Registry No.—**2**, 93-55-0; **3**, 4393-06-0; **12**, 33716-94-8; 1-phenyl-1-propanol, 93-54-9; sodium amide, 7782-92-5; 1-methoxy-1-phenylpropane, 59588-12-4; benzaldehyde-*formyl-d*, 3592-47-0; α-vinylbenzyl alcohol-*O-d*, 59588-11-3.

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(6) The exact reason for this large isotope effect is unknown. It is conceivable that dianion generation could have a large isotope effect, based on the evidence that certain monoanion formations have exhibited isotope effects of $k_H/k_D = 24$ at −50 °C [A. Wright and R. West, *J. Am. Chem. Soc.*, **96**, 3227 (1974)]. In the allyl phenyl ether case the α deuteriums appear to not only retart isomerization but also divert the starting material toward competing reactions.
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(18) The multiplet pattern consisted of an intense triplet ($J = 7$ Hz, vicinal H–H), which was further split (equal intensity triplet, $J = 0.7$ Hz, vicinal H–D), and a weaker quartet ($J = 7$ Hz, vicinal H–H).
(19) The pattern is definitely that of a triplet ($J \approx 7$ Hz), which is further split. It appears that there is some unsplit triplet superimposed on a triplet which is further split into an equally intense triplet ($J \approx 2$ Hz, geminal H–D).
(20) The patterns of the methylene and methyl groups were similar to the previously described deuterated propiophenone,[18,19] but obviously different with the respect to the amount of deuterium on the methyl group. The methylene quartet (reflecting the nondeuterated propiophenone component) and triplet, which was further split (reflecting the $-CH_2CH_2D$ unit), were closer to the same intensity.

Synthesis of Optically Active Dialkylarylsulfonium Salts from Alkyl Aryl Sulfoxides[1]

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Treatment of alkoxysulfonium salts, prepared by O-alkylation of optically active methyl, ethyl, and *n*-butyl *p*-tolyl sulfoxides, with alkyl Grignard or alkylcadmium reagents gave optically active *n*-butylmethyl-*p*-tolyl-, *n*-butylethyl-*p*-tolyl-, and ethylmethyl-*p*-tolylsulfonium salts. Racemic phenyl-*o*-tolyl-*p*-tolyl- and ethylphenyl-*p*-tolylsulfonium salts were formed from optically active alkoxyphenyl-*p*-tolylsulfonium salts. Trialkylsulfonium salts were not formed when alkoxydialkylsulfonium salts were treated with alkyl Grignard or alkylcadmium reagents. The chiroptic properties of the dialkyl-*p*-tolylsulfonium salts are discussed.

Optically active sulfonium salts, formerly accessible only by resolution, may be synthesized by treating optically active O-alkylated sulfoxides with organocadmium or Grignard reagents (eq 1).[3] This reaction has recently been shown to proceed with inversion of configuration

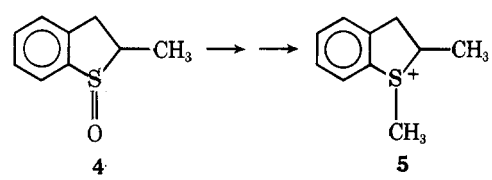
$$RR'S{=}O \rightarrow RR'S^+{-}OR''' \rightarrow RR'R''S^+ \qquad (1)$$

although partial racemization of the alkoxysulfonium salt may lower the enantiomeric purity of the product.[4]

This article reports on the study of this reaction for the synthesis of dialkylaryl-, triaryl-, alkyldiaryl-, and trialkylsulfonium salts and on the chiroptic properties of dialkylarylsulfonium salts. In principle, a given sulfonium salt may be prepared from any one of three sulfoxides. That is, any one of the three groups around sulfur could come from the organometallic reagent while the other two originate from the sulfoxide. But in fact, only alkoxyalkylaryl- and alkoxydiarylsulfonium salts ($RArS{-}OR^+$, $Ar_2S{-}OR^+$) react as in eq 1; alkoxydialkyl sulfonium salts (R_2SOR^+) do not.

