mmol (87%) of benzenesulfinic acid.

In another experiment 1.1 g (4.0 mmol) of *p*-tolyl *p*-toluenethiolsulfonate,[12] dissolved in 30 ml of dioxane was added with stirring to a solution of 0.52 g of 30% hydrogen peroxide (4.6 mmol of H_2O_2) and 2.2 g (20.8 mmol) of sodium carbonate in 100 ml of water and 25 ml of dioxane. The final solution was allowed to stand for 15 min. At the end of that time the still-alkaline reaction mixture was extracted with diethyl ether; the ether extracts were discarded. The water layer was then made quite strongly acid by the addition of sulfuric acid and immediately extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure. After drying at room temperature under high vacuum for 0.5 hr the residue was recrystallized from ether–hexane, affording 0.9 g (72%) of *p*-toluenesulfinic acid, mp 84–84.5° (lit.[24] 85°).

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Nucleophilic Substitution at Tricoordinate Sulfur(IV). Stereochemistry of Dialkylarylsulfonium Salt Formation from Alkyl Aryl Sulfoxides[1]

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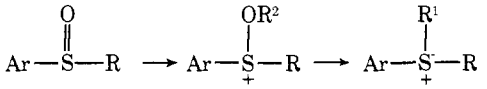
Abstract: The cis and trans isomers of 2-methyl-2,3-dihydrobenzothiophene 1-oxide (**1** and **2**) were alkylated with trimethyloxonium tetrafluoroborate and treated with methylmagnesium bromide at −78° or dimethylcadmium at room temperature to yield the cis and trans isomers of 1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate (**10** and **11**). The reaction proceeds with inversion of configuration at sulfur, but loss of stereospecificity may occur owing to isomerization of the starting material. The assignments of configuration to **1**, **2**, **10**, and **11** are presented.

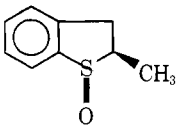
Optically active dialkylarylsulfonium salts can be prepared from optically active alkyl aryl sulfoxides by alkylation followed by reaction with a dialkylcadmium or an alkyl Grignard reagent[4] (eq 1).



(1)

The aim of this present work was to determine the stereochemistry of this conversion, which, although assumed to proceed with inversion of configuration at sulfur analogous to most other nucleophilic substitutions on tricoordinate sulfur(IV) compounds had never been established. Nucleophilic displacement of alkoxy groups from sulfinate esters and alkoxysulfonium salts usually proceeds with inversion, thus providing the analogies to eq 1.[5]

We now wish to report the first experimental evidence concerning the stereochemical pathway followed in eq 1, beginning with the cis and trans isomers of 2-methyl-2,3-dihydrobenzothiophene 1-oxide (**1** and **2**), the preparation



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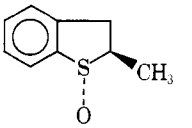

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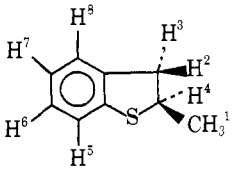
and characterization of which are described below. The diastereomeric sulfoxides, **1** and **2**, were chosen as substrates for the reaction since they not only fulfilled the basic requirement of being alkyl aryl sulfoxides but also converted the problem from one involving a determination of the absolute configuration of a chiral, acyclic sulfonium salt, with which a correlation to the starting sulfoxide could be made,[6] into one involving the experimentally easier assignment of configuration to cis-trans cyclic stereoisomers. Sul-

Table I. Pmr Parameters of 2-Methyl-2,3-dihydrobenzothiophene and Derivatives[a]



Compd	Solvent[b]	H^1	H^2	H^3	H^4	H^5	H^6, H_7, H_8	$\Delta(H^1)$[c]	$\Delta(H^4)$[c]
1	$CDCl_3$	1.57 d (6.2)	—— 3.41 bs ——			7.95 m	7.55 bs		
	C_6H_6	1.23 d	2.98 dd	—— ~2.6 m ——				0.34	0.8
2	$CDCl_3$	1.43 d (7.3)	2.95 dd (5.0, 16.0)	3.93 dd (6.9, 16.0)	~3.60 dq (5.0, 7.0)	7.90 m	7.54 bs		
	C_6H_6	0.92 d	2.20 dd	—— ~3.2 m ——				0.51	0.4
4[d]	$CDCl_3$	1.31 d (6.8)	2.79 dd (6.7, 15.2)	3.21 dd (7.5, 15.2)	3.83 h (6.8)	—— ~6.9 m ——			
6[d]	$CDCl_3$	1.48 d (6.6)	2.93 dd	~3.45 m	~3.55 m	—— ~7.6 m ——			

[a] All measurements were performed on a Jeolco HA-100 instrument at ordinary probe temperature. The protons are numbered as shown above. Chemical shifts are given in parts per million downfield from internal tetramethylsilane. The following abbreviations are used for the coupling patterns: bs, broad singlet; dd, doublet of doublets; dq, doublet of quintets; h, hextet; m, multiplet. Values in parentheses are coupling constants in hertz. [b] Concentration of **1** and **2** was 0.32 *M*. [c] ASIS (parts per million) of H^1 and H^4 calculated as $\delta(CDCl_3) - \delta(C_6H_6)$. [d] The relative assignment of H^2 and H^3 does not apply.

