nism may be urethan despite our failure to isolate it from I and II even at 0°.[3] Furthermore, the first step, and not the second, may be the rate-determining step for isocyanate disappearance. Our data do not clearly differentiate the two possibilities. The relative rates for the different carbinols should be the same whether urethan or carbonium ion formation is rate controlling.[9]

$$ArSO_2NCO + Ar_3COH \xrightarrow{\text{rate determining}} [ArSO_2NHCOCAr_3] \longrightarrow \text{ions, etc.}$$

Electron-withdrawing groups probably cause slow urethan formation because of the reduced nucleophilicity of the carbinol oxygen. Also, the carbinol oxygen would have a partial positive charge on it in the transition state.

In summary, we do not believe that the results obtained prove or disprove a common intermediate for the different reactions. While a common step involving urethan formation is the simplest explanation, it is still disturbing that urethan cannot be isolated at low temperatures in most cases. If, on the other hand, the mechanisms are different for consumption of isocyanate, it might be concluded that three nitro groups have approximately the same effect in the urethan reaction as they would have in the amide-producing reaction.

It is interesting to note that 4-toluenesulfonyl isocyanate (I) is slightly less reactive than is benzenesulfonyl isocyanate[3] toward triphenylmethanol (II). (The rate constants are 0.209 and 0.296, respectively, at 100°.) Apparently, the methyl group destabilizes the transition state (which may have partial negative charges on the carbon or nitrogen of the isocyanate) or the subsequent ions. As expected from the above result, we have found that 4-chlorobenzenesulfonyl isocyanate is considerably more reactive than is I toward hindered phenols.[10]

Registry No.—I, 4083-64-1; VIII, 21112-03-8; IX, 22566-46-7; X, 22566-47-8; XI, 22566-48-9; XII, 22566-49-0.

(9) A reviewer suggested that the Hammett value is too small in absolute magnitude if carbonium ion formation is rate determining, but is consistent with urethan formation.

(10) Unpublished results obtained in this laboratory by Mr. Samuel Gaskins.

The Synthesis and Stereochemistry of Triarylsulfonium Salts[1]

KENNETH K. ANDERSEN, MAURO CINQUINI, AND NICHOLAS E. PAPANIKOLAOU[2]

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

Received July 8, 1969

Several triarylsulfonium salts were prepared from the reaction of arylmagnesium halides with diarylethoxysulfonium salts. Optically active diarylethoxysulfonium salts gave only racemic triarylsulfonium salts. Possible reasons for the cause of racemic products are discussed. A series of 9,9-dihydro- and 9,9-dimethyl-10-aryl- and alkylthioxanthylium perchlorates were synthesized. A variable-temperature nmr study was done on 9,9-dimethyl-10-phenylthioxanthylium perchlorate. Coalescence of the 9,9-dimethyl doublet occurred at 200 ± 5° in benzophenone. A value for $\Delta G^{\ddagger}$ of 25.4 kcal/mol was calculated for the barrier to pyramidal sulfur inversion for this molecule.

The synthesis of triarylsulfonium salts from the reaction of arylmagnesium halides with diarylethoxysulfonium salts was reported in a preliminary communication (eq 1).[3] When optically active diaryl-

$$ArAr'SOC_2H_5^+ + Ar''MgX \longrightarrow ArAr'Ar''S^+ \quad (1)$$

ethoxysulfonium salts were used, inactive triarylsulfonium salts were obtained, which was surprising, since other examples of nucleophilic substitution at sulfur involving optically active tricoordinate sulfur compounds proceeded with inversion to give optically active products (eq 2,[4] 3,[5] 4,[6] and 5[7]). This article presents the details of additional research into the causes of racemization as well as the details of our earlier work.

$$ArS(O)OR + RMgX \longrightarrow ArRSO \quad (2)$$

$$ArS(O)OR + R'OH \longrightarrow ArS(O)OR' + ROH \quad (3)$$

$$ArRSO + Ar'SONH_2 \xrightarrow[(C_2H_5)_3N]{P_4O_{10}} ArRSNSO_2Ar' \quad (4)$$

$$ArAr'SOC_2H_5^+ + OH^- \longrightarrow ArAr'SO \quad (5)$$

The sulfonium salts synthesized as in eq 1 are listed in Table I together with their physical properties. The sulfonium salts synthesized starting with optically active sulfoxides as the source of the ethoxysulfonium salt showed no optical activity between 600 and 300 mμ.

