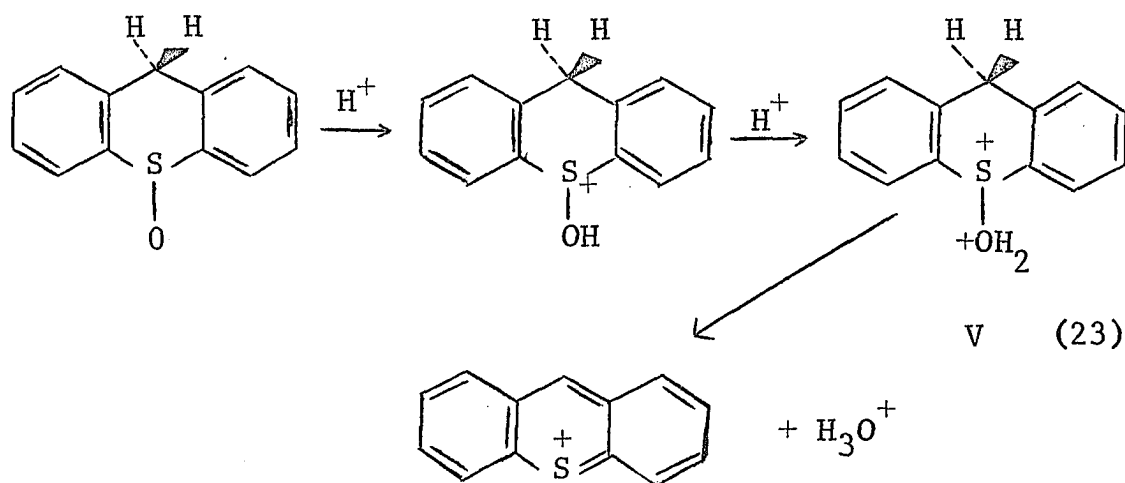
Temp., °C	Solvent	Half-Widths (cps)					c ^b
		$\frac{-\text{CH}_2-}{\text{CH}_3(1)^a}$	$\frac{-\text{CH}_3(2)^a}{\text{CH}_3(1)^a}$	$\frac{-\text{CH}_2-/\text{CH}_3(1)^a}{\text{CH}_3(2)^a}$	$\frac{-\text{CH}_2-}{\text{CH}_3(1)^a}$	$\frac{-\text{CH}_2-/\text{CH}_3(2)^a}{\text{CH}_3(1)^a}$	
32°	CDCl ₃	5.5	3	3	1.83	1.83	10%
32°	CHCl ₂ CHCl ₂	5	3.5	3.5	1.43	1.43	20%
40°	CHCl ₂ CHCl ₂	4(4.5) ^c	3(3.5)	3(3.5) ^c	1.33(1.29)	1.33(1.29)	20%
65°	CHCl ₂ CHCl ₂	3.2(3.2) ^c	3(3) ^c	3(3) ^c	1.07(1.07)	1.07(1.07)	20%
85°	CHCl ₂ CHCl ₂	4.5(3) ^c	4.5(3.5) ^c	5.5(3.5) ^c	1(0.86)	0.82(0.86)	20%
95°	CHCl ₂ CHCl ₂	3(3) ^c	3(3) ^c	3(3.5) ^c	1(1)	1(0.86)	20%

^a -CH₃(1) lower field peak; -CH₃(2) higher field peak. ^b Concentration by weight.

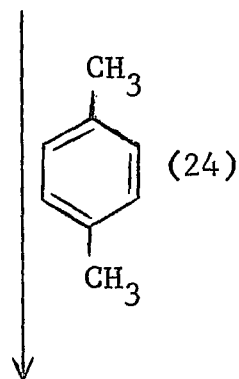
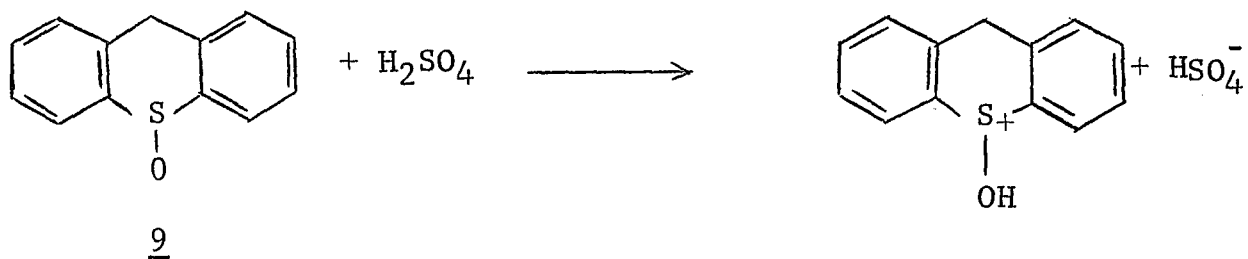
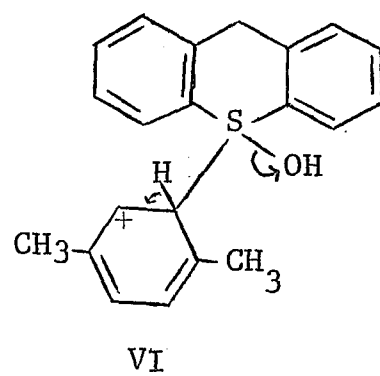
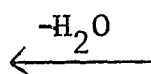
^c Numbers in parentheses are repeated measurements, after instrument was returned. They serve as a double check.

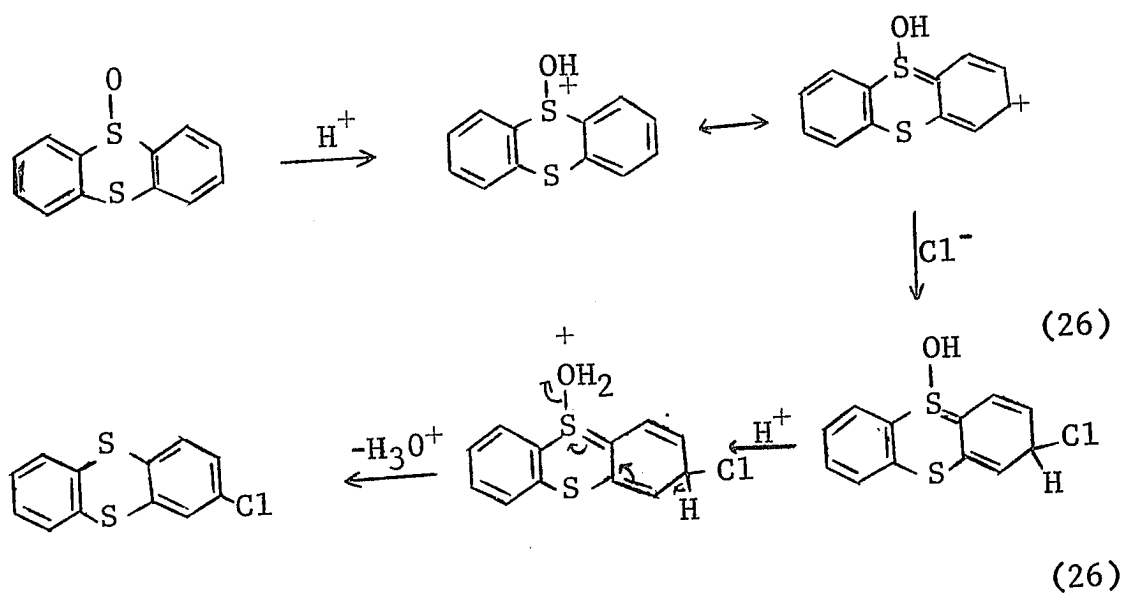
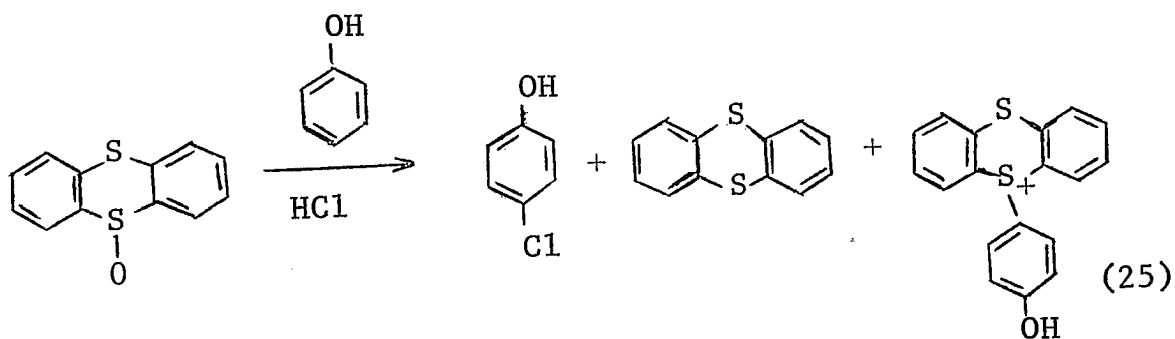
At low temperatures, both ring interconversion and sulfur inversion might be affected, and the situation would be complex. An attempt was made to run the spectrum at low temperatures; however, 11 precipitated out from both deuteriochloroform and acetone solvents.