Table II. Eu(dpm)$_3$-Induced Shifts of *cis*- and *trans*-2-Methyl-2,3-dihydrobenzothiophene 1-Oxide[a]

Compd	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8
1	-8.26 ± 0.05	-6.55 ± 0.09	-5.37 ± 0.06	-9.48 ± 0.08	-3.98 ± 0.02	-1.4 ± 0.1	-2.38 ± 0.06	-3.50 ± 0.03
	0.9999	0.9997	0.9998	0.9998	1.0000	0.9894	0.9988	0.9999
2	-3.40 ± 0.04	-4.18 ± 0.07	-6.5 ± 0.1	-10.2 ± 0.2	-5.49 ± 0.06	-1.85 ± 0.05	-2.30 ± 0.04	-2.83 ± 0.07
	0.9998	0.9994	0.9995	0.9995	0.9997	0.9988	0.9993	0.9986

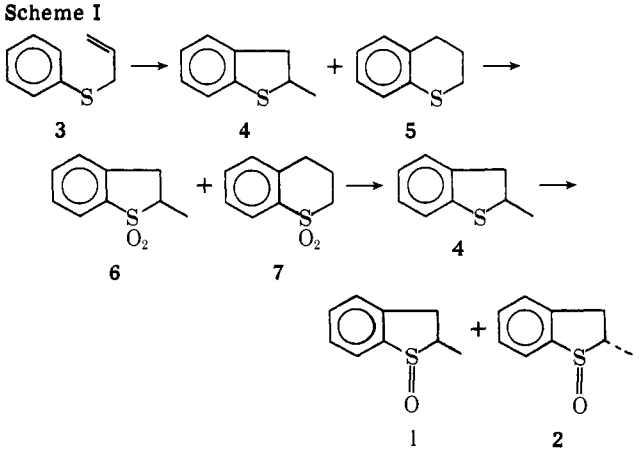
[a] All measurements were performed at constant substrate concentration (0.32 *M*) in $CDCl_3$ solutions with increasing amounts of freshly sublimed tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), Eu(dpm)$_3$, added. The instrument used, temperature, and numbering of protons are as in Table I. The induced shifts were extrapolated to 100 mol % Eu(dpm)$_3$ from observed shifts at 0, 5, 15, 25, 35, and 45 mol % (compd **1**) or 0, 10, 20, 30, 35, and 45 mol % (compd **2**) by the method of least-squares and are presented as $\Delta_{Eu(dpm)_3}$ values in parts per million[12] along with the standard errors and correlation coefficients.

foxides **1** and **2** had been prepared and separated previously, but their configurations had never been assigned.[7,13]

Results and Discussion

Synthesis of *cis*- and *trans*-2-Methyl-2,3-dihydrobenzothiophene 1-Oxide (1 and 2). The syntheses of **1** and **2** are outlined in Scheme I. Allyl phenyl sulfide (**3**) was cyclized to give a mixture of the two sulfides **4** and **5**, according to the procedure of Kwart and Evans.[8] Oxidation with potassium permanganate yielded 55% of the sulfone mixture (48 parts of **6** and 52 parts of **7**). Following the procedure of Whitney and Cram,[7] this mixture was treated with lithium aluminum hydride in ether-benzene to give a mixture of **4** and **7** which was easily separated by distillation. Oxidation of **4** with hydrogen peroxide in acetic acid gave the desired sulfoxides **1** and **2** as a 40:60 mixture, which were separated by column chromatography on silica gel. [6]

Scheme I



Assignment of Configuration. *cis*- and *trans*-2-Methyl-2,3-dihydrobenzothiophene 1-Oxide (1 and 2). The structural assignments of the sulfoxides **1** and **2** were based on chromatographic retention times and nmr spectroscopy including aromatic solvent induced shifts (ASIS) and lanthanide induced chemical shifts (LIS). Except for the LIS, these methods were used by Johnson, *et al.*,[9] in the configurational assignments of the closely related 2-methylthiolane 1-oxides, and the results we have obtained are consistent with those of Johnson. The isomer produced in lesser amount has the shorter retention time (larger R_f value) on column and thin-layer chromatography, suggesting that in this isomer the sulfoxide oxygen is more sterically hindered and therefore of cis configuration (**1**). The more abundant isomer with the longer retention time is consequently assigned the trans configuration (**2**).

This assignment is strongly supported by the ASIS and LIS studies. The aromatic solvent used in the ASIS study, in this case benzene, forms a collision complex with the polar solute, the sulfoxide, in which the benzene molecule is located at the positive end of the dipole,[8] *i.e.*, at the sulfur atom. This would give a larger deshielding relative to an inert solvent, in this case chloroform, of the *C*-methyl group in the trans isomer, while a larger deshielding should occur for the methine proton in the cis isomer. This is indeed observed (Table I) using the assignment given above (*C*-methyl:$\Delta_2/\Delta_1 = 1.5$; methine:$\Delta_1/\Delta_2 = 2.0$).