Results and Discussion

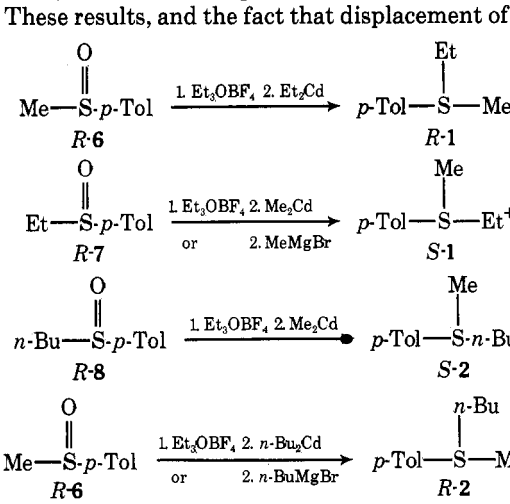
Dialkylarylsulfonium Salts. Treatment of alkoxysulfonium salts, derived from (*R*)-alkyl *p*-tolyl sulfoxides, with alkylcadmium or Grignard reagents yields optically active dialkyl-*p*-tolylsulfonium salts (Table I). Since the cyclic analogues *cis*- and *trans*-**4** yield sulfonium salts *trans*- and *cis*-**5** with predominant inversion at sulfur (eq 2), we assume that acyclic compounds behave similarly.[4] This assumption is



(2)

4 **5**

strengthened by the reactions depicted by eq 3–6. Enantiomeric sulfonium salts are produced in each pair of reactions (eq 3 and 4, 5 and 6) from sulfoxides of known absolute configuration, thus establishing a common stereochemical process. These results, and the fact that displacement of alkoxy



(3)

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Table I. Dialkyl-*p*-tolylsulfonium Salts (*p*-TolR′R″SX) Prepared from (*R*)-Alkoxyalkyl-*p*-tolylsulfonium Salts (*p*-TolR″SOR‴$^+$)

Sulfonium salt[a]	R′	R″	R‴O	X$^-$	Mp, °C	$[\alpha]^{25}D$	Yield, %[b]	Registry no.
R-1	Et	Me	EtO	TNBS$^-$	199–200	−5.6[c]	57[d]	59710-76-8
			MeO	BF_4^-	Oil	−15.8[e]	51[f]	59710-77-9
			MeO	Ph_4B^-	168–170	−10.5[c]	39[f]	59710-78-0
			EtO	Br^-	Oil	−115[g,e]	25[f]	59710-79-1
S-1	Me	Et	EtO	TNBS$^-$	208–209	19.2[c]	16[h]	59710-81-5
			MeO	BF_4^-	Oil	21.2[e]	59[f]	59710-82-6
			MeO	Ph_4B^-	168–170	9.0[c]	53[f]	59710-83-7
			EtO	Ph_4B^-	167–169	4.8[c]	7[h]	
			EtO	Ph_4B^-	165–166	7.8[c]	9[i]	
			EtO	Br^-	Oil	230[g,e]	72[f]	59710-84-8
R-2	*n*-Bu	Me	EtO	TNBS$^-$	136–142	−6.6[c]	10[h]	59751-79-0
			EtO	Ph_4B^-	100–110	−10.7[c]	10[h]	59751-80-3
			EtO	Ph_4B^-	119–121	−17.5[c]	9[i]	
S-2	Me	*n*-Bu	EtO	TNBS$^-$	149–150	7.6[c]	75[j]	34586-95-3
R-3	*n*-Bu	Et	EtO	TNBS$^-$	148–150	−6.2[c]	11[i]	59710-86-0
S-3	Et	*n*-Bu	MeO	BF_4^-	Oil	8.7[e]	59[k]	59710-88-2
			MeO	Ph_4B^-	140–142	10.2[c]	64[f]	59710-89-3

[a] The TNBS (2,4,6-trinitrobenzenesulfonate) and tetraphenylborate salts analyzed within 0.3% of theory for C and H. [b] Based on sulfoxide. [c] In acetone. [d] Distilled Et_2Cd, room temperature, 3 h (ref 3). [e] In ethanol. [f] Distilled R'_2Cd, room temperature, 2 h. [g] 290 nm. [h] Undistilled R'_2Cd, room temperature, 20 min. [i] R′MgBr, −78 °C, 1 h. [j] Distilled Me_2Cd, room temperature, 40 h (ref 3). [k] Distilled R'_2Cd, room temperature, 20 min.

groups from acyclic tricoordinate S(IV) generally proceeds with inversion, justify our generalization.[5]