About the Mechanism of Formation of 11. The behavior of thioxanthene 10-oxide (9) in concentrated sulfuric acid is different from the behavior of other sulfoxides, such as diphenyl sulfoxide, in the same acid.^{7,36,37} Unlike the latter, 9 goes beyond the monoprotinated stage^{38a,b}, and suffers dehydroxylation, presumably via intermediate V (eq. 23).



The mechanism for the formation of 11, might be as shown in eq. 24, via a tetravalent intermediate or transition state VI. This is similar to the mechanism proposed by Shine and Dais³⁹ for the reaction of thianthrene monoxide and phenol in the presence of concentrated hydrochloric acid (eq. 25). The mechanism was based on the observation that thianthrene in the presence of only concentrated hydrochloric acid produced 2-chlorothianthrene (eq. 26).

11



Ultraviolet Spectra. The ammonium or trimethylammonio group is known to have almost no chromophoric effect on the ultraviolet absorption spectra of aromatic compounds.⁴⁰ However, the dimethylsulfonio⁴⁰ group shifts the primary band of benzene from 203.5 m μ to 220 m μ . These facts indicate that, contrary to the ammonio groups, the dimethylsulfonio group does conjugate with and stabilizes the photoexcited state.

It was found⁴⁰ that ortho substituents in a benzene ring have very little influence on the conjugative characteristics of the sulfonio group in photoexcitation. This means that the conjugative interaction of the sulfonio group with the benzene ring in the photoexcited state does not have a preferred steric or angular arrangement, and thus presumably involves 2p-3d overlap for the interaction.

The ultraviolet spectra of triphenylsulfonium bromide, phenyl-p-tolyl-m-tolyl sulfonium perchlorate, and phenyl-p-tolyl-o-anisylsulfonium perchlorate, in 95% ethanol, were taken at two different concentrations to make certain that Beer's law was followed. It was reported⁴¹ that certain sulfonium salts had not obeyed Beer's law. However, all of the above examined sulfonium salts obeyed the law. The ultraviolet spectra of these sulfonium salts are shown in Fig. 1. The spectrum of phenyl-p-tolyl-o-anisylsulfonium salt is somewhat different in as much as it has a long wavelength low intensity band, that is not present in the other two compounds. This band must be due to the ortho methoxy substituent present.

The ultraviolet spectra of thioxanthene (8), thioxanthene 10-oxide (9), thioxanthene 10,10-dioxide (10), and 9,10-dihydro-10-(2,5-dimethylphenyl)thioxanthylum perchlorate (11), were obtained in 95% ethanol, and are shown in Fig. 2.

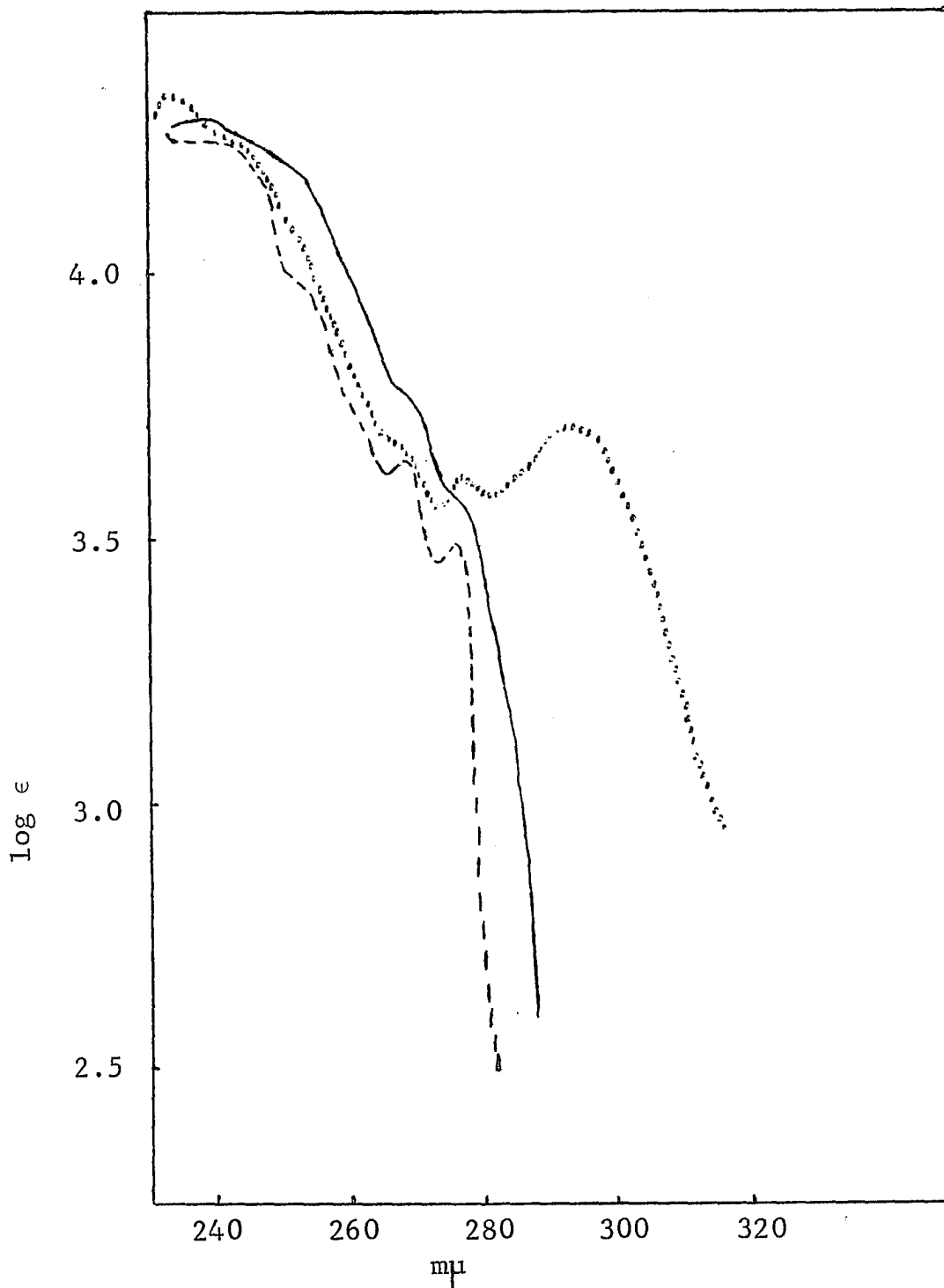


Fig. 1 - Ultraviolet spectra of triphenylsulfonium Bromide (----), phenyl-p-tolyl-m-tolyl-sulfonium perchlorate(—), and phenyl-p-tolyl-o-anisylsulfonium perchlorate(····)