LIS studies have previously been found to be valuable tools in work on organic sulfur compounds, especially sulfoxides.[10] Here the complexing between the shift reagent (Eu(dpm)$_3$) and the sulfoxide takes place at the oxygen atom causing the largest shifts for protons cis to the oxygen.[11] Our results (Table II) show full agreement with the assignment made from the ASIS study (*C*-methyl:Δ_1/Δ_2 =

Table III. Reaction Products[a]

Reaction no.	Starting sulfoxide	Methoxysulfonium salt, % yield (8:9)	Sulfonium salt, % yield (10:11)	% yield of 4, 1, and 2[b]
A[c]-1	1	75 (100:0)	45 (90:10)	20[d]
A[c]-2	1	79 (100:0)	50 (95:5)	16[d]
A[c]-3	2	81 (0:100)	40 (50:50)	60[d]
A[c]-4	2	79 (0:100)	30 (35:65)	70[d]
B[e]-1	1	77 (95:5)	31 (92:8)	55[f]
B[e]-2	2	62 (15:85)	32 (15:85)	50[f]
C[g]-1	2	100 (0:100)	45 (15:85)	36[f]

[a] Yields determined by nmr analysis. [b] A mixture of **1** and **2** was obtained in all cases. [c] Methylmagnesium bromide, −78°, 60 min. [d] Greater than 90% **4**. [e] Dimethylcadmium, room temperature, 20 min. [f] Greater than 90% **1** and **2**. [g] Dimethylcadmium, room temperature, 60 min.

2.4 methine:Δ_2/Δ_1 = 1.08 benzylic, cis to *C*-methyl:Δ_1/Δ_2 = 1.6 benzylic, trans to *C*-methyl:Δ_2/Δ_1 = 1.2).

Therefore, we assign the cis configuration (**1**) to the liquid isomer and the trans configuration (**2**) to the solid isomer of 2-methyl-2,3-dihydrobenzothiophene 1-oxide.[13]

Assignment of Configuration. *cis*- and *trans*-1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (10 and 11). The configurations of **10** and **11** were assigned on the bases of an equilibration study, a kinetic study, and ^{13}C nmr.

1,2-Dimethyl steric interactions are larger in the cis isomer relative to those in the trans isomer. For this reason, the thermal equilibration of **10** and **11** should yield a predominance of the less hindered isomer. The equilibrium composition, determined by thermal equilibration of a 93:7 **10**:**11** mixture at 110° in 96% acetic acid,[14] was 60% **10** and 40% **11**. Therefore, **10** was assigned the trans geometry and **11** the cis.

The alkylation of sulfide **4** with either trimethyloxonium tetrafluoroborate in nitromethane or in methylene chloride or by methyl fluorosulfonate in methylene chloride gave in all three cases an approximately 80:20 mixture of sulfonium salts **10**:**11**, respectively. The most stable epimer is formed most rapidly.

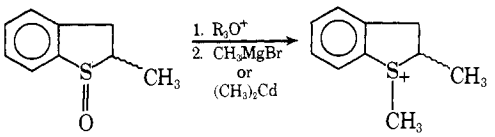
One would expect the trans isomer to react with nucleophiles more rapidly at the *S*-methyl carbon than would the cis in which the carbon is more sterically crowded and therefore less accessible to nucleophilic attack. When a mixture of **10** and **11** was treated with pyridine at room temperature,[15] the rate of attack on **10** relative to **11** was *ca.* 2:1 which is as expected based on the argument above and the assignment made by thermal equilibration.

These three studies are internally consistent. The $\Delta\Delta G^*$ for alkylation, assuming identical reaction mechanism for the formation of both isomers, is *ca.* 0.8 kcal/mol. The $\Delta\Delta G$ value for the difference in ground-state energies based on the equilibration study, albeit at 110°, is *ca.* 0.3 to 0.2 kcal/mol. Assuming dealkylation transition states similar to those of alkylation, the predicted $\Delta\Delta G^*$ for the pyridine dealkylation is 0.5 to 0.6 kcal/mol which gives a rate ratio of *ca.* 2:1 as found experimentally.

Because of their steric proximity, the C-CH_3 and S^+-CH_3 ^{13}C nmr shifts of the cis methyl groups are expected to be upfield by *ca.* 6 ppm from those of the trans isomer.[16] The value for C-CH_3 (δ(**10**) − δ(**11**)) was 4.89 ppm and for S-CH_3 (δ(**10**) − δ(**11**)) 6.82 ppm in agreement with the previous assignments.

Reaction of *cis*- and *trans*-1-Methoxy-2-methyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (8 and 9) with Organometallics. Sulfoxides **1** and **2** were alkylated to their corresponding alkoxysulfonium salts, **8** and **9**, using trimethyloxonium tetrafluoroborate in nitromethane. Nmr showed formation of only one alkyoxysulfonium salt from its sulfoxide precursor in most cases. The small amount of epimer formation occasionally observed is attributed to the presence of water which was not completely excluded from the starting sulfoxide. The salts, obtained as oils, were purified by precipitation from methylene chloride by ether, followed by several ether washings.

Separate treatment of **8** and **9** with dimethylcadmium and with methylmagnesium bromide gave the sulfonium salts **10** and **11** which were isolated as the tetrafluoroborates (oils) and subsequently converted into their tetraphenylborates (solids). Nmr analysis of the tetrafluoroborate sulfonium salts obtained from the reactions yielded the cis:trans ratios based on the relative areas of a clearly resolved S^+-CH_3 singlet and a C-CH_3 doublet for each isomer. The reactions are shown by eq 2, while the products and yields are tabulated in Table III.



(2)

Turning now to the results given in Table III, one can see that the reactions are divided into three groups: (A) the reactions of **8** and **9** with methylmagnesium bromide at −78°; (B) the reactions with dimethylcadmium at room temperature for 20 min; and (C) those for 60 min. Except for B-1 and B-2, where moisture caused some isomerization, the alkylation of sulfoxides **1** and **2** gave only one isomer, assumed to have retained configuration at sulfur, and did so in good yield. However, treatment of **8** or **9** with the organometallic reagents gave mixtures of **10** and **11** in 30 to 50% yields.