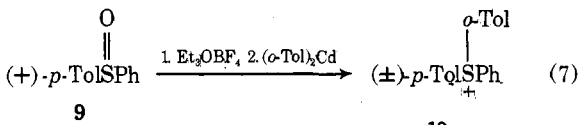
If Grignard reagents or organocadmium reagents are used, the chemical yields of sulfonium salts are around 10%; but if distilled, halide-free alkylcadmiums are employed, the yields improve to ca. 50–70% (Table I). Competing racemization reactions of the alkoxysulfonium salts may be important so the sulfonium salts produced are probably not optically pure. This is particularly true in the case of the distilled organocadmium reagents which react more slowly than Grignard reagents. In any event, the sulfonium salts are of unknown optical purity no matter which organometallic is used in their synthesis.

The sulfonium salts do not racemize at room temperature, nor are they destroyed by the organometallic reagents under the reaction conditions, but isolation as the bromide should be avoided. Use of the nonnucleophilic tetrafluoroborate anion is prefered to minimize any decomposition of the sulfonium salt during workup.[4]

Other systems were employed in an attempt to prepare dialkylarylsulfonium salts. When *N*-tosyl-*S*-methyl-*S*-phenylsulfilimine was alkylated with methyl fluorosulfonate and treated with *n*-butylmagnesium bromide, none of the desired sulfonium salt was obtained. The products isolated include the parent sulfilimine, *N*-methyl-*p*-toluenesulfonamide, and methyl phenyl sulfoxide. An analogous reaction with *N*-tosyl-*S*-phenyl-*S*-ethylsulfilimine gave similar results.

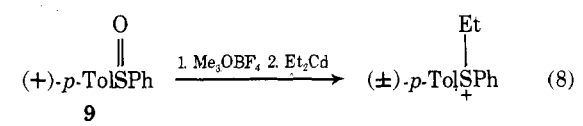
Several sulfoxides have been alkylated with a 1-bromoadamantane.[6] Treatment of 1-adamantoxymethyl-*p*-tolylsulfonium salts with ethylcadmium over a 20-min period at room temperature gave the desired sulfonium salt 1 in only 6% yield, but after 15 h the yield was 100%.

Triarylsulfonium Salts. Triarylsulfonium salts have been prepared from the reaction of alkoxydiarylsulfonium salts with aryl Grignard reagents, but the salts obtained were always racemic.[7] The evidence suggested a low barrier to pyramidal inversion with consequent rapid racemization at room temperature although other causes could not be completely ruled out. We carried out a synthesis using an arylcadmium reagent and also obtained a racemic product (eq 7). Since Grignard and organocadmium reagents both react with inversion at sulfur (eq 3–6) in the synthesis of dialkylarylsulfonium salts and would be expected to do so in the analogous triaryl case, the formation of a racemic product further supports the idea of a low barrier. Darwish recently estimated the half-life for triarylsulfonium salts undergoing pyramidal inversion to be 15 min in methanol at 25 °C.[8]



9 10 (7)

Alkyldiarylsulfonium Salts. One alkyldiarylsulfonium salt was prepared (eq 8), but it was racemic. Darwish and Scott studied the racemization of ethyl-*p*-anisylphenylsulfonium salt and observed a half-life of about 2.3 h in methanol at 25 °C.[8]



9 11 (8)

Trialkylsulfonium Salts. The alkylation of racemic or optically active dialkyl sulfoxides (cyclic or acyclic) followed by treatment with Grignard or organocadmium reagents at varying temperatures and reaction times failed to yield any sulfonium salt. The main product was the parent sulfoxide, which was often isolated as a 1:1 adduct of sulfoxide and 2,4,6-trinitrobenzenesulfonic acid, the anion used in the attempted isolation of the sulfonium salt.

A number of model experiments were undertaken to explain this observation. The reaction of (±)-methoxy-*n*-butylmethylsulfonium tetrafluoroborate with ethylcadmium indicated that propane was formed, so attack at the alkoxy carbon was definitely occurring. Triethylsulfonium tetrafluoroborate was stable to treatment with methylcadmium; no propane or ethylene was formed and the salt was recovered in quantitative yield. The same result was obtained on treatment with methoxide ion (methylcadmium followed by the addition of an aliquot of methanol).