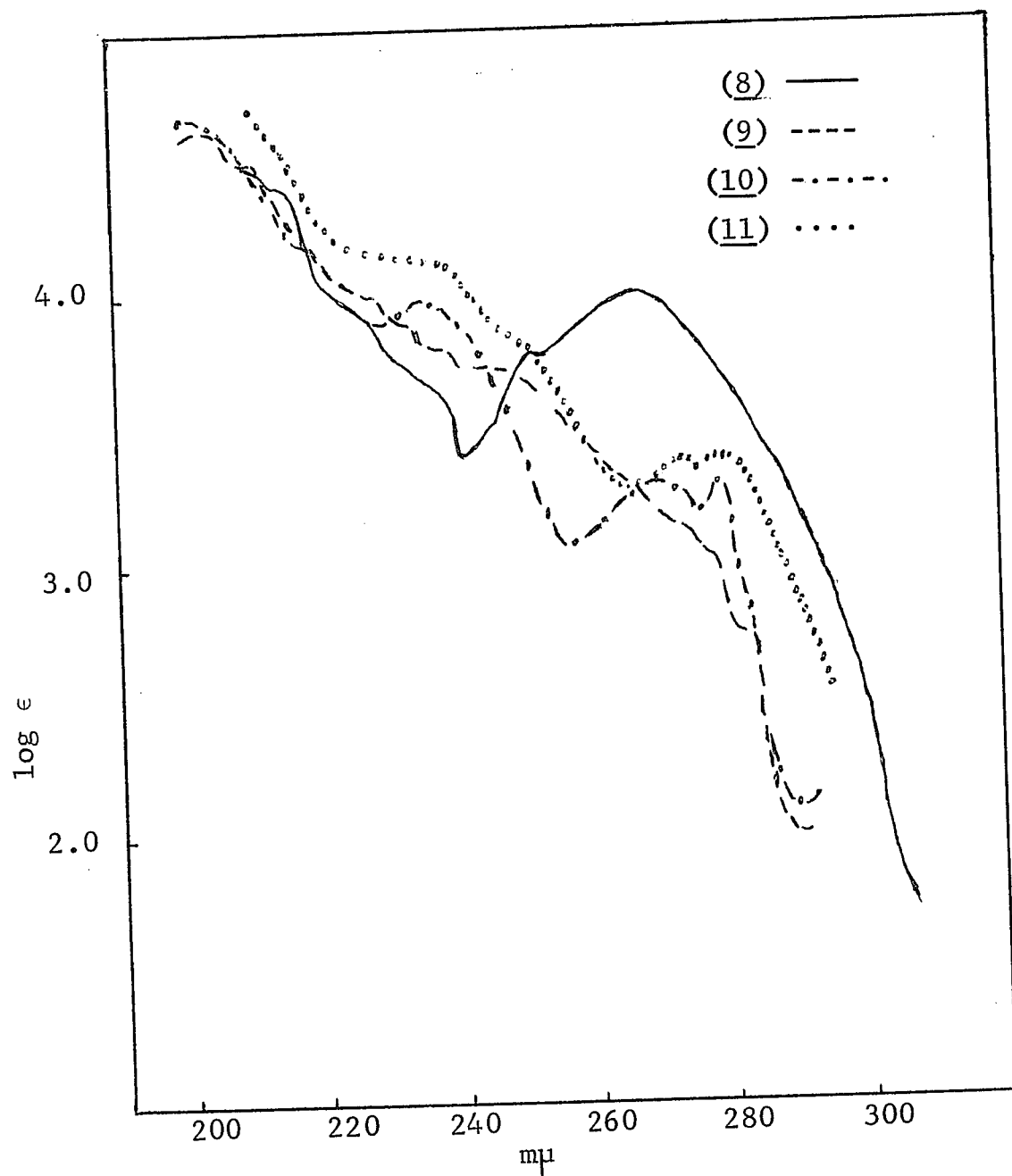
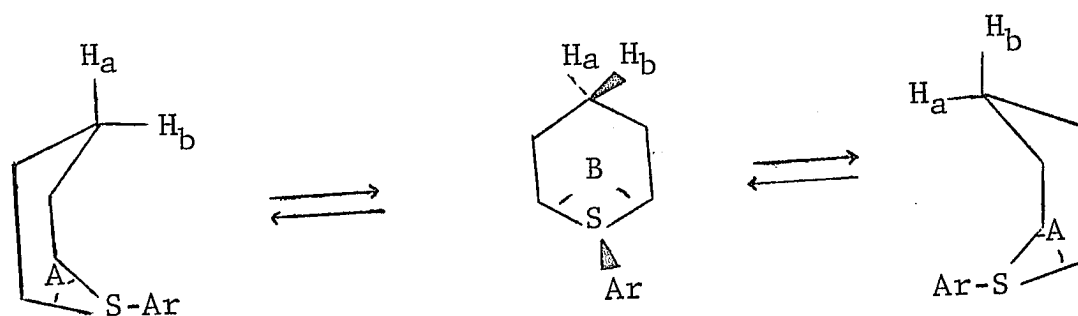


Fig. 2 - Ultraviolet spectra of (8), (9), (10) and (11).

CONCLUSION

The nuclear magnetic resonance behavior of 11, combined with the experimental observation of Darwish and Tourigny²⁵, that racemization of trialkylsulfonium salts was facilitated by bulky groups, indicates that the energy barrier for inversion of triarylsulfonium salts is low, and therefore, the isolation of optically active triarylsulfonium salts seems to be difficult at room temperature. However, the results obtained by the nuclear magnetic study of 11 might not reflect the exact behavior of an unbridged triarylsulfonium salt, since the interconversion of 11 from one boat conformation to the other, would involve a planar transition state (eq. 27). This means that the angle C-S-C, i.e., angle A, of the bridged part of the molecule becomes larger (B>A) in the planar form. This enlargement of the angle might cause the inversion at sulfur to become more rapid, since the differences between the ground and the transition states for this process would be smaller. It is difficult to ascertain the effect of the enlargement of the angle on the sulfur inversion, because ring interconversion and sulfur inversion might be independent processes. The fact that one process (ring interconversion) goes through a planar form does not require the other process (sulfur inversion) to go through the same form simultaneously.



Planar Form

(27)

DESCRIPTION OF EXPERIMENTS

The infrared absorption spectra were determined with a Perkin-Elmer Model 337 grating infrared spectrophotometer. The nuclear magnetic resonance spectra were determined with a Varian Model A-60 nuclear magnetic resonance spectrometer. The ultraviolet absorption spectra were measured with a Model 4000 Spectracord, or a Cary Model 14.