Looking first at reactions B-1 and B-2, one sees that **8** and **9** gave **10** and **11** with complete inversion at sulfur. The cis:trans ratios are reversed in going from starting material to product. When the reaction time is increased (C-1), so is the chemical yield, but the stereospecificity drops. Fifteen per cent of the sulfonium salt is of retained configuration. The origin of the other reaction products will be discussed subsequently.

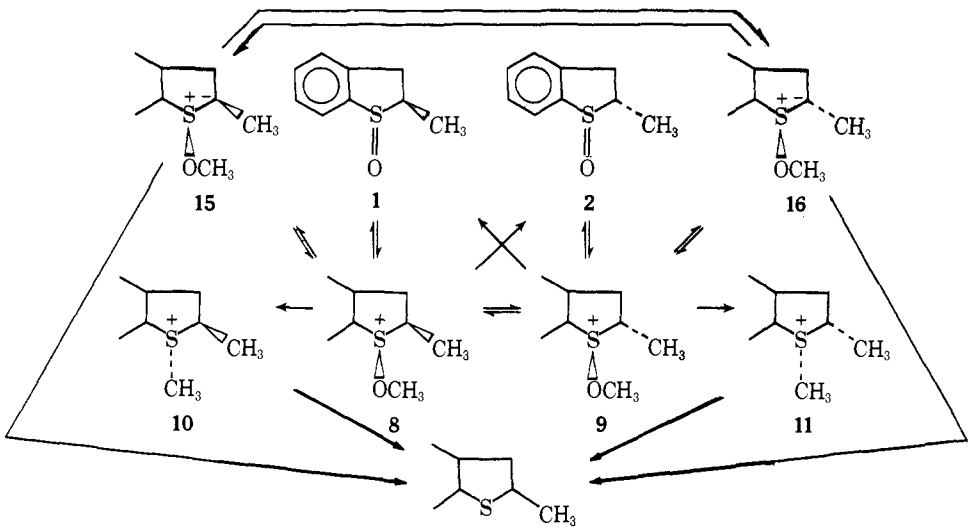
With methylmagnesium bromide (A-1 and A-2), **8** also reacted with high stereospecificity (inversion), but **9** (A-3 and A-4) did not. The stereospecificity ranged from 0 to 30%. What caused this isomerization?

Product isomerization by Grignard reagent can be ruled out since **10** and **11** are stable under the reaction conditions. They were recovered unchanged in quantitative yield after being treated with either the Grignard reagent or magnesium methoxide for 1 hr at −78°.

Ligand permutation (pseudorotation) of a tetravalent tetracoordinate intermediate, a sulfurane, formed by bonding of a methyl group to the sulfur atom of **8** or **9**, with possible coordination of the magnesium or cadmium at the methoxy oxygen, could, in principle, lead to isomerization before the methoxy group departed to give **10** or **11**. But this does not explain the loss of stereospecificity in going from reaction B-2 to C-1 where the only difference is one of reaction time.

So the explanation for isomerization seems to lie with the methoxysulfonium salts **8** and **9** which might be isomerized by the basic organometallic reagent, by alkoxide ion formed during the reaction, or by bromide ion present in the Grignard reagent. Treatment of the methoxysulfonium salt **12**, derived from (*R*)-methyl *p*-tolyl sulfoxide (**13**), used as a model for **8** and **9**, with magnesium bromide and with magnesium methoxide was carried out in order to investigate these possibilities.

Scheme II



When **12,** derived from 98% optically pure **13,** was stirred with magnesium methoxide for 1.5 hr at room temperature and then hydrolyzed with 1% aqueous sodium hydroxide, a hydrolysis which normally converts alkoxysulfonium salts into sulfoxides with 90 to 100% inversion of configuration at sulfur,[17] a quantitative yield of **13** was obtained but with 59% inversion. No methyl *p*-tolyl sulfide (**14**) was observed. The methoxide ion may attack the methoxy carbon of **12,** the sulfur atom, or the proton α to sulfur. Carbon attack leads to retention of configuration; sulfur attack leads initially to inverted **12** or retained **13** after hydrolysis but eventually to racemization after enough alkoxide exchanges have taken place. Johnson and Phillips have shown that alkoxysulfonium salts undergo exchange with a variety of alkoxides accompanied by sulfide formation *via* the ylide.[18]

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

Treatment of alkoxysulfonium salt **12** with magnesium bromide for 1.5 hr at room temperature followed by hydrolysis as above gave a 33% yield of sulfoxide **13** of 59% retained configuration and a 46% yield of sulfide **14.** Similar results had been obtained previously with (+)-ethoxybenz-*p*-tolylsulfonium tetrafluoroborate.[19]

Bromide ion attack on the methoxy carbon leads to **13** of retained configuration. Bromide ion attack on sulfur yields a bromosulfonium ion which, if attacked on bromine by nucleophiles, would lead to sulfide **14.** When a stream of ethylene was passed into a stirred mixture of methoxymethyl-*p*-tolylsulfonium tetrafluoroborate and anhydrous magnesium bromide in methylene chloride, dibromoethane was formed. Thus, bromine or a brominating agent (perhaps the bromosulfonium salt) was formed in the reaction mixture.

Utilizing the results from these model studies, reaction Schemes II and III were written which explain the observations recorded in Table III.