Thus, the reaction of O-alkylated dialkyl sulfoxides with alkylmagnesium, alkylcadmium, or dialkylmagnesium reagents does not form trialkylsulfonium salts. If the salts were formed, they would have been isolated since they are stable under the reaction conditions.

When the *O*-adamantyl derivatives of dimethyl, di-*n*-butyl, methyl *n*-butyl, and pentamethylene sulfoxides were treated with alkylcadmiums, no trialkylsulfonium salts were isolated; the products were the parent sulfoxide, adamantanol, and uncharacterized substances, probably sulfides.

Chiroptic Properties of Dialkyl-*p*-tolylsulfonium Salts. The first reported ORD and CD spectral data for sulfonium salts are listed in Table II.

The uv spectra of dialkyl-*p*-tolylsulfonium salts exhibit primary or ^1L_a bands at ca. 230 nm and less intense secondary or ^1L_b bands at 250–280 nm arising from the aromatic chromophore.[9] Cotton effects (CE) were recorded in the 250–280-nm region, but the low rotation and high absorptivity of the salts made measurements at lower wavelengths difficult. We were successful in measuring only one short wavelength CE, the one for (−)-*R*-1 bromide. The longer wavelength data exhibited a fair amount of experimental error as can be seen by comparing the ORD and CD data for enantiomers.

The longer wavelength (^1L_b) CE correspond fairly well with the uv maxima, e.g., Figure 1, while the oppositely signed shorter wavelength CE observed for (−)-*R*-1 tetrafluoroborate corresponds to the ^1L_a absorption.

Table II. ORD, CD, and Uv Measurements on Dialkyl-*p*-tolylsulfonium Salts

Mode	Salt[a]	Anion	Concn[b]	P[c]	T[c]	P	T	P	T	P	T
ORD	*S*-1	BF_4^-	0.004–0.04	272 (400)	269 (200)	260 (815)	258 (800)	240 (1200)			
ORD	*R*-1	BF_4^-	0.006–0.06	272 (−500)	269 (−350)	262 (−700)	257.5 (−600)	238 (−3400)			
ORD	*S*-1	Br^-	0.05	271.5 (480)	269.5 (340)	267.8 (580)	265.5 (560)	241.6 (1820)			
ORD	*R*-1	Br^-	0.05	271 (−176)	267.5 (−120)	262.5 (−355)	260 (−352)	241.5 (−724)			
ORD	*S*-3	BF_4^-	0.045	275.5 (130)	270.5 (110)	265 (120)	258.5 (64)	237 (660)			
CD	*S*-1	BF_4^-	0.004–0.04	274 (−1800)	272 (−1300)	265 (−2120)	258 (−1600)	255 (−1700)			
CD	*R*-1	BF_4^-	0.006–0.06	270 (1750)	268 (1720)	265 (2130)	263 (1200)	255 (3330)			
CD	*S*-1	Br^-	0.05	274 (−2940)	269 (−1470)	267.5 (−2500)	255 (−494)	252.5 (−611)			
CD	*R*-1	Br^-	0.05	273.2 (1400)	268 (1175)	265 (1410)	263 (423)	250 (1434)			
CD	*S*-3	BF_4^-	0.045	273.5 (−2500)	271 (−2200)	264 (−2900)	257 (−2750)	250 (−3600)			
CD	*R*-1	BF_4^-	0.04						200[d] (−8600)		
Uv	1	BF_4^-	0.0004–0.004	274.5 (1800)	272 (1460)	266.5 (1900)	262.5 (1700)	255 (1720)	253.5 (1700)	230 (34 000)	215 (22 000)
Uv	1	Br^-	0.002–0.009	274 (1375)	272 (1050)	266 (1615)	257.5 (1350)	254 (1375)	251 (1300)	229 (20 000)	218 (11 000)
Uv	3	BF_4^-	0.0046	275 (1100)	273 (950)	266 (1350)	263 (1320)	254 (1650)	253 (1630)	230 (9000)	

[a] Configuration of predominant enantiomer. [b] g/ml in ethanol. [c] P = peak; T = trough. Wavelengths are in nm; values in parentheses are for molecular rotation (ORD), molecular ellipticity (CD), and molar extinction coefficients (uv). [d] In methanol.