The optical rotations at the sodium D line were determined with a Franz Schmidt and Haensch polarimeter. The optical rotatory dispersions were determined on a Cary Model 60 recording spectropolarimeter, or a Rudolph Model 260/655/850/810-614 recording spectropolarimeter.

Microanalyses were determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The boiling points and melting points are in degrees centigrade and are uncorrected.

Triethyloxonium Tetrafluoroborate.⁴² Boron tri-fluoride etherate (2.5 g., 0.016 mole) was diluted with anhydrous ether (30 ml.), and placed into a 300 ml. 3-neck round bottom flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser with a calcium chloride drying tube. Epichlorohydrin (1.5 g., 0.016 mole) was added dropwise, at a rate that kept the reaction mixture boiling. After an additional stirring of 2 hours, the reaction mixture was allowed to stand at room temperature for 5 hours. The organic liquid was forced out through a V-shape bent tube by means of nitrogen. The white salt was prevented from being forced out by means of glass-wool at one end of the tube. The salt was washed three times with anhydrous ether (40 ml.), which was forced out by means of nitrogen.

(+)-m-Tolyl-p-tolyloethoxysulfonium Tetrafluoroborate.^{14,18}

A solution of (+)-m-tolyl p-tolyl sulfoxide (2.7 g., 0.012 mole, $[\alpha]_D^{25} +16.9^\circ$, c 2.015, acetone) in anhydrous methylene chloride (20 ml.) was added at room temperature with stirring to the solid triethyloxonium salt, all at once. A cooling effect was felt. The homogeneous yellow solution was stirred for an additional 1 hour and then it was allowed to stand overnight. Anhydrous tetrahydrofuran (100 ml.), freshly distilled from sodium hydride, was added to the slightly darkened methylene chloride solution, and the mixed solvent was concentrated (10-15 ml.) by means of an aspirator. Two yellow layers appeared. The bottom layer was quite thick.

Phenyl-m-tolyl-p-tolyloethoxysulfonium Salt. (+)-m-Tolyl-p-tolyloethoxysulfonium salt in tetrahydrofuran (10-15 ml.) was added at 0°C over a 40 min. period with stirring to a solution of phenylmagnesium bromide (0.0625 mole) in anhydrous tetrahydrofuran (130 ml.). The Grignard reagent had been prepared from bromobenzene (12.5 g., 0.0795 mole), and

magnesium (1.5 g., 0.0625 mole). After stirring for an additional ten minutes at 0°, the mixture was hydrolyzed with 20% hydrobromic acid (80 ml.). The organic layer was washed twice with 5% hydrobromic acid (30 ml.), while the combined aqueous solution was washed with ethyl ether (50 ml.). The sulfonium salt was extracted with six 50 ml. portions and one 100 ml. portion of chloroform. After concentration of the chloroform solution at 30-40° at aspirator pressure, excess ether was added at 0° to precipitate the sulfonium salt. A thick oil was obtained which failed to crystallize on cooling or on standing at room temperature for two days. The sulfonium salt gave the qualitative test for water soluble sulfonium salts with cobalt and bismuth.¹⁶ The optical rotation at the sodium D line was difficult to observe due to the colored impurities present. The sulfonium salt was dissolved in distilled water (50 ml.), filtered, and converted into the corresponding crystalline sulfonium perchlorate¹⁹ as follows: The aqueous solution was cooled in an ice-bath, slightly acidified with dilute sulfuric acid, and precipitated with excess aqueous sodium perchlorate solution and few drops of 70% perchloric acid. After several hours at 0°, the solution was filtered, and the precipitate was washed with distilled water, dissolved in chloroform, and reprecipitated with excess ethyl ether. The sulfonium salt did not rotate light at the sodium D line (α 2.110, 95% ethanol). Recrystallization was effected by dissolving the sulfonium salt in acetone-water, and allowing the solvent to evaporate slowly. M.p. 133-135°C. Infrared spectra no. 1251 and no. 1273. Ultraviolet absorption in 95% ethanol occurred at λ_{\max} (log ϵ), 238.5 (4.29), 268.5 (3.90), 277.5 (3.67).

o-Anisylphenyl-p-tolylsulfonium Salt. a) (+)-Phenyl-p-tolylethoxysulfonium tetrafluoroborate was prepared as in the case of (+)-m-tolyl-p-tolylethoxysulfonium tetrafluoroborate from triethyloxonium tetrafluoroborate salt (0.0158 mole), and (+)-phenyl p-tolyl sulfoxide (3.6 g., 0.016 mole; $[\alpha]_D^{27} +21^\circ$, c 2.005 in acetone, lit.¹⁷, $[\alpha]_D^{23} +22^\circ$, c 2.00 in acetone) in anhydrous methylene chloride (25 ml.). The system was in a nitrogen atmosphere at all times. After addition of anhydrous tetrahydrofuran (100 ml.) and concentration of the solvent (50 ml.), a homogeneous solution was obtained. A solution of o-anisylmagnesium bromide (0.0320 mole), prepared from o-bromoanisole (6 g., 0.0320 mole) and magnesium, (1.5 g., 0.0625 g. atom) in anhydrous tetrahydrofuran (80 ml.) was added at 0° over a half an hour period with stirring. After stirring for an additional 8 hours, the mixture was hydrolyzed at 0° with saturated aqueous ammonium chloride. After separation of the layers, the aqueous layer was washed with ether, and the sulfonium salt was extracted with seven 100 ml. portions of chloroform. Concentration of the chloroform solution at room temperature at aspirator pressure yielded a brown oil. The optical rotation at the sodium D line was difficult to observe due to the colored impurities present. The cobalt and bismuth tests indicated the presence of a sulfonium salt. The perchlorate salt was prepared as in the case of phenyl-m-tolyl-p-tolylsulfonium salt, with the exception of omitting the addition of perchloric acid. The salt was dissolved in methanol-water and the solvent was allowed to evaporate slowly. M.p. 86-88°; $[\alpha]_D^{24} 0.0$, c 1.989, 95% ethanol. The optical rotatory dispersion curve up to 300 m μ gave zero rotation. Infrared spectrum no. 1521. Ultraviolet absorption in 95% ethanol occurred at λ_{\max} (log ϵ) 233 (4.32), 268

(3.66), 277 (3.61), 293 (3.71).

Anal. calcd. for $C_{20}H_{19}ClO_4S$: C, 59.04%; H, 4.71%.
Found: C, 59.12%, H, 4.75%.

b) A solution of (-)-o-anisyl p-tolyl sulfoxide (1.0 g., 0.0042 mole) in anhydrous methylene chloride was added at 0°C with stirring to triethyloxonium tetrafluoroborate salt (0.0079 mole). After stirring for 2 hours, and 3 hours of standing at 0°C, dimethoxyethane (50 ml.), freshly distilled over sodium hydride was added. The solution was concentrated (30 ml.) by means of nitrogen, and then diluted with anhydrous dimethoxyethane (50 ml.). A solution of phenylmagnesium bromide (0.01 mole) prepared from bromobenzene (1.57 g., 0.0100 mole) and magnesium (0.5 g., 0.030 g. atom), in anhydrous ether (50 ml.) was added at -10° to -20°C with stirring over a thirty minute period. After hydrolysis with saturated aqueous ammonium chloride, the mixture was filtered and the layers were separated. The sulfonium salt was extracted with five 50 ml. portions of chloroform. A small amount of the chloroform solution (30 ml.) was stirred with an aqueous solution of sodium tetraphenylboron.⁴⁵ After filtering, the solution was concentrated and the water insoluble solid was filtered and washed with plenty of distilled water. The optical rotation of the sulfonium tetraphenylborate at the sodium D line was zero (c 2, acetone).