Racemization could conceivably occur in various ways. The ethoxysulfonium salt might racemize before it reacts with the Grignard reagent to form products. The reaction (eq 1) could proceed through a symmetrical intermediate or transition state. For example, if a tetracoordinate intermediate analogous in structure to sulfur tetrafluoride is formed, it might undergo pseudorotation before going on to products, with the consequent formation of racemic sulfonium salts.[8] Finally, an optically active sulfonium salt might be formed but suffer rapid loss of optical

(1) The authors gratefully acknowledge support from the U. S. Public Health Service, Grant GM-10800. Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969.

(2) Part of this research is from the Ph.D. thesis of N. E. P., University of New Hampshire, 1966.

(3) K. K. Andersen and N. E. Papanikolaou, *Tetrahedron Lett.*, 5445 (1966).

(4) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968), and references cited therein.

(5) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

(6) J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, **87**, 4398 (1965).

(7) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965), and references cited therein.

(8) P. C. Lauterbur and F. Ramirez, *ibid.*, **90**, 6722 (1968).

TABLE I

TRIARYLSULFONIUM SALTS SYNTHESIZED FROM DIARYLETHOXYSULFONIUM SALTS

Compd no.	Sulfonium salt ArAr'Ar''S$^+$	Sulfonium salt X$^-$	Precursors ArAr'SO	Precursors Ar''MgX	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1	Ph_3	Br^-	Ph_2SO	PhMgBr	284–286[a]	62.96	4.40	63.06	4.17
2	Ph-*m*-Tol-*p*-Tol[b]	ClO_4^-	(+)-*m*-Tol-*p*-Tol	PhMgBr	133–135	61.45	4.90	61.28	4.77
3	Ph-*p*-Tol-*o*-An	ClO_4^-	(+)-Ph-*p*-Tol	*o*-AnMgBr	86–88	59.04	4.71	59.12	4.75
4	Ph-*p*-Tol-*o*-An	ClO_4^-	(−)-*o*-An-*p*-Tol	PhMgBr	85–87	59.04	4.71	59.30	4.72
5	Ph_2-*p*-Tol	ClO_4	Ph_2SO	*p*-TolMgBr	207–208	60.55	4.55	60.81	4.70

[a] Literature mp 285–286° [B. S. Wilde, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, **73**, 1965 (1951)]; 292.5° [W. A. Bonner, *ibid.*, **74**, 5078 (1952)]. [b] Ph = phenyl, Tol = tolyl, An = anisyl.

activity through processes such as aryl-group exchange with the arylmagnesium halide or pyramidal inversion.[9] These various possibilities will be discussed in turn.

If the diarylethoxysulfonium salts are to racemize before they react with the arylmagnesium bromide, this racemization must take place in the Grignard solution, for the diarylethoxysulfonium salts are otherwise optically stable. This was demonstrated by forming an ethoxysulfonium salt from (+)-phenyl *p*-tolyl sulfoxide and hydrolyzing it with aqueous sodium hydroxide, whereupon (−)-phenyl *p*-tolyl sulfoxide was formed. We were also able to duplicate Johnson's results using (+)-*p*-tolyl benzyl sulfoxide.[7,10] In this case we also isolated the ethoxysulfonium salt and measured its rotation before hydrolyzing it in basic solution to form the inverted (−)-*p*-tolyl benzyl sulfoxide.

To see whether the magnesium bromide in the Grignard solution reacted with the ethoxysulfonium salt, a solution of magnesium bromide in ether was added to phenyl-*p*-tolylethoxysulfonium tetrafluoroborate prepared from phenyl-*p*-tolyl sulfoxide, $[\alpha]D$ −15°. After basic hydrolysis, the recovered sulfoxide was still levorotatory, $[\alpha]D$ −10.8°. A similar sequence was carried through using (+)-*p*-tolyl benzyl sulfoxide, $[\alpha]D$ +106°. The sulfoxide recovered in 30% yield after hydrolysis had the same sign of rotation, $[\alpha]D$ +59°. The intermediate ethoxysulfonium salt was 87% optically pure; the recovered sulfoxide was 55% optically pure.

Nucleophilic attack of the bromide ion on the ethyl group of the ethoxysulfonium salt with consequent formation of ethyl bromide and the sulfoxide of retained configuration can explain our observations. Since the recovered sulfoxide is lower in optical purity than the starting material, it seems that such a displacement reaction is fairly slow. Some unreacted ethoxysulfonium salt remains in the reaction mixture and is subsequently converted into the inverted sulfoxide, forming a partially racemic product. In the case of the *p*-tolylbenzylethoxysulfonium salt, *ca.* 80% of the reaction product was due to bromide ion attack and 20% to hydroxide ion attack. The low recovery of sulfoxide (30%) is puzzling. Perhaps another side reaction is taking place.