Table III. ^1H NMR Parameters of Sulfonium Tetraphenylborates[a]

Sulfonium salt	SCH_3	SCH_2CH_3	$S(CH_2)_3CH_3$	SCH_2	SCH_2CH_2-CH_2CH_3	$-C_6H_4CH_3$	ArH	Anion Ph
1	3.28 s	1.24 t (8)		3.64 m		2.44 s	7.8 q (8.5)	7.04 m
2	3.19 s		0.81 t (5.5)	3.52 m	1.37 m	2.33 s	7.5 q (8)	6.8 m
3		1.17 t (6)	0.84 t (6)	3.72 m	1.44 m	2.44 s	7.8 q (8)	7.08 m
10						2.44 s 2.52	7.7 m	7.02 m
11		1.24 t (8)		2.9 m		2.68 s	7.52 m	7.52 m

[a] Chemical shifts are in parts per million from internal Me_4Si in Me_2SO-d_6 except for **11**, which was run in CH_2Cl_2 with external Me_4Si. Coupling constants are in hertz and enclosed in parentheses.

Although positive ORD curves are associated with the (+)-*S* enantiomers, the CD curves are negative, showing that the ^1L_b CE are actually negative. The positive rotation at 589 nm is caused by the tail of a strong positive CE associated with the primary bands. Thus, the (+)-*S* enantiomers give rise to negative CE in the 250–280-nm region and the (−)-*R* isomer to positive CE.

Experimental Section

Instrumentation. NMR spectra, obtained on a Varian A-60 or Jeolco HM-100 spectrometer, are reported in Table III. Optical rotations, optical rotatory dispersion curves, and circular dichroism curves were obtained on a Cary 60 recording spectrophotopolarimeter; optical rotations were also taken on a Carl Zeiss 0.005° photoelectric precision polarimeter. Uv spectra were recorded on a Cary Model 14 recording spectrophotometer. Ir spectra were obtained on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Melting points, determined on a Hoover capillary melting point apparatus, are uncorrected. Microanalyses were determined by Mrs. L. Heavner, Mrs. D. Cardin, and Miss G. Lambert on a F & M Model 185 carbon, hydrogen, nitrogen analyzer.

Dialkyl-*p*-tolylsulfonium salts were prepared from optically active O-methylated and O-ethylated sulfoxides in three ways: by the use of distilled methyl- or ethylcadmium,[10] by undistilled organocadmium reagents, or by Grignard reagents. An example of each method is given. Racemic salts were prepared by alkylation of sulfides with triethyl- or trimethyloxonium tetrafluoroborate or methyl fluorosulfonate. Optically active sulfoxides of high optical purity were synthesized by treating (−)-menthyl-(*S*)-*p*-toluenesulfinate with the appropriate Grignard reagent.[11]

1. (*S*)-(+)-Ethylmethyl-*p*-tolylsulfonium Tetraphenylborate (1). (*R*)-Ethyl *p*-tolyl sulfoxide (1.0 g, 5.9 mmol, $[\alpha]^{25}D$ 186.6°, acetone) was methylated using trimethyloxonium tetrafluoroborate (0.96 g, 6.5 mmol) in nitromethane.

The solution was concentrated and (*R*)-methoxyethyl-*p*-tolylsulfonium tetrafluoroborate was precipitated by addition of an excess of ether. The salt was purified by dissolution in methylene chloride followed by precipitation with ether. After several repetitions, 1.27 g (80%) of the salt was obtained as a thick yellow oil.

Distilled methylcadmium in ether (3 ml, 6.18 mmol, 30% excess, 2.08 M) was added with rapid stirring to a methylene chloride solution of the oil. After 20 min at room temperature, the excess cadmium reagent was hydrolyzed with 5% sulfuric acid, and the entire mixture was extracted with water. The aqueous layers were saturated with ca. 20 g of sodium tetrafluoroborate and extracted with five 25-ml portions of methylene chloride. The organic layer was dried over magnesium sulfate and concentrated on the rotary evaporator to give the tetrafluoroborate as a thick yellow oil. It was purified by dissolution in methylene chloride followed by precipitation with ether as above. After drying in vacuo, 0.88 g (73%) of (*S*)-(+)-ethylmethyl-*p*-tolylsulfonium tetrafluoroborate was obtained.