The remaining chloroform solution was concentrated and the sulfonium salt was precipitated as a semisolid (0.50 g., 0.0014 mole, 36% yield) with excess ether in a Dry-Ice acetone bath. The sulfonium salt was dissolved in distilled water, slightly acidified with dilute sulfuric acid, and precipitated as the perchlorate at 0°C with aqueous sodium

perchlorate solution. The sulfonium salt was filtered, washed with distilled water, and dissolved in acetone-water. Slow evaporation yielded white crystals. M.p. 85-87°.

Infrared spectrum no. 3211.

Anal. calcd. for $C_{20}H_{19}ClO_4S$: C, 59.04%; H, 4.71%.

Found: C, 59.30%; H, 4.72%.

o-Anisylphenyl-p-tolylsulfonium Nitrate. (+)-

Phenyl-p-tolyloethoxysulfonium tetrafluoroborate (.0158 mole) was prepared from triethyloxonium tetrafluoroborate (0.0158 mole), and (+)-phenyl p-tolylsulfoxide (3.6 g., 0.017 mole, $[\alpha]_D^{27} +21^\circ$), in anhydrous methylene chloride (30 ml.). After stirring for half an hour, the solution was allowed to stand overnight in a nitrogen atmosphere. Anhydrous tetrahydrofuran (100 ml.) was added and the solution was concentrated (20 ml.) at aspirator pressure. More anhydrous tetrahydrofuran was added (40 ml.). Two layers were present. A solution of o-anisylmagnesium bromide (0.0161 mole), prepared from o-bromoanisole (3.0 g., 0.016 mole) and magnesium (1.5 g., 0.063 mole), in anhydrous tetrahydrofuran (100 ml.) was added at 0° with stirring over a 2 hour period. The system was in a nitrogen atmosphere at all times. Hydrolysis at 0° with 10% aqueous nitric acid (50 ml.), gave a homogeneous yellow solution. After washing twice with 100 ml. and 50 ml. portions of ether, the sulfonium salt was extracted with seven 50 ml. portions of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. Addition of chilled ethyl ether precipitated a white sticky paste, which changed to yellow with time. The sulfonium salt gave the cobalt and bismuth tests, and it did not rotate light at the sodium D line (c 10.215, 95% ethanol). Infrared spectrum no. 1643.

A solution of the sulfonium salt in distilled water was stirred with an aqueous solution of sodium tetraphenylboron. The sulfonium tetraphenylborate was washed with distilled water, dissolved in acetonitrile, reprecipitated with distilled water, and finally washed with ethyl ether. M. p. 177-178°. Infrared spectrum no. 1643.

From the ether solution, phenyl p-tolyl sulfoxide was recovered (0.5 g., 0.0023 mole) which was recrystallized from ligroin (b.p. 65-75°). The sulfoxide rotated light at the sodium D line $[\alpha]_D +16^\circ$, $n_D 1.895$, acetone).

Triphenylsulfonium Bromide. a) Diphenylethoxysulfonium tetrafluoroborate (0.0215 mole) was prepared from triethyloxonium tetrafluoroborate (0.0215 mole), and diphenyl sulfoxide (Aldrich) (7.0 g., 0.035 mole) in anhydrous methylene chloride (35 ml.). After 9 hours, anhydrous tetrahydrofuran was added (100 ml.), and the solution was concentrated (50 ml.) at aspirator pressure. The solution was added at 0° over a two hour period with stirring to a solution of phenylmagnesium bromide (0.178 mole), prepared from bromobenzene (32 g., 0.20 mole) and magnesium (4.3 g., 0.18 g. atom), in anhydrous tetrahydrofuran (100 ml.), the layers were separated. The aqueous layer was washed with five 50 ml. portions of ether, and the sulfonium bromide extracted with eight 50 ml. portions of chloroform. The chloroform solution upon concentration gave white crystals (4.39 g., 0.0128 mole, 60% yield). The sulfonium compound gave the cobalt and bismuth tests, and it reacted with aqueous silver nitrate to give a precipitate. It was recrystallized once by dissolving in chloroform and precipitating with excess ethyl ether, and once by dissolving in acetone and precipitating again with excess ether. Infrared spectra no.

1150, 1196. Ultraviolet absorption in 95% ethanol: λ_{\max} (log ϵ), 237.5 (4.25), 268.5 (3.64), 276.5 (3.49). M.p. 284-286°, lit.^{10,44}, 285-286° and 292.5°.

Anal. calcd. for $C_{18}H_{15}BrS$: C, 62.96%, H, 4.40%.
Found: C, 63.06%; H, 4.17%.

b) Diphenylethoxysulfonium tetrafluoroborate (0.0188 mole) was prepared from triethyloxonium tetrafluoroborate (0.0188 mole) and diphenyl sulfoxide (5.0 g., 0.024 mole) in anhydrous methylene chloride (20 ml.). Anhydrous tetrahydrofuran was added (30 ml.), and the solvent was concentrated at aspirator pressure. More tetrahydrofuran was added (100 ml.). Two layers were present. A solution of phenylmagnesium bromide (0.1250 mole), prepared from bromobenzene (22 g., 0.14 mole) and magnesium (3.0 g., 0.130 g. atom), in anhydrous tetrahydrofuran (80 ml.) was added at 0° over a 20 minute period with stirring. After hydrolysis with 20% hydrobromic acid (80 ml.) at 0°, the layers were separated. The aqueous layer was washed with five 50 ml. portions of ether, and the sulfonium salt was extracted with eight 50 ml. portions of chloroform. After concentration of the chloroform solution, addition of chilled ether precipitated a white solid (2.0 g., 0.0059 mole, 31% theory). The sulfonium salt was recrystallized from acetone-chloroform (5:2 by volume). M.p. 285-288°, lit.^{10,44}, 285-286° and 292.5°.

o-Anisylphenyl-p-tolylsulfonium Tetraphenylborate.

a) A solution of (+)-phenyl p-tolyl sulfoxide (1.5 g., 0.0070 mole, $[\alpha]_D^{26} +21^\circ$, $d_4^{20} 2.090$, acetone) in anhydrous methylene chloride was added at 0° with stirring to triethyloxonium tetrafluoroborate (0.00791 mole). After stirring for an additional 3 hours at 0°, anhydrous dimethoxyethane (70 ml.), freshly distilled over sodium hydride, was added, and the solution was stirred for 1 hour. After concentration (30

ml.) at aspirator pressure, addition of anhydrous ethyl ether precipitated a white solid. Anhydrous sodium tetraphenylboron (1.5 g., 0.0044 mole) was added and the mixture was stirred at 0° for one hour. A solution of o-anisylmagnesium bromide (0.008 mole), prepared from o-bromoanisole (1.5 g., 0.008 mole) and excess magnesium in anhydrous ether (70 ml.), was added at 0° with stirring over a twenty minute period. The reaction mixture was hydrolyzed with distilled water (70 ml.), filtered, and the solid obtained was dissolved in acetonitrile. The acetonitrile was concentrated at aspirator pressure at room temperature and the white solid thus obtained was dried in a drying pistol at 40°. The compound did not rotate light at the sodium D line (c 2.035, acetonitrile), and the optical rotatory dispersion (1% in acetonitrile) gave zero rotation up to 320 m μ . M.p. 173-175°. Infrared spectrum no. 2707.