Dimethylcadmium reacts with alkoxysulfonium salts **8** or **9** (Scheme II) at sulfur with inversion of configuration to give sulfonium salts **10** and **11,** respectively, which are resistant toward further reaction, although, given time, they will form sulfide **4** by losing an *S*-methyl group to a nucleophile.[20] The dimethylcadmium may also attack at the methoxy carbon to regenerate the precursor sulfoxide. The methoxide ion liberated in the former reaction may also react with the alkoxysulfonium salt, as shown by the model studies, to give sulfoxide of retained configuration as well as inverted alkoxysulfonium salt. But these processes manifest themselves only during more vigorous conditions of time and temperature (C-1) and are not obvious under milder conditions (B-1 and B-2). The mixture of sulfoxides **1** and **2** isolated in 36 to 55% yield must arise primarily from reaction with dimethylcadmium at carbon and upon hydrolysis of unreacted **8** or **9.** While it is conceivable that **8** or **9** could form ylides **15** and **16,** which lead to sulfide **4,** this appears, in view of the small amount of **4** produced, to be of no importance.

The reactions of **8** and **9** with the Grignard reagent (Scheme III) appear to be slightly more complex. Very little sulfoxide was produced, but the quantity of sulfide **4** increased dramatically as a result, in view of the model experiments, of the intermediate bromosulfonium ions **17** and **18,** although the ylides **15** and **16** cannot be ruled out as possible sulfide precursors.

In summary, our results indicate that alkylarylalkoxysulfonium salts yield dialkylarylsulfonium salts with inversion of configuration at sulfur, but loss of stereospecificity may occur owing to isomerization of the starting material.

The absolute configurations may now be assigned to dialkylarylsulfonium salts synthesized from alkyl aryl sulfoxides.[4]

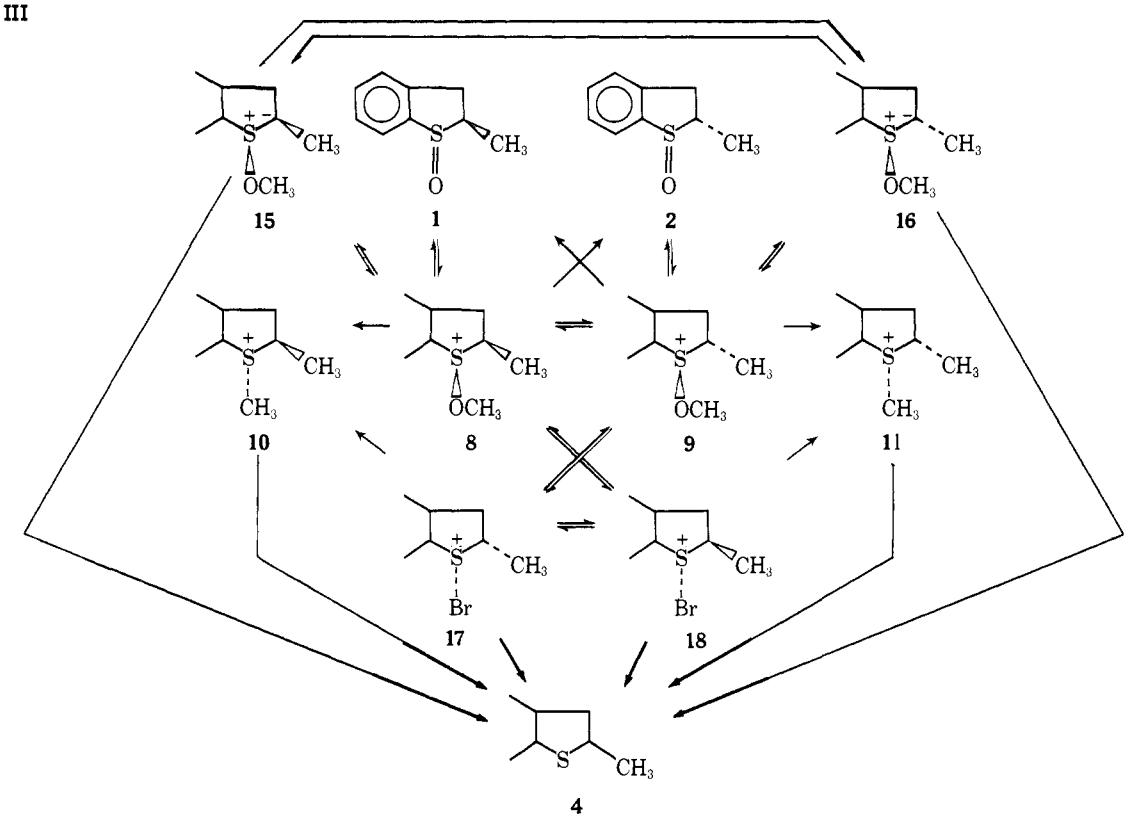
Experimental Section

Instrumentation. Nmr spectra, obtained from a Jeolco HM-100 spectrometer, are in parts per million downfield from TMS. Ir spectra were obtained from a Perkin-Elmer Model 337 grating infrared spectrophotometer. Melting points, determined on a Hoover capillary melting point apparatus, are uncorrected. A Radiometer Model 25 pH meter was used in the acid-base titrations of the organometallic reagents. Microanalyses were determined on a F & M Model 185 carbon, hydrogen, nitrogen analyzer.