The tetrafluoroborate (0.2 g, 0.79 mmol) was converted to the tetraphenylborate by mixing acetone solutions of the sulfonium salt and sodium tetraphenylborate and adding ether. After several reprecipitations there remained 0.33 g (90% yield).

2. (*S*)-(+)-Ethylmethyl-*p*-tolylsulfonium Salt (1). (*R*)-Ethyl *p*-tolyl sulfoxide (1.00 g, 5.94 mmol, $[\alpha]^{25}D$ +185.7°, acetone) was ethylated with triethyloxonium tetrafluoroborate (1.19 g, 6.26 mmol) in methylene chloride. Methylcadmium prepared from cadmium chloride (2.00 g, 10.9 mmol) and methylmagnesium bromide (7.4 ml, 21.8 mmol, 3.0 M in ether) was added at 0 °C. After 15 min, the mixture was poured into water and extracted with ether. Several grams of sodium bromide were added. The aqueous layer was acidified with 5% hydrochloric acid and then extracted several times with chloroform. Concentration on the rotary evaporator without external warming gave 1.06 g (72.3%) of crude bromide.

The 2,4,6-trinitrobenzenesulfonate salt was obtained from the crude bromide (0.53 g) in acetone–ether using 2,4,6-trinitrobenzenesulfonic acid to yield 0.22 g (22%).

The tetraphenylborate salt was prepared in a similar way from sodium tetraphenylborate (0.74 g) and the crude bromide (0.53 g) in acetone, yield 0.10 g (9.6%).

3. (*S*)-(+)-Ethylmethyl-*p*-tolylsulfonium Tetraphenylborate (1). (*R*)-Ethyl *p*-tolyl sulfoxide (1.0 g, 5.9 mmol, $[\alpha]^{25}D$ 185.7°, acetone) was ethylated with triethyloxonium tetrafluoroborate (1.32 g, 6.6 mmol) in methylene chloride. Methylmagnesium bromide (2.0 ml, 6 mmol, 3.0 M) was added slowly at −78 °C. After hydrolysis with 5% sulfuric acid, the entire mixture was extracted with an equal volume of ether and the two layers were separated. The aqueous layer was saturated with sodium bromide (ca. 35 g) and extracted with chloroform. Concentration gave 0.52 g (40%) of the crude sulfonium bromide as a yellow oil. The bromide was converted to the tetraphenylborate as above.

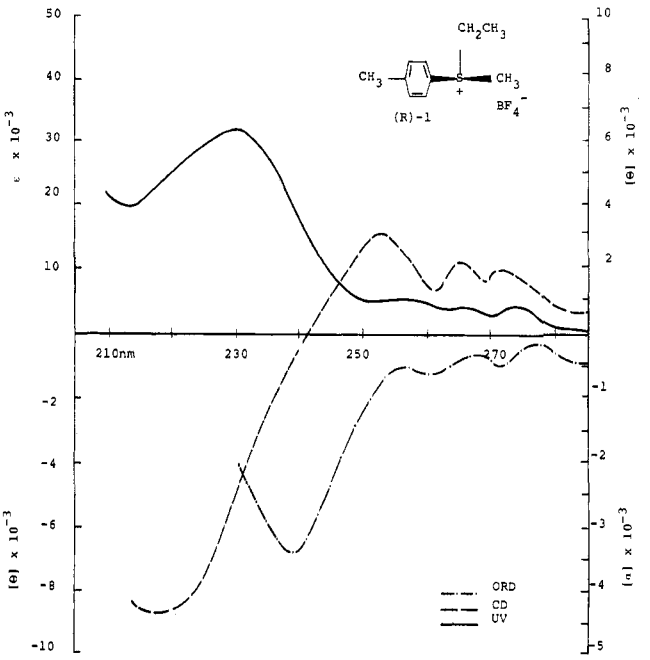


Figure 1. ORD, CD, and uv spectra of *R*-1.

(*S*)-(+)-Ethylmethyl-*p*-tolylsulfonium Tetraphenylborate (1) via Adamantoxysulfonium Salts. (+)-Adamantoxymethyl-*p*-tolylsulfonium hexafluoroantimonate (0.45 g, 0.856 mmol) in methylene chloride was treated with diethylcadmium (0.32 ml, 0.856 mmol, 2.75 M). After 24 h at room temperature, the mixture was worked up as above. (+)-Ethylmethyl-*p*-tolylsulfonium tetrafluoroborate was isolated as a thick yellow oil, yield 0.22 g (100%). The tetrafluoroborate was converted to the tetraphenylborate in the normal way with a 70% recovery, mp 169–171 °C (EtOH).