The organic solution from the reaction mixture was dried over magnesium sulfate, filtered and concentrated to give (+)-phenyl p-tolyl sulfoxide (0.5 g., 0.00231 mole), $[\alpha]_D^{24}$ +15 (c 2.415, acetone) (unrecrystallized).

b) A solution of (-)-anisyl p-tolyl sulfoxide (2.2 g., 0.0090 mole), $[\alpha]_D^{25}$ -232°, c 2.060, acetone) in anhydrous methylene chloride (40 ml.) was added at 0° with stirring to triethyloxonium fluoroborate (0.0120 mole). After 2 hours of stirring and 2 hours of standing at 0°, anhydrous ether was added (100 ml.) to precipitate the ethoxysulfonium salt. However, a colloidal suspension was obtained, and it was necessary to concentrate the solution (2-3 ml.) at aspirator pressure. The last traces of solvent were removed by passing nitrogen through the system. Anhydrous 1,2-dimethoxyethane (200 ml.) freshly distilled over sodium hydride, and anhy-

drous sodium tetraphenylboron (Fisher, 3.0 g., 0.0088 mole) were added at 0° with stirring. A very small quantity of white crystals failed to dissolve in dimethoxyethane. The solution was transferred to an addition funnel, and added to a filtered solution of phenylmagnesium bromide (0.0270 mole) prepared from bromobenzene (4.27 g., 0.0270 mole) and anhydrous 1,2-dimethoxyethane (200 ml.). The addition took 2 hours. The mixture was hydrolyzed at 0° with distilled water (200 ml.), filtered, and the solid obtained was washed with acetone. Concentration of the acetone solution gave a white solid, m.p. 176-178°. The optical rotatory dispersion (2.5%, acetone) showed that the sulfonium tetraphenylborate was inactive up to 330 m μ . Infrared spectrum no. 3001.

Hydrolysis of (-)-o-Anisyl-p-tolyloethoxysulfonium Tetrafluoroborate. Triethyloxonium tetrafluoroborate (0.0079 mole) was prepared from boron trifluoride etherate (1.67 g., 0.0118 mole) and epichlorohydrin (1.00 g., 0.0107 mole). A solution of (-)-o-anisyl p-tolyl sulfoxide (0.45 g., 0.0018 mole, $[\alpha]_D^{23}$ -172°, c 2.040, acetone, 70% optically pure) in anhydrous methylene chloride (10 ml.) was added at 0°C with stirring. After half an hour, 5 ml. of the solution was poured into distilled water (30 ml.), and the rest of the solution was poured into 5% aqueous sodium hydroxide solution (50 ml.). The solutions were stirred, and the sulfoxide was extracted with ethyl ether. After drying over anhydrous magnesium sulfate, the solutions were filtered and then concentrated. The rotations of the recovered sulfoxide were as follows: Water hydrolysis, $[\alpha]_D^{24}$ -157° (c 0.7750, acetone); basic hydrolysis, $[\alpha]_D^{24}$ = 0.0 (c 2.020, acetone).

Hydrolysis of (+)-Phenyl-p-tolyloethoxysulfonium Tetrafluoroborate. Triethyloxonium tetrafluoroborate (0.0158 mole) was prepared from boron trifluoride etherate (3.00 g., 0.021 mole) and epichlorohydrin (2.5 g., 0.027 mole). A solution of (+)-phenyl p-tolyl sulfoxide (1.5 g., 0.0069 mole, $[\alpha]_D^{22} +16$, c 2.0, acetone, 73% optically pure) in anhydrous methylene chloride was added and the reaction mixture was stirred for half an hour. Anhydrous benzene (100 ml.) was added and the solution was concentrated (50 ml.) by means of an aspirator. Five per cent aqueous sodium hydroxide solution (50 ml.) was added and the mixture was stirred at 0° for 10 minutes. The layers were separated and the organic was diluted with ethyl ether and dried over anhydrous magnesium sulfate. After filtering, the organic solution was concentrated to give (-)-phenyl p-tolyl sulfoxide (1.2 g., 0.0056 mole, 80% theory) $[\alpha]_D^{22} -15.4 \pm 1^\circ$ (c 2.015, acetone).

Reaction of (-)-Phenyl p-tolyloethoxysulfonium Tetrafluoroborate with Magnesium Bromide Etherate. Triethyloxonium tetrafluoroborate (0.0158 mole) was prepared from boron trifluoride ethyl ether (3.0 g., 0.021 mole) and epichlorohydrin (2.5 g., 0.027 mole). A solution of (-)-phenyl p-tolyl sulfoxide (1.00 g., 0.00463 mole, $[\alpha]_D^{22} -15^\circ$, c 2.040, acetone, 69% optically pure) in anhydrous methylene chloride (20 ml.) was added, and the reaction mixture was stirred for half an hour. Anhydrous benzene was added (75 ml.) and the solvent was concentrated (50 ml.) at aspirator pressure. A solution of magnesium bromide etherate (0.0212 mole), prepared from ethylene dibromide (4.00 g., 0.021 mole) and excess magnesium, in anhydrous ethyl ether (50 ml.), was added over a fifteen minute period. After stirring for

fifteen minutes, the mixture was hydrolyzed with 5% aqueous sodium hydroxide solution (50 ml.). The layers were separated, and the organic layer was dried over anhydrous magnesium sulfate. After filtering, the organic solution was concentrated to give a very small amount of sulfoxide, $[\alpha]_D^{22} -10.8^\circ$ (c 2.015, acetone). The rotation of the sulfoxide above is that of unrecrystallized compound.

Condensation of (+)-Phenyl p-Tolyl Sulfoxide and Anisole by Means of Phosphorus Pentoxide.⁶ (+)-Phenyl p-tolyl sulfoxide (2.0 g., 0.0092 mole) and anhydrous anisole (1.0 g., 0.0093 mole) were placed in a 1-neck 100 ml. round bottom flask, equipped with a calcium drying tube. Phosphorus pentoxide (1.9 g., 0.0134 mole) was added, and the mixture was heated in a water bath for 1 1/2 hours. The mixture turned red in color. After cooling to 0°, distilled water (50 ml.) was added, and the mixture was warmed. The solution was washed with three 50 ml. portions of ethyl ether, and then with three 50 ml. portions of chloroform. The aqueous layer was concentrated (5 ml.) at aspirator pressure. The aqueous solution gave the cobalt test for sulfonium salts. Methanol was added (40 ml.), and then excess saturated aqueous barium hydroxide solution. The solution was filtered and carbon dioxide was passed into it to precipitate the excess barium. The solution was refiltered and acidified with six 50 ml. portions of chloroform which was concentrated to a small volume. Addition of excess ether precipitated an oil. The oil was dissolved in 25 ml. of methanol and the optical rotation at the sodium D line was taken and found to be zero. An aqueous solution of the solution of the sulfonium salt reacted with dilute aqueous silver nitrate to give a precipitate.

Evaporation of the ether solution gave sulfoxide (0.8 g., 0.004 mole), which was recrystallized from ligroin. The sulfoxide was racemic at the sodium D line (c 0.0512 g., acetone). Infrared spectrum no. 1894.