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

Allyl Phenyl Sulfide (3). Allyl bromide (121 g, 1.0 mol) was added dropwise with stirring to a solution of thiophenol (110 g, 1.0 mol) and aqueous sodium hydroxide (45 g, 1.1 mol) over a 40-min period at 40–50°. The stirring was continued for 18 hr, while the reaction mixture was slowly cooled to room temperature. Extraction with 250 ml of methylene chloride followed by drying over magnesium sulfate and evaporation of the solvent *in vacuo* at 70° yielded 150 g (1.0 mol, 100%) of crude **3**; nmr [(CCl_4) δ 3.41 (dd, J_{vic} = 6.4, J_{allyl} = 1.0 Hz, 2, SCH_2), 4.8–5.2 (m, 2, $=CH_2$), 5.83 (ddt, J_{cis} = 9.2, J_{trans} = 17.2, J_{vic} = 6.4 Hz, 1, CH), 7.2 (m, 5,

Scheme III



C_6H_5)] revealed no impurities.

2-Methyl-2,3-dihydrobenzothiophene (4).[8] A mixture of 150 g (1.0 mol) of crude allyl phenyl sulfide and 129 g (1.0 mol) of quinoline was heated at reflux (225–240°) for 4 hr. The solution was then poured into 500 ml of 6 *N* hydrochloric acid and extracted once with 500 ml and two times with 250-ml portions of heptane. The combined heptane extracts were concentrated to *ca.* 300 ml and washed three times with 250 ml of 5 *N* hydrochloric acid. Drying over magnesium sulfate and concentration *in vacuo* at 75° yielded 90 g of crude oil which was shown by nmr to consist of **4**, **5**, and thiophenol. Distillation yielded 83 g (0.55 mol, 55%) of a colorless oil consisting of 40% **4** and 60% **5**, bp 73–100° (1.5 mm).[21]

This mixture of sulfides (83 g, 0.55 mol) was suspended in 100 ml of water, and a solution of 160 g (1.0 mol) of potassium permanganate in 2 l. of water was slowly added with stirring at room temperature. The reaction mixture was acidified with concentrated hydrochloric acid, and solid sodium bisulfite was added until a colorless solution containing a white precipitate was obtained. Filtration, extraction of the filtrate with methylene chloride, drying over magnesium sulfate of the combined precipitate and extracts, and concentration of the solvent *in vacuo* gave a yellow oil, which crystallized upon trituration with cyclohexane. Filtration yielded 55 g (0.30 mol, 55%) of a white crystalline solid, mp 79–99°, consisting of 48% **6** and 52% **7** as shown by nmr.

A solution of 16.3 g (90 mmol) of this sulfone mixture in 300 ml of benzene and 200 ml of ether was added dropwise to a stirred suspension of 4.0 g (105 mmol) of lithium aluminum hydride in 135 ml of ether and benzene at room temperature over a 75-min period. After continued stirring for another 75 min, excess lithium aluminum hydride was decomposed by dropwise addition of 4 ml of water, 4 ml of 15% sodium hydroxide, and 12 ml of water, in that order. Filtration and evaporation of the solvent *in vacuo* gave 15.7 g of a white, semicrystalline product, which was vacuum distilled to yield 5.1 g (34 mmol, 38%) of **4** as a colorless oil: bp 48–50° (0.2 mm); ir (neat) ν_{max} 3070 (m), 2970 (m), 2930 (m), 2900 (m), 2870 (m), 2835 (m), 1595 (m), 1465 (s), 1450 (s), 1375 (m), 1255 (m), 1120 (m), 1065 (m), 1000 (m), 745 (s), 695 (m) cm^{-1}. The **2-methyl-2,3-dihydrobenzothiophene 1,1-dioxide (6)** had mp 110–112° (benzene–cyclohexane) (lit.[8] mp **115–116°**). The yield of **4** based on the amount formed in the original cyclization of allyl phenyl sulfide (**3**) was 52%.

The residue from the distillation was recrystallized from 200 ml of cyclohexane–benzene (3:2) to yield 6.2 g (34 mmol, 38%) of **1-thiachroman 1,1-dioxide** (7): mp 84–85° (ethanol) (lit.[8] mp 88–89°); nmr ($CDCl_3$) δ 2.53 (m, 2, $CH_2CH_2CH_2$), 3.10 (t, J = 6.5 Hz, 2, $ArCH_2$), 3.42 (m, 2, SO_2CH_2), 7.6 (m, 3, ArH meta and para to SO_2), 8.12 (dd, J = 6, 2 Hz, 1, ArH ortho to SO_2).

***cis*- and *trans*-2-Methyl-2,3-dihydrobenzothiophene 1-oxide** were prepared from 4.5 g (30 mmol) of sulfide **4** as described.[7] The crude mixture (40:60 of **1**:**2** by nmr) of diastereomeric sulfoxides (4.6 g, 28 mmol, 92%) was purified by chromatography on a 3.5 × 115 cm column packed with 425 g of Baker silica gel. Elution with 300 ml of cyclohexane, 600 ml of cyclohexane–ether (1:1), 3800 ml of ether, and 1600 ml of ether–methanol (9:1) yielded first a fraction of pure **1** (1.47 g, 8.9 mmol, 30%) as a viscous oil [ir (neat) ν_{max} 3065 (w), 2970 (m), 2930 (m), 2870 (w), 1590 (w), 1570 (w), 1460 (m), 1445 (m), 1370 (w), 1120 (m), 1105 (m), 1055 (s), 1030 (s), 980 (s), 815 (m), 750 (s), 710 (m), 690 (w) cm^{-1}], then a mixed fraction (0.30 g, 1.8 mmol, 6%), and finally pure **2** (2.00 g, 12.0 mmol, 40%) as a viscous oil which crystallized on standing. Recrystallization from 10 ml of cyclohexane–ether (1:1) yielded 1.66 g of pure crystalline **2**, mp 42–44°.