(*R*)-(−)-Ethylmethyl-*p*-tolylsulfonium tetrafluoroborate was prepared in a similar way (54% yield). It contained very slight amounts of impurities which could not be removed even after repeated recrystallizations. No further work was performed on the compound.

Attempted Preparation of Optically Active Phenyl-*o*-tolyl-*p*-tolylsulfonium Tetraphenylborate (10). (*R*)-Phenyl *p*-tolyl sulfoxide (1.3 g, 6.02 mmol, $[\alpha]^{25}D$ 21.05°, acetone) was ethylated with triethyloxonium tetrafluoroborate (1.25 g, 6.6 mmol) in methylene chloride. Undistilled di-*o*-tolylcadmium (6.02 mmol) was introduced at 0 °C. After 1.5 h, the usual workup yielded 2.6 g (100%) of the crude sulfonium bromide as a thick yellow oil.

The bromide (oil) was converted to the tetraphenylborate (solid) as above yielding 0.5 g (20%) of the desired product, mp 171–174 °C (acetone–ether), $[\alpha]^{25}D$ 0°.

(±)-Phenyl-*o*-tolyl-*p*-tolylsulfonium Tetraphenylborate (10). (±)-Phenyl *p*-tolyl sulfoxide (1.3 g, 6.0 mmol) was ethylated with triethyloxonium tetrafluoroborate (1.25 g, 6.6 mmol) in methylene chloride and then treated with *o*-tolylmagnesium bromide (2.22 ml, 6 mmol, 2.7 M) according to the procedure outlined for the attempted preparation of optically active phenyl *o*-tolyl-*p*-tolylsulfonium tetraphenylborate (see above) with the following modification: the organometallic and alkylated sulfoxide were allowed to react at −78 °C for 1 h. (±)-Phenyl-*o*-tolyl-*p*-tolylsulfonium tetraphenylborate was isolated in 46% yield (1.42 g), mp 172.5–174 °C (acetone–ether).

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

Attempted Preparation of Optically Active Ethylphenyl-*p*-tolylsulfonium Tetraphenylborate (11). (*R*)-Phenyl *p*-tolyl sulfoxide (0.63 g 2.87 mmol, $[\alpha]^{25}D$ 15.24°, acetone) was ethylated as above and the ethoxysulfonium salt purified by precipitation from methylene chloride–ether, to give 0.55 g (60%) as a thick oil. Diethylcadmium (4.32 ml, 2.66 mmol, 0.6 M, 50% excess) was added to the oil in methylene chloride. After 20 min at room temperature, the mixture was worked up using sodium tetrafluoroborate to give 0.4 g (73%) of (±)-ethylphenyl-*p*-tolylsulfonium tetrafluoroborate (11), which was converted to the tetraphenylborate as above, 0.7 g (80% yield).

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

Attempted Preparation of Racemic and Optically Active Trialkylsulfonium Salts from O-Alkylated Sulfoxides. Treatment of O-alkylated dialkyl sulfoxides (racemic or optically active) with Grignard reagents at −78 °C for 1 h or alkylcadmium reagents for 20 min at room temperature using the procedure for the preparation of dialkylarylsulfonium salt (see above) failed to yield the desired trialkylsulfonium salts. The products isolated include starting sulfoxide (partially racemized in the case of optically active sulfoxides), the corresponding sulfide, and some unidentified products. The sulfoxides were often isolated as a 1:1 complex with 2,4,6-trinitrobenzenesulfonic acid, the anion which was used in the attempted isolation of the sulfonium salt. A number of variations in the reaction conditions including changes in temperature, reaction time, organometallic, leaving group, and anion resulted in no sulfonium salt.

Attempted Preparation of Racemic Sulfonium Salts from N-Methylated Sulfilimines. *N*-Tosyl-*S*-methyl-*S*-phenylsulfilimine (1 g, 3.4 mmol) in methylene chloride was methylated with methyl fluorosulfonate (0.52 g, 3.4 mmol). *n*-Butylmagnesium bromide (1.45 ml, 3.4 mmol, 2.4 M) was added at −78 °C. Workup as above using sodium bromide yielded a crude yellow oil which consisted of *N*-tosyl-*S*-methyl-*S*-phenylsulfilimine, *N*-methyl-*p*-toluenesulfonamide, and methyl phenyl sulfoxide (TLC, NMR). None of the desired product was obtained.