Racemization of (-)-o-Anisyl p-Tolyl Sulfoxide with Phosphorus Pentoxide. (-)-o-Anisyl p-tolyl sulfoxide (1.0 g., 0.004 mole, $[\alpha]_D^{23}$ -248°, c 2.250, acetone) and anhydrous 1,3-dimethoxybenzene (0.5 ml., 0.5 g., 0.0036 mole) were placed in 1-neck 100 ml. round bottom flask equipped with a calcium chloride drying tube. Phosphorus pentoxide (0.28 g., 0.0020 mole) was added and the mixture was warmed in a water bath, kept at 80°, for 15 minutes. Distilled water was added and the sulfoxide was extracted with ethyl ether. The ether solution was dried over anhydrous magnesium sulfate, filtered and then concentrated. The solid obtained was recrystallized from ligroin (b.p. 65-75°), $[\alpha]_D^{23}$ -110 ± 1° (c 2.070, acetone).

Condensation of (-)-o-Anisyl p-Tolyl Sulfoxide with Benzene by Means of Aluminum Chloride.⁹ Anhydrous benzene (2.0 g., 0.025 mole) was placed in a 1-neck 50 ml. round bottom flask, equipped with a condenser and a calcium chloride drying tube. Anhydrous aluminum chloride (1.25 g., 0.00725 mole) was added at ice temperatures and the mixture was mixed well. (-)-o-Anisyl p-tolyl sulfoxide (1.25 g., 0.00405 mole) was added at the above temperature and the reaction flask was immersed in an oil bath kept at 40°. After three days, the reaction mixture was poured onto crushed ice and the sulfonium salt was extracted with eight 50 ml. portions of chloroform. The chloroform solution was concentrated (20 ml.) and then excess ether was added. The mixture was cooled in a Dry Ice acetone-bath, and the solvent was decanted from

the white solid. The solid was washed four more times with ether and then it was dried in a pistol over phosphorus pentoxide. Yield: 1.0 g., (0.0029 mole, 73% theory). The crispy material became semisolid when it was exposed to air. Infrared spectrum no. 4580. An aqueous solution of the sulfonium salt gave the cobalt test for sulfonium salts.

The semisolid (1 g.) was dissolved in distilled water, filtered, and then cooled in an ice bath. Perchloric acid (1 ml., 70%) was added dropwise with stirring. The white fluffy solid was allowed to stand for 1 hour at 0°, and then it was filtered. The solid was washed with distilled water and then dissolved in acetone. A little water was added and the solution was allowed to slowly evaporate. White crystals appeared, m.p. 86-88°, $[\alpha]_D^{25}$ 0.0 (2.070, acetone). Infrared spectrum no. 4643.

The solvent that was used to wash the sulfonium salt obtained initially (chloroform and ether), was concentrated and washed with distilled water. The aqueous solution was filtered and stirred with sodium tetraphenylboron (Fisher). A white colloidal suspension appeared which coagulated when a little sodium chloride was added. The solid was washed with distilled water and dried in a pistol over phosphorus pentoxide at 60°. The sulfonium tetraphenylborate was recrystallized twice by dissolving in acetone and precipitating with excess ligroin (b.p. 65-75°). M.p. 175-177°. Infrared spectrum no. 4605.

Condensation of (+)-Phenyl p-Tolyl Sulfoxide with p-Xylene by Means of Aluminum Chloride. p-Xylene (4 ml., 3.4 g., 0.032 mole) was placed in a dry 1-neck 50 ml. round bottom flask, equipped with a magnetic stirrer and a calcium chloride drying tube. Anhydrous aluminum chloride (1.33 g., 0.00928

mole) was added at ice temperatures. (+)-Phenyl p-tolyl sulfoxide (1.0 g., 0.0046 mole) was added and the reaction mixture was stirred at 40-42° for six hours and then poured onto crushed ice. The aqueous solution was washed with ether and the sulfonium salt was extracted with five 50 ml. portions of chloroform. Concentration of the chloroform solution gave an oil (1.5 g., 0.0044 mole, 50% theory). The sulfonium salt gave the bismuth test for sulfonium salts. The oil was dissolved in distilled water, filtered, and treated with a solution of sodium tetraphenylboron (1.0 g., 0.0030 mole) in distilled water. The white solid was washed with distilled water but this process changed it into a semisolid. After drying in the air, the semisolid was dried in a desiccator over calcium chloride, dissolved in acetone, filtered, and the solvent evaporated at aspirator pressure at room temperature. A very white crispy material appeared. The solid was dried at 40° in a pistol over phosphorus pentoxide for half an hour. (0.40 g., 0.00064 mole, 22% yield), m.p. 87-90°. The sulfonium salt did not rotate light at the sodium D line (c 1.875, acetone) and its optical rotatory dispersion (2.5% in acetone) gave no zero rotation up to 330 $m\mu$. Infrared spectrum no. 3059.

Concentration of the ether used to wash the aqueous solution originally, gave (+)-phenyl p-tolyl sulfoxide (0.2 g., 0.0009 mole, $[\alpha]_D +31^\circ$ (c 2.200, acetone).

The Reaction of o-Anisylmagnesium Bromide with (+)-p-Anisyl p-Tolyl sulfoxide. The procedure was that of Wildi, et al.¹⁰ A solution of o-anisylmagnesium bromide (0.040 mole), prepared from magnesium (2.0 g., 0.080 mole) and o-bromoanisole (7.5 g., 0.040 mole) in anhydrous ether (80 ml.) was diluted with anhydrous benzene (100 ml.). The

ether was distilled off and a solution of (+)-p-anisyl p-tolyl sulfoxide¹⁷ (1.0 g., 0.0050 mole, $[\alpha]_D^{20} +24$, c 2.005, acetone) in anhydrous benzene (100 ml.) was added with stirring over a 10 minute period. The reaction mixture was refluxed for 21 hours by means of a heating mantle, cooled to 0°, and hydrolyzed with 24% hydrobromic acid (20 ml.). The sulfonium salt was removed from the aqueous layer with chloroform.¹⁹ Evaporation of the solvent gave a negligible amount of an oil, which did not rotate light at the sodium D line. The positive cobalt test¹⁶ confirmed the presence of the sulfonium salt. Infrared spectrum no. 598.

Methylphenylbenzylsulfonium Perchlorate.⁴⁵ A solution of methyl phenyl sulfide (4.00 g., 0.0322 mole) and benzyl alcohol (3.48 g., 0.0322 mole) in nitromethane (150 ml.) was placed in a 1-neck 500 ml. round bottom flask. Seventy per cent perchloric acid (4.64 g., 0.0322 mole) was added dropwise at room temperature. The reaction mixture changed from colorless to yellow to maroon. After standing for 70 hours at room temperature, the mixture was cooled for 1 hour at 0° and then diluted with ether. The sulfonium salt precipitated as a white solid which was removed by filtration and washed with distilled water and then pentane. Yield 6.0 g. (0.019 mole); 60% theory. M.p. 124-126°. Nuclear magnetic resonance (no. 1580 and 1582) revealed a singlet at 6.77 τ (methylene) and a singlet at 7.10 τ (methyl). Infrared spectrum no. 3945.

Thioxanthene. Thioxanthene was purchased from Aldrich Co. The nuclear magnetic resonance spectrum of this substance (no. 1524) in deuteriochloroform exhibited a singlet at 6.18 τ for the protons of C₉. The aromatic region occurred as a multiplet with the highest peak at 2.80 τ . The spectrum was in agreement with that reported in the literature.²⁹

Ultraviolet absorption in 95% ethanol: λ_{\max} (log ϵ), 268.5 (3.99), 251 (3.76), 238.5 (3.63), 226 (3.95), 216 (4.39).