Alternatively, one could postulate nucleophilic attack by bromide ion on sulfur with displacement of the ethoxy group to give a bromosulfonium salt (eq 6).

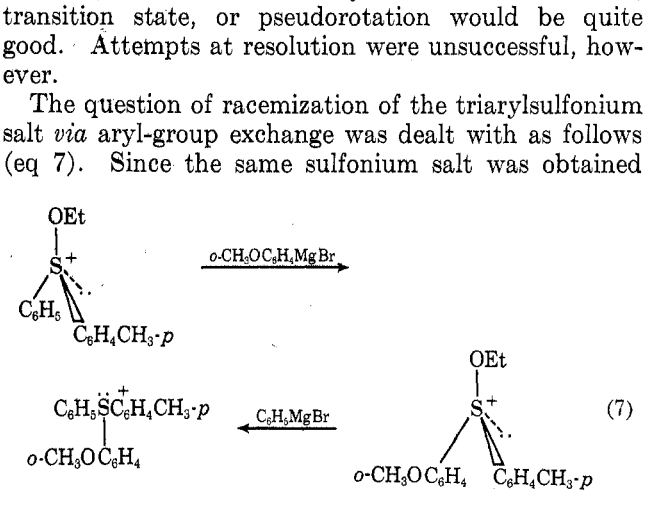
$$ArAr'SOC_2H_5^+ + Br^- \longrightarrow ArAr'SBr^+ + C_2H_5O^- \quad (6)$$

This bromosulfonium salt might undergo bromide ion exchange with consequent racemization followed by reaction with either Grignard reagent or hydroxide ion to give racemic products.

No matter what the exact nature of the reaction of magnesium bromide with the diarylethoxysulfonium salt, it might be the cause of racemization. Removal of the magnesium bromide from a Grignard solution by precipitation with dioxane prior to adding the Grignard solution to the diarylethoxysulfonium salt made no difference; the triarylsulfonium salt obtained was racemic.

In principle, it would be easy to see if the reaction (eq 1) proceeds through a symmetrical intermediate or transition state. Provided that the ethoxysulfonium salt did not undergo a base-catalyzed elimination or rearrangement reaction, one could synthesize a trialkylsulfonium salt from an optically active dialkylethoxysulfonium salt and an alkylmagnesium halide and see if the product is active. Trialkylsulfonium salts have been resolved and are thermally stable at room temperature.[11] Unfortunately, the usual trialkylsulfonium salts undergo base-catalyzed elimination reactions with Grignard reagents; we were not successful in synthesizing them by the above procedure. Alternatively, one could attempt the resolution of a triarylsulfonium salt. If it could be resolved and remained optically active under the conditions of the reaction, then the case for a symmetrical intermediate, transition state, or pseudorotation would be quite good. Attempts at resolution were unsuccessful, however.

The question of racemization of the triarylsulfonium salt *via* aryl-group exchange was dealt with as follows (eq 7). Since the same sulfonium salt was obtained



(7)

in two ways, scrambling of the aryl groups does not take place.

Since other tricoordinate sulfur compounds, including ethoxysulfonium salts, react with nucleophiles with inversion of configuration, it seems probable that racemization occurs after the formation of a triaryl-

(9) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

(10) C. R. Johnson and D. McCants, Jr., *ibid.*, **89**, 1764 (1967).

(11) D. Darvish, S. H. Hui, and Tomilson, *ibid.*, **90**, 5631 (1968).