Repetition of the reaction with *N*-tosyl-*S*-phenyl-*S*-ethylsulfilimine and ethylcadmium yielded analogous results.

Dialkyl- and Adamantoxyalkylarylsulfonium Salts.[6] The procedure outlined for the preparation of (±)-adamantoxymethyl-*p*-tolylsulfonium perchlorate will serve to illustrate the general method employed in the synthesis of the title compounds.

Methyl *p*-tolyl sulfoxide (1.08 g, 7 mmol) in methylene chloride was added to silver perchlorate (1.44 g, 7 mmol). 1-Bromoadamantane (1.5 g, 7 mmol) in methylene chloride was added with the exclusion of light over a 15-min period. After the addition, the mixture was allowed to stand for 1 h at room temperature. The silver bromide produced was removed by filtration. Adamantoxymethylsulfonium perchlorate (1.42 g, 53%) was obtained as a fluffy white solid by precipitation from methylene chloride–ether, mp 153–155 °C dec.

Anal. Calcd for $C_{18}H_{25}O_5SCl$: C, 55.59; H, 6.48. Found: C, 55.7; H, 6.58.

The hexafluoroantimonate salts were prepared and purified in an analogous way by use of silver hexafluoroantimonate. Other salts prepared according to this procedure include (+)-adamantoxymethyl-*p*-tolylsulfonium hexafluoroantimonate (53%), mp 124–126 °C (methylene chloride–ether), $[\alpha]^{25}D$ 68.37° (*c* 1, acetone).

Anal. Calcd for $C_{18}H_{25}SSbF_6$: C, 41.16; H, 4.80. Found: C, 41.12; H, 4.80.

(±)-Adamantoxymethyl-*n*-propylsulfonium hexafluoroantimonate (20%), mp 110–112 °C (methylene chloride–ether).

Anal. Calcd for $C_{14}H_{25}SSbF_6$: C, 35.24; H, 5.28. Found: C, 35.17; H, 5.11.

Attempted Preparation of Racemic Trialkylsulfonium Salts from Adamantoxydialkylsulfonium Salts. Treatment of adamantoxydialkylsulfonium salts with dialkylcadmium reagents at room temperature for ca. 24 h, using the procedure described for the preparation of dialkylarylsulfonium salts, failed to yield the desired trialkylsulfonium salts. Starting sulfoxides, adamantanol, and several unidentified by-products were isolated (TLC, NMR). The sulfoxides were often isolated as a 1:1 complex with 2,4,6-trinitrobenzenesulfonic acid, the anion used in the attempted isolation of the sulfonium salt. Reactions were also attempted for a 20-min period at room temperature with negative results.

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Registry No.—*S*-**2** Ph_4B^-, 59751-81-4; *R*-**3** Ph_4B^-, 59710-90-6; *R*-**6**, 1519-39-7; *R*-**7**, 1519-40-0; *R*-**8**, 20288-49-7; **9**, 16491-20-6; (±)-**10** Br^-, 59710-91-7; (±)-**10** Ph_4B^-, 59710-93-9; **11** BF_4^-, 59710-95-1; **11** Ph_4B^-, 59710-96-2; trimethyloxonium tetrafluoroborate, 420-37-1; (*R*)-methoxyethyl-*p*-tolylsulfonium BF_4^-, 59710-98-4; sodium Ph_4B^-, 143-66-8; triethyloxonium BF_4^-, 368-39-8; sodium bromide, 7647-15-6; 2,4,6-trinitrobenzenesulfonic acid, 2508-19-2; (+)-adamantoxymethyl-*p*-tolylsulfonium hexafluoroantimonate, 59711-00-1; silver perchlorate, 7783-93-9; 1-bromoadamantane, 768-90-1; (±)-adamantoxymethyl-*p*-tolylsulfonium perchlorate, 59711-02-3; silver hexafluoroantimonate, 26042-64-8; (±)-adamantoxymethyl-*n*-propylsulfonium hexafluoroantimonate, 59711-04-5.

References and Notes

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