***cis*- and *trans*-1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate and Tetraphenylborate (10 and 11).** The title compounds were prepared by several procedures; one example, typical of each method, is described below.

Procedure A. Trimethyloxonium tetrafluoroborate (0.59 g, 4.02 mmol, 10% excess) was dissolved in *ca.* 20 ml of nitromethane in a 125-ml erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. *cis*-2-Methyl-2,3-dihydrobenzothiophene 1-oxide (0.6 g, 3.65 mmol), dissolved in nitromethane, was introduced by means of a syringe, and the reaction mixture was stirred for 1 hr. The solution was concentrated on the rotary evaporator, and the methoxysulfonium salt was precipitated from the nitromethane by the addition of ether. The salt was purified by dissolution in methylene chloride followed by precipitation from ether several times, followed by several washings with ether which yielded 0.72 g (75%) of the desired product as a thick oil. The oil was dissolved in methylene chloride in a 125-ml erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. The flask was immersed in an acetone–Dry Ice bath, and methylmagnesium bromide (1.36 ml, 4.02 mmol, 2.95 *M*) was introduced by means of a syringe. After 1 hr, the reaction mixture was hydrolyzed with 5% sulfuric acid. The entire

mixture was extracted with two equal volumes of ether, and the ethereal layers were combined and washed with two 25-ml portions of water. The aqueous layers were combined, saturated with sodium tetrafluoroborate (*ca.* 25 g), and extracted with five 25-ml portions of methylene chloride. The methylene chloride extracts were dried over magnesium sulfate and concentrated on the rotary evaporator. The crude oil was washed several times with ether and dried *in vacuo*, yielding 0.42 g (45%) of the desired product consisting of a 90:10 mixture of **10**:**11** as a yellow oil.

Sodium tetraphenylborate (0.57 g, 1.7 mmol) was dissolved in a minimum amount of acetone in an erlenmeyer flask. The sulfonium tetrafluoroborate (prepared above) was dissolved in a second flask in the same way, and the two solutions were combined. The desired product was obtained by precipitation from the acetone solution by ether. The product obtained was purified by dissolution in acetone followed by precipitation with ether repeated several times yielding 0.8 g (100%) of the 1-2-dimethyl-2,3-dihydrobenzothiophenium tetraphenylborate (fluffy white crystals), mp 168–170°. Nmr (DMSO-d_6): **10**, δ 1.47 (d, J = 2 Hz, 3, CCH_3), 3.06 (s, 3, SCH_3), 4.46 (m, 1, CH), 6.52–8.24 (m, 24, Ar); **11**, δ 1.58 (d, J = 2 Hz, 3, CCH_3), 2.88 (3, SCH_3), 4.76 (m, 1, CH), 6.52–8.24 (m, 24, Ar). All spectra of **10** and **11** are of mixtures of the two isomers. Ir (KBr): **10** and **11** (80:20), ν_{max} 3070 (m), 3030 (m), 2990 (m), 2950 (s), 1595 (s), 1495 (s), 1445 (s), 1410 (m), 1275 (m), 1158 (m), 1040 (m), 850 (m), 745 (m), 695 (m), 615 (m), 420 (m).

Anal. Calcd for $C_{34}H_{33}BS$: C, 84.28; H, 6.87. Found: C, 84.01; H, 6.81.

The reaction was repeated several times; the results are given in Table III.

Procedures B and C. Distilled dimethylcadmium was used in place of methylmagnesium bromide. The reaction was carried out at room temperature for 20 min or 1 hr. The reaction procedure is otherwise identical with that given in procedure A (*vide supra*), and the results are listed in Table III.

Procedure D. Trimethyloxonium tetrafluoroborate (2.96 g, 0.02 mol) was dissolved in *ca.* 50 ml of methylene chloride in a 125-ml erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. 2-Methyl-2,3-dihydrobenzothiophene (3 g, 0.02 mol), dissolved in methylene chloride, was introduced by means of a syringe, and the reaction was stirred for 4 hr at room temperature. Unreacted oxonium salt was removed by filtration, and the desired product was precipitated from the reaction mixture by the addition of ether. The crystalline material obtained was purified by several precipitations from methylene chloride by ether followed by several washings with ether. The solid was decanted and dried *in vacuo* yielding 4.36 g (87%) of the desired product consisting of a 83:17 mixture of **10**:**11**, mp 168–170° (reported above, mp 168–170°).

The reaction was repeated several times with trimethyloxonium tetrafluoroborate in nitromethane or in methylene chloride or by methyl fluorosulfonate in methylene chloride yielding in all cases an approximately 80:20 mixture of **10**:**11**, respectively.

Thermal Equilibration of 1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (10 and 11). A 93% trans and 7% cis mixture of **10**:**11** (0.04 g) was dissolved in 96% acetic acid (0.5 ml) in an nmr tube. The sample was equilibrated in a bath of refluxing toluene (bp 110°). The apparatus consisted of a 250-ml round-bottom flask equipped with a two-neck adapter, thermometer, and pipet inlet adapter in which the nmr tube was placed. The nmr tube was removed at periodic intervals over a 9-day period and the nmr spectrum recorded. The cis:trans ratio of the two isomers was determined from the *S*-methyl singlets which were clearly resolved in all spectra. Very little decomposition of the starting material was observed: $k = 2.18 \times 10^{-2}$ hr^{-1}, $k' = 3.42 \times 10^{-2}$ hr^{-1}

$$\text{trans} \underset{k'}{\overset{k}{\rightleftharpoons}} \text{cis}$$

and $t_{1/2}$ 20.39 hr.