TABLE II
ANALYTICAL AND NMR DATA

Compd no.	Compd	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Nmr[a]
6	Thioxanthene	...	...		...		6.18 (s, $CDCl_3$)
7	Thioxanthene 10-oxide	118–119[b]	...		...		5.88, 6.26 (q, J_{AB} = 16.8 Hz, $CDCl_3$[c])
8	2-Chlorothioxanthene 10-oxide	124–125	62.78	3.65	63.03	3.61	5.89, 6.24 (q, J_{AB} = 16.8 Hz, $CDCl_3$)
9	9,9-Dimethylthioxanthene 10-oxide	116–117[d]	74.35	5.82	74.23	5.80	8.03, 8.65 (d, CCl_4)[e]
10	Thioxanthene 10,10-dioxide	171–173[f]	...		...		5.77 (s, $CDCl_3$)[g]
11	9,9-Dimethylthioxanthene 10,10-dioxide	165–167[h]	69.74	5.46	69.89	5.58	8.12 (s, $CDCl_3$)[i]
12	9,9-Dihydro-10-(2,5-xylyl)thioxanthylium perchlorate	158	62.60	4.75	62.36	4.75	5.52 (s, $CDCl_3$)
13	9,9-Dihydro-10-mesitylthioxanthylium perchlorate	>245	63.38	5.08	63.09	5.19	5.43, 5.50 (d, $CHCl_2CHCl_2$)
14	9,9-Dimethyl-10-phenylthioxanthylium perchlorate	197–198	62.60	4.75	62.58	4.74	7.97, 8.29 (d, $CHCl_2CHCl_2$)
15	9,9-Dihydro-10-methylthioxanthylium perchlorate	199–200 dec	53.76	4.19	53.48	4.17	5.44, 5.48 (6.65) (d, $CHCl_2CHCl_2$), 5.44 (6.78) (s, CH_3CN)
16	2-Chloro-9,9-dihydro-10-methylthioxanthylium perchlorate	178–179 dec	48.43	3.48	48.53	3.59	5.40, 5.45 (6.62) (d, $CHCl_2CHCl_2$)
17	9,9-Dihydro-10-ethylthioxanthylium perchlorate	123–125	55.12	4.33	55.18	4.52	5.43 (s, $CDCl_3$)
18	Methyldiphenylsulfonium perchlorate	75–76[j]	...		...		(6.39) (s, $CDCl_3$)

[a] In τ units; chemical shifts refer to the 9,9-dihydro or 9,9-dimethyl groups except for **15**, **16**, and **18**, for which values for the CH_3S group are given in parentheses; s = singlet, d = doublet, q = quartet. [b] Literature mp 119° [H. J. Shine and L. Hughes, *J. Org. Chem.*, **31**, 3142 (1966)]. [c] Literature τ 5.84, 6.23 (J = 17 Hz) [A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 941 (1969)]. [d] Literature mp 121–122° (footnote *c*). [e] Literature τ 8.02. 8.64 (footnote *c*). [f] Literature mp 170° [T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, **99**, 145 (1911)]. [g] Literature 5.77 (footnote *c*). [h] Literature mp 169–170° (footnote *c*). [i] Literature τ 9.14 (footnote *c*). [j] Literature mp 73–74° [V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961)].

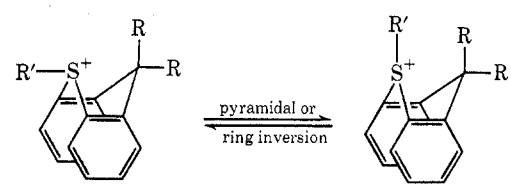
sulfonium salt. Pyramidal inversion is a possible explanation for such a racemization. Although trialkylsulfonium salts can be resolved, Darwish and coworkers recently demonstrated that they do racemize by pyramidal inversion.[11] Their conclusions were confirmed by Mislow and Scartazzini.[12] While trialkylsulfonium salts do not racemize rapidly at room temperature, it is conceivable that this is not so for triarylsulfonium salts. Their barrier to inversion might be so low that they racemize readily at room temperature. This would explain the lack of stereochemistry in our synthesis of triarylsulfonium salts (eq 1).

In order to test this hypothesis, we synthesized a number of model compounds for which an nmr study might provide evidence for or against the inversion process.

These compounds, listed in Table II, are derivatives of thioxanthene and have the general structure shown in eq 8. The three triaryl compounds, 9,9-dihydro-10-(2,5-xylyl)thioxanthylium perchlorate (**12**), 9,9-dihydro-10-mesitylthioxanthylium perchlorate (**13**), and 9,9-dimethyl-10-phenylthioxanthylium perchlorate (**14**), were prepared from the sulfoxide, the proper aromatic hydrocarbon (*p*-xylene, mesitylene, or benzene), and concentrated sulfuric acid. The alkyldiarylsulfonium salts, 9,9-dihydro-10-methylthioxanthylium perchlorate (**15**), 2-chloro-9,9-dihydro-10-methylthioxanthylium perchlorate (**16**), 9,9-dihydro-10-ethylthioxanthylium perchlorate (**17**), and methyldiphenylsulfonium perchlorate (**18**), were prepared from the parent sulfide, alkyl iodide, and silver tetrafluoroborate in 1,2-dichloroethane.

(12) R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967).

The central sulfur-containing ring in these compounds is probably boat shaped.[13] The possible conformational and configurational equilibria are shown below.