Thioxanthene 10,10-Dioxide. 30% Hydrogen peroxide (2.50 g., 0.0198 mole) was added dropwise (ten drops after a 3 minute interval) to a boiling solution³⁰ of thioxanthene (1.0 g., 0.0051 mole) in glacial acetic acid (20 ml.). The solution was boiled until the volume was reduced to 5 ml. and then it was poured onto ice water. Filtration gave a white solid which was washed with cold distilled water and then dissolved in methylene chloride. After drying over magnesium sulfate, the solution was concentrated at aspirator pressure and the solid obtained (1.0 g.) was recrystallized once from ligroin (b.p. 60-75°)-chloroform to yield 0.60 g. (0.0026 mole, 52% yield) of a white solid, m.p. 171-173°, lit.³⁰, m.p. 170°. Thin layer chromatography on silica G gel in chloroform showed only one spot. Nuclear magnetic resonance (no. 2203) in deuteriochloroform showed a sharp singlet for the protons of C₉ at 5.77 τ . The aromatic region occurred as a multiplet, centered at about 1.98 τ , and as a doublet with peaks at 2.53 τ , and 2.58 τ . Also the spectrum in chloroform revealed a sharp singlet at 5.78 τ . Infrared spectrum no. 5295. Ultraviolet absorption in 95% ethanol: λ_{\max} (log ϵ), 283.5 (2.71), 278.5 (2.97), 248.5 (3.69), 211 (4.48), 203.5 (4.61).

Thioxanthene 10-Oxide. 30% Hydrogen peroxide (1.272 g., 0.0102 mole) was added dropwise at room temperature with stirring to a solution of thioxanthene (1.0 g., 0.0051 mole) in acetic anhydride (60 ml.). After the lapse of a short time the temperature rose to 33°. The temperature should not be allowed to rise above 35°. When the temperature started to drop, the solution was poured onto crushed ice. The

product was extracted with five 50 ml. portions of methylene chloride, dried over magnesium sulfate, and the solution was concentrated at aspirator pressure. Addition of ligroin (b.p. 60-75°), and cooling precipitated a white solid (0.80 g., 0.0047 mole, 91.5% yield), which was recrystallized once from carbon tetrachloride, m.p. 114-115°, lit.³⁰ m.p. 109-110° and^{38a} 119°. Thin layer chromatography on silica G gel in chloroform showed one spot. Nuclear magnetic resonance (no. 2202) in deuteriochloroform revealed a quartet for the protons of C₉, centered at about 6.03τ, and with peaks at 5.70τ, 5.98τ, 6.17τ, and 6.45τ. The aromatic region occurred as a multiplet centered at about 2.17τ, and a doublet with peaks at 2.62τ, and 2.67τ. Infrared spectrum no. 5344. Ultraviolet absorption in 95% ethanol: λ_{\max} (log ϵ), 278.5 (3.30), 271 (3.29), 236 (3.97), 202 (4.66).

9,10-Dihydro-10-(2,5-dimethylphenyl)thioxanthylum
Perchlorate. Concentrated sulfuric acid⁶ (98%; 2 ml.) was added dropwise at 15° with stirring to a mixture of thioxanthene sulfoxide (1.0 g., 0.0047 mole) and p-xylene (10 ml.). The dark red mixture was stirred for half an hour at 20° and then poured onto crushed ice. The aqueous solution was washed with three 50 ml. portions of ether, and the sulfonium salt was extracted with five 50 ml. portions of methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate, filtered and then concentrated at room temperature at aspirator pressure. The sulfonium salt was extracted with two 30 ml. portions of distilled water, filtered and cooled to 0°. Addition of 70% perchloric acid (3 ml.) precipitated a white solid which was filtered, washed with distilled water, and then dried in an evacuated pistol over phosphorus pentoxide. Yield 0.50 g. (0.0012

mole, 26% theory). M.p. 148-150°. Nuclear magnetic resonance (no. 2152) in deuterochloroform revealed two singlets at 7.28 τ , and 7.72 τ , and a singlet at 5.52 τ for the protons of C₉. The aromatic region occurred as a multiplet, centered at about 2.08 τ , and as two singlets with peaks at 2.55 τ and 3.20 τ . Similarly, the spectrum in chloroform (no. 2144) revealed two singlets at 7.32 τ , and 7.75 τ , and a singlet at 5.50 τ . The high temperature study (no. 2249) in 1,1,2,2-tetrachloroethane at 60 Mc revealed that the half-width of the singlet observed for the protons of C₉ became sharper (see Table 1). Infrared spectrum no. 5207. Ultra-violet absorption in 95% ethanol: λ_{\max} (log ϵ), 281 (3.39), 273.5 (3.38), 238.5 (4.13).

Anal. calcd. for C₂₁H₁₉ClO₄S: C, 62.60%; H, 47.75%.
Found: C, 62.36%; H, 4.75%.

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SUMMARY

I. The reaction of (-)-menthyl (-)-arenesulfinate esters with Grignard reagents proceeds with inversion to yield optically active sulfoxides in high yields. In an effort to find out something about the stereospecificity of this reaction, the following reactions were carried out: a) (-)-Menthyl S-(-)-p-toluenesulfinate was reacted with p-anisylmagnesium bromide to yield S-(-)-p-anisyl p-tolyl sulfoxide, $[\alpha]_D^{30} -25^\circ$. b) (-)-Menthyl S-(-)-p-methoxybenzenesulfinate was reacted with p-tolylmagnesium bromide to give R-(+)-p-anisyl p-tolyl sulfoxide, $[\alpha]_D^{20} +24^\circ$. The above results, combined with the fact that pure sulfoxides are obtained in high yields, indicate that any reactions leading to racemization or retention must be minor. The literature also indicates that in the case of (+)-ethyl p-tolyl sulfoxide, the reaction between (-)-menthyl S-(-)-p-toluenesulfinate and ethylmagnesium bromide proceeded with 96% inversion and 4% retention.

II. Although optically active trialkylsulfonium salts have been known for many years, a literature survey showed that optically active triarylsulfonium salts had never been prepared. In an effort to convert optically active diaryl sulfoxides into optically active triarylsulfonium salts the following methods were investigated: a) Condensation of (+)-phenyl p-tolyl sulfoxide with anisole in the presence of phosphorus pentoxide at 85° . b) Condensation of (-)-o-anisyl p-tolyl sulfoxide with anisole in the presence of anhydrous aluminum chloride at 40° . c) Condensation of (+)-methyl p-tolyl sulfoxide with anisole in the presence of 70% perchloric

acid at room temperature. d) Reaction of (+)-p-anisyl p-tolyl sulfoxide with phenylmagnesium bromide. e) Reaction of optically active diarylethoxysulfonium tetrafluoroborates such as (-)-o-anisyl-p-tolyloethoxysulfonium salt, with arylmagnesium bromide at, or below 0°. The sulfonium salts were inactive in all cases. Methods a and c were found to racemize diaryl sulfoxides.

Condensation of thioxanthene 10-oxide with p-xylene in the presence of concentrated sulfuric acid at 15° yielded 9,10-dihydro-10-(2,5-dimethylphenyl)thioxanthylum salt. The nuclear magnetic resonance spectrum of the latter compound exhibited a singlet for the protons at C₉ and this indicated that both ring interconversion and sulfur inversion were probably rapid. This fact, combined with evidence found in the literature that racemization of optically active trialkylsulfonium salts is facilitated by bulky groups, indicates that optically active triarylsulfonium salts may racemize rapidly at room temperature.