(8)

R = CH_3 or H
R′ = aryl or alkyl

The rate of ring flipping is believed to be fast for systems of this type. For example, 9,9-dimethylthioxanthene-10,10-dioxide (**11**) gave only one nmr signal for the *gem*-dimethyl group from −70 to 35°. Had the ring flipping for the sulfone been slow, one would have expected the anisotropy of the S=O bond to manifest itself in the nmr signal for the two methyl groups as it did in the sulfoxide case. For the sulfoxide, the diastereotopic relationship of the two methyls is clearly revealed in their spectrum. For the sulfone, these methyls are equivalent on the nmr time scale. One can consider pyramidal inversion of the tricoordinate sulfur atom superimposed on this rapid ring flipping. This inversion process is slow for the sulfoxide, as revealed by the diastereotopism of the *gem*-dimethyls in the nmr spectrum. A similar diastereotopic relationship is also demonstrated for several of the sulfonium salts by their nmr spectra.

(13) For discussion of this problem, see A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969).

One of these sulfonium salts, **14**, proved stable enough at high temperatures so that coalescence of the *gem*-dimethyl doublet could be observed. This occurred at 200 ± 5° in benzophenone as a solvent. A value of k for this exchange process of 17.8 sec^{-1} was calculated from the equation $k = (\pi \Delta \nu)/\sqrt{2}$, where $\Delta\nu$ is the separation between the *gem*-dimethyl signals in hertz under conditions of no exchange.[14] The free energy of activation was calculated to be 25.4 kcal/mol.

Mislow and Scartazzini[12] report $\Delta H^{\pm}$ for the racemization of 1-adamantylethylmethylsulfonium perchlorate as 26 kcal/mol and $\Delta S^{\pm}$ as 8 eu. Darwish and Tomilson report $\Delta H^{\pm}$ values of 25–29 kcal/mol for several other trialkylsulfonium salts.[15] These values were obtained by measuring rates of racemization of the resolved compounds.

Since we do not have values for $\Delta H^{\pm}$ and $\Delta S^{\pm}$, we cannot calculate a value for $\Delta G^{\pm}$ at room temperature. Mislow did report a value for $\Delta S^{\pm}$ of 8 eu as mentioned above for a sulfonium salt racemization and values of +4 to −8 eu for a series of sulfoxide thermal racemizations.[16] If we assume a value of $\Delta S^{\pm} \geq 0$, then $\Delta G^{\pm} \geq 25.4$ kcal/mol at 25°. The half-life for pyramidal inversion is then on the order of several weeks. An entropy term of *ca.* −30 eu would be required to reduce the half-life for inversion to several minutes and *ca.* −15 eu for a half-life of several hours.

It seems we are left with two alternative possibilities. First, our cyclic triarylsulfonium salt may be a poor model for the noncyclic compounds. If the ideal transition state for pyramidal inversion is planar and has CSC bond angles of 120°, one can see that this condition might be more difficult to achieve in the cyclic case compared with the noncyclic case owing to steric constraints imposed by the rings in the former.[9] Alternatively, the cyclic compound may be an accurate model for the noncyclic compounds. This would argue for some sort of symmetrical intermediate, transition state, or pseudorotation. These possibilities seem unlikely in view of the stereospecific nature of other examples of nucleophilic substitution at tetravalent tricoordinate sulfur (eq 2–5), At present we favor the first explanation.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer; ORD spectra were recorded on Rudolph and Cary 60 recording spectropolarimeters. Analytical and spectral data are recorded in Tables I and II.

Triarylsulfonium Perchlorates.—The general procedure for the synthesis of triarylsulfonium salts is exemplified by the synthesis of phenyl-*p*-tolyl-*o*-anisylsulfonium perchlorate (**4**).

Phenyl-*p*-tolyl-*o*-anisylsulfonium Perchlorate (4).—A solution of (*S*)-(−)-*p*-tolyl-*o*-anisyl sulfoxide[17] (1.0 g, 0.0042 mol) in anhydrous methylene chloride was added at 0° with stirring to triethyloxonium tetrafluoroborate[18] (0.0079 mol). After the solution had been stirred for 3 hr at 0°, 1,2-dimethoxyethane (50 ml), freshly distilled from sodium hydride, was added. The solution was concentrated to *ca.* 30 ml by means of a current of dry nitrogen and then diluted with dimethoxyethane (50 ml).

A solution of phenylmagnesium bromide, prepared from bromobenzene (1.57 g, 0.00100 mol) and magnesium (0.5 g, 0.03 g-atom) in ether (50 ml), was added at −10 to −20° with stirring to the ethoxysulfonium salt over a 30-min period. After hydrolysis with saturated aqueous ammonium chloride, the mixture was filtered and the layers were separated. The sulfonium salt was extracted from the aqueous layer with five 50-ml portions of chloroform. The chloroform solution was concentrated and the sulfonium salt was precipitated as a semisolid, presumably the bromide, yield 0.50 g (0.0014 mol, 36%), with excess ether and cooling in a Dry–acetone bath. The sulfonium salt was dissolved in distilled water, acidified, and precipitated as the perchlorate at 0° by the addition of aqueous sodium perchlorate. The sulfonium salt was filtered, washed with distilled water, and dissolved in acetone–water. Slow evaporation of the solvent gave white crystals.

This sulfonium salt as well as those in Table I exhibited no optical activity when examined from 600 to 300 mμ in the purified state or in the crude state directly after isolation.

Thioxanthene 10-oxide (7) was prepared from thioxanthene in 75% yield by oxidation with iodobenzene dichloride in moist pyridine[19] and recrystallized from carbon tetrachloride.

2-Chlorothioxanthene 10-oxide (8) was prepared as for **7** in 87% yield and recrystallized from cyclohexane.

9,9-Dimethylthioxanthene 10-Oxide (9).—A suspension of 9-methylthioxanthylium perchlorate[20] (3.11 g, 0.0100 mol) in anhydrous ethyl ether (200 ml) was added to a solution of methylmagnesium iodide prepared from methyl iodide (4.26 g, 0.0300 mol) and magnesium (0.73 g, 0.030 g-atom) in ether (200 ml). The mixture was refluxed for 2 hr, cooled to 0°, and then hydrolyzed with saturated aqueous ammonium chloride. The organic layer was washed twice with water, dried over sodium sulfate, and concentrated *in vacuo* to give 9,9-dimethylthioxanthene[20] as a crude oil. This was dissolved in a mixture of water (2 ml) and pyridine (15 ml) and the solution was cooled to 40°. Iodobenzene dichloride (2.75 g, 0.0100 mol) in pyridine[20] (15 ml) was added over a 15-min period with stirring at −40°. After 15 min of additional stirring, the mixture was allowed to warm to room temperature and then stirred for an additional 1 hr. The solution was neutralized with 30% sulfuric acid with cooling and then extracted five times with chloroform. The chloroform solution was washed twice with water, dried over sodium sulfate, and concentrated *in vacuo*. Addition of petroleum ether (bp 30–60°) to the residual oil precipitated a solid, yield 1.87 g (0.00771 mol, 77%), which was recrystallized from cyclohexane.

Thioxanthene 10,10-dioxide (10) was prepared from thioxanthene by oxidation with 30% hydrogen peroxide in glacial acetic acid.

9,9-Dimethylthioxanthene 10,10-Dioxide (11).—Hydrogen peroxide (30%, 2.5 equiv) was added dropwise with stirring at 0° to a solution of crude 9,9-dimethylthioxanthene, prepared as described above from 9-methylthioxanthylium perchlorate (3.11 g, 0.0100 mol) in glacial acetic acid (20 ml). The mixture was heated overnight on a steam bath and concentrated *in vacuo*, and the residual oil was dissolved in chloroform. The chloroform solution was washed with sodium bicarbonate (5%), dried over calcium chloride, and concentrated to give a solid, yield 2.5 g (0.010 mol, 100%), which was recrystallized from ethanol.

9,9-Dihydro-10-(2,5-xylyl)thioxanthylium Perchlorate (12).—Concentrated sulfuric acid (4 ml) was added at 0° with stirring to a mixture of thioxanthene 10-oxide (2.0 g, 0.0093 mol) and *p*-xylene (20 ml).[21] The mixture was allowed to warm to room temperature, stirred for an additional 2 hr, and then poured onto crushed ice. The mixture was extracted three times with ether. Perchloric acid (70%, 5 ml) was added to the aqueous solution previously cooled to 0°. After 1 hr at 0°, the mixture was filtered and the solid was washed with cold water and ether and then

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

(15) D. Darwish and R. L. Tomilson, *J. Amer. Chem. Soc.*, **90**, 5938 (1968).

(16) D. R. Rayner, A. J. Gordon, and K. Mislow, *ibid.*, **90**, 4854 (1968).

(17) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *ibid.*, **86**, 5637 (1964).

(18) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).

(19) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc., C*, 659 (1968).

(20) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(21) S. Smiles and R. Le Rossignol [*J. Chem. Soc.*, 696 (1906)] have used this procedure to synthesize triarylsulfonium salts.

recrystallized from acetone–ether, yield 1.7 g (0.0042 mol, 45%).

9,9-Dihydro-10-mesitylthioxanthylium Perchlorate (13).—Concentrated sulfuric acid (4 ml) was added at 0° with stirring to a mixture of thioxanthene 10-oxide (2.0 g, 0.0093 mol) and mesitylene (10 ml). The mixture was stirred at room temperature for 8 days and then worked up as for **12**, yield 0.8 g (0.002 mol, 20%).

9,9-Dimethyl-10-phenylthioxanthylium Perchlorate (14).—Concentrated sulfuric acid (2.5 ml) was added with stirring at 0° to a mixture of 9,9-dimethylthioxanthene 10-oxide (2.42 g, 0.0100 mol) and benzene (15 ml). The mixture was stirred at room temperature for 2 days and then worked up as described for **12** except that **14** was recrystallized from ethanol, yield 3.4 g (0.0084 mol, 85%).

9,9-Dihydro-10-methylthioxanthylium Perchlorate (15).—Silver tetrafluoroborate (1.95 g, 0.0100 mol) was added slowly at room temperature with stirring to a solution of thioxanthene (1.98 g, 0.0100 mol) and methyl iodide (14.2 g, 0.100 mol) in 1,2-dichloroethane (60 ml). The mixture was stirred overnight at room temperature and filtered, and the solid was washed with acetone. The combined filtrates were concentrated and residual solid was washed with ether. The solid was dissolved in warm water, and perchloric acid (70%, 10 ml) was added dropwise with stirring. The mixture was cooled to 0° and the solid was removed by filtration, yield 2.4 g (0.0077 mol, 77%). The solid was recrystallized from acetone–ether.

Compound **15** was also obtained as follows. Thioxanthene 10-oxide (2.14 g, 0.0100 mol), *p*-dimethoxybenzene (6.9 g, 0.050 mol), and aluminum chloride (2.67 g, 0.0200 mol) were stirred together at 60° for 15 hr. The mixture was cooled, poured onto crushed ice, and extracted with ether. Perchloric acid (70%, 6 ml) was added to the aqueous layer and the solid was removed by filtration, yield 2.14 g (0.00684 mol, 68%). It was recrystallized from acetone–ether or from ethanol.

2-Chloro-9,9-dihydro-10-methylthioxanthylium perchlorate (16) was prepared in the same manner as **15** from 2-chlorothioxanthene (2.31 g, 0.010 mol), methyl iodide (14.2 g, 0.100 mol), and silver tetrafluoroborate (1.95 g, 0.0100 mol) in 1,2-dichloroethane (70 ml), yield 3.1 g (0.0090 mol, 90%).

9,9-Dihydro-10-ethylthioxanthylium perchlorate (17) was prepared in the same manner as **15** from thioxanthene (1.98 g, 0.0100 mol), ethyl iodide (15.5 g, 0.100 mol), and silver tetrafluoroborate (1.95 g, 0.0100 mol) in 1,2-dichloroethane (60 ml), yield 1.3 g (0.0040 mol, 40%).

Methyldiphenylsulfonium perchlorate (18) was prepared in the same manner as **15** from diphenyl sulfide (1.86 g, 0.0100 mol), methyl iodide (14.2 g, 0.100 mol), and silver tetrafluoroborate (1.95 g, 0.0100 mol) in 1,2-dichloroethane, yield 2.1 g (0.0068 mol, 68%).

Reaction of (*R*)-(+)-Benzyl-*p*-tolylethoxysulfonium Tetrafluoroborate with Hydroxide Ion and with Magnesium Bromide.—(*R*)-(+)-Benzyl-*p*-tolylethoxysulfonium tetrafluoroborate, mp 116–117°, $[\alpha]^{24}D$ +202.6° (*c* 2, $CHCl_3$), was prepared from (*R*)-(+)-benzyl-*p*-tolyl sulfoxide, mp 166–167°, $[\alpha]^{23}D$ +105.8° (*c* 2, $CHCl_3$). The sulfoxide was 98% optically pure based on the value of $[\alpha]^{22}D$ +107.8° for the pure compound, while the sulfonium salt was 88% optically pure based on the value of $[\alpha]^{22}D$ +203° for an 88% optically pure compound.

Hydrolysis of the sulfonium salt (1.0 g) with water and sodium hydroxide as described by Johnson gave (*S*)-(−)-benzyl *p*-tolyl sulfoxide, mp 164–165°, $[\alpha]^{28}D$ −93.4°, which was calculated to be 87% optically pure.

(*R*)-(+)-Benzyl-*p*-tolylethoxysulfonium tetrafluoroborate (3.43 g, 0.0100 mol) in anhydrous tetrahydrofuran (50 ml) was added to magnesium bromide (0.015 mol) in tetrahydrofuran (50 ml) at room temperature followed by stirring for 1 hr. Aqueous sodium hydroxide (5%) was added until the mixture was slightly basic, the tetrahydrofuran was removed *in vacuo*, and the aqueous mixture was saturated with sodium chloride and then extracted four times with chloroform–ether (9:1). The organic layers were dried over sodium sulfate and concentrated *in vacuo*, and the residual solid was washed twice with petroleum ether (bp 35–60°) to give (*R*)-(+)-benzyl *p*-tolyl sulfoxide, yield 0.7 g (30%), mp 156–159°, $[\alpha]^{24}D$ +59.2° (*c* 2, $CHCl_3$), calculated to be 55% optically pure.

Reaction of (*S*)-Phenyl-*p*-tolylethoxysulfonium Tetrafluoroborate with Magnesium Bromide—A solution of (*S*)-(−)-phenyl *p*-tolyl sulfoxide (1.00 g, 0.00463 mol), $[\alpha]^{22}D$ −15° (*c* 2.04, acetone), 69% optically pure, in anhydrous methylene chloride (20 ml) was added to triethyloxonium tetrafluoroborate (0.0158 mol) and stirring was continued for 30 min. Anhydrous benzene (75 ml) was added and the solution was concentrated to 50 ml *in vacuo*. A solution of magnesium bromide etherate, prepared from ethylene dibromide (4.00 g, 0.0212 mol) and excess magnesium, in anhydrous ether (50 ml) was added with stirring over a 15-min period. After an additional 15 min of stirring, the mixture was hydrolyzed with 5% aqueous sodium hydroxide (50 ml). The organic layer was dried over magnesium sulfate, filtered, and concentrated to give a small amount of sulfoxide, $[\alpha]^{22}D$ −10.8° (*c* 2.015, acetone).

Reaction of (*R*)-Phenyl-*p*-tolylethoxysulfonium Tetrafluoroborate with a Di-*m*-tolylmagnesium–Magnesium Bromide Dioxanate Mixture.—(*R*)-Phenyl-*p*-tolylethoxysulfonium tetrafluoroborate was prepared from (*R*)-(+)-phenyl *p*-tolyl sulfoxide (1.93 g, 0.0100 mol), $[\alpha]^{30}D$ +20.1° (*c* 2.48, acetone), and triethyloxonium tetrafluoroborate. A Grignard reagent was prepared from *m*-bromotoluene (17.1 g, 0.100 mol) and magnesium (3.0 g, 0.12 g-atom) in tetrahydrofuran (100 ml). Dioxane (25 ml) distilled from lithium aluminum hydride was added to the Grignard reagent. A copious white precipitate formed. The entire mixture was added to the sulfonium salt in tetrahydrofuran (50 ml). After stirring for 1 hr, the mixture was hydrolyzed with 10% hydrobromic acid. Ether (50 ml) was added and the two layers were separated. The ether layer was extracted with 10% hydrobromic acid. The aqueous layer was extracted with ether. The combined acidic aqueous layers were extracted with seven 50-ml portions of chloroform. The chloroform solution was concentrated to 5 ml of ether (100 ml) was added. The oil which formed upon standing was taken up in water (35 ml) and filtered. A solution of sodium perchlorate (17 g) in water (10 ml) was added. After cooling, the phenyl-*m*-tolyl-*p*-tolylsulfonium perchlorate was removed by filtration and purified by dissolving in chloroform and reprecipitation with ether, yield 0.30 g (7.7%), mp 134–136°. It showed no optical rotation from 578 to 365 mμ.

Registry No.—**2**, 22837-45-2; **3**, 22837-46-3; **5**, 22837-47-4; **6**, 261-31-4; **8**, 90-37-9; **12**, 22837-50-9; **13**, 22837-51-0; **14**, 22837-52-1; **15**, 22837-53-2; **16**, 22837-54-3; **17**, 22837-55-4; **18**, 10504-64-0.

Acknowledgment.—The authors wish to thank G. G. Lyle and W. Gaffield for obtaining the ORD spectra.