Reaction of (*R*)-Methoxymethyl-*p*-tolylsulfonium Tetrafluoroborate (12) with Magnesium Bromide and Magnesium Methoxide. Anhydrous magnesium bromide (0.52 g, 2.8 mmol) was placed in a 125-ml erlenmeyer flask equipped with a magnetic stirrer, fitted with a septum, and flushed with nitrogen. Methylene chloride (10 ml) was introduced, and stirring was initiated. (*R*)-Methoxymethyl-*p*-tolylsulfonium tetrafluoroborate (0.72 g, 2.8 mmol, $[\alpha]^{23}$D 186°), prepared from (*R*)-(+)-methyl *p*-tolyl sulfoxide [1 g, 6.48 mmol; $[\alpha]^{23}$D 140.9° (*c* 0.9, acetone)] and trimethyloxonium tetrafluoroborate, dissolved in 10 ml of methylene chloride, was added using a syringe, and the mixture was stirred for 1.5 hr. The magnesium bromide was filtered off, and the filtrate was hydrolyzed with *ca.* 50 ml of 1% sodium hydroxide. The two layers were separated, and the aqueous layer was saturated with *ca.* 20 g of sodium bromide and then extracted with four 25-ml portions of methylene chloride. The methylene chloride extract was dried over magnesium sulfate, concentrated on the rotary evaporator, and dried *in vacuo* yielding 0.18 g (46%) of methyl *p*-tolyl sulfide (**14**) and 0.15 g (33%) of (*R*)-(+)-methyl *p*-tolyl sulfoxide (**13**); $[\alpha]^{22}$D 25.3° (*c* 1, acetone), 18.0% optically pure.

Also, **12** was treated with magnesium methoxide. Following reaction and work-up as above, (*S*)-(−)-methyl *p*-tolyl sulfoxide (**13**) (0.43 g, 100%) was isolated, $[\alpha]^{23}$D −24.2° (*c* 1, acetone), 17.2% optically pure.

Stability of 1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (10 and 11) to Magnesium Methoxide. Magnesium methoxide (86 mg, 1.0 mmol) was added to a solution of sulfonium salt (**11**:**10**, 7:93) (252 mg, 1.0 mmol) in methylene chloride (5 ml). The solution was stirred for 1 hr, undissolved magnesium methoxide was filtered off, and the nmr spectrum of the resulting solution was recorded. This showed an unchanged ratio of **11**:**10** (7:93) and revealed no decomposition products.

Stability of 1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate (10 and 11) to Methylmagnesium Bromide. Methylmagnesium bromide (0.34 ml, 1.0 mmol) in ether was added to a cooled solution (−78°) of sulfonium salt (**11**:**10**, 7:93) (756 mg, 3.0 mmol) in methylene chloride (15 ml) under nitrogen. The solution was stirred for 1 hr in the cold, then acidified with 5% sulfuric acid, and warmed to room temperature. After the usual work-up, 695 mg (2.8 mmol, 92%) of sulfonium salt, which was shown by nmr to consist of **11** and **10** in unchanged ratio (7:93) and to contain no decomposition products, was recovered.

Reaction of 1,2-Dimethyl-2,3-dihydrobenzothiophenium Tetrafluoroborate with Pyridine. Pyridine (39.5 mg, 0.50 mmol) was added to a solution of sulfonium salt (25.2 mg, 0.10 mmol) in methylene chloride (0.30 ml) in an nmr tube. The reaction was followed by integration of the 2-methyl signals of **10**, **11**, and **4** over a period of 21 hr at room temperature (hr, % **11**, % **10**): 0.0, 17.8, 82.2; 0.7, 13.6, 76.5; 1.3, 13.0, 72.5; 1.8, 14.3, 64.9; 2.7, 16.3, 55.5; 3.4, 14.0, 49.3; 5.7, 12.1, 37.0; 9.8, 10.7, 36.5; 21.2, 6.2, 13.2. The results were fitted to the rate equation[22] by the method of least squares giving $k_{11}/k_{10} = 0.47 \pm 0.08$ (correlation coefficient 0.91). After 44 hr, the nmr spectrum showed the presence of the sulfide **4**, exclusively.

Reaction of (+)-Methoxymethyl-*p*-tolylsulfonium Tetrafluoroborate with Magnesium Bromide in the Presence of Ethylene. Racemic methyl *p*-tolyl sulfoxide (91 mg, 5.9 mmol) was methylated with trimethyloxonium tetrafluoroborate (96 mg, 6.5 mmol) in methylene chloride (20 ml). Anhydrous magnesium bromide (*ca.* 1.5 g) prepared from magnesium and bromine in ether was added. A stream of ethylene was passed in for 1 hr with stirring. After 1 additional hr of stirring, the supernatant liquid was shown by gc (10 ft × 0.25 in., 10% Apiezon M on Chromosorb W 60–80 column, 200°) to contain 1,2-dibromoethane and methyl *p*-tolyl sulfide.

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References and Notes

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(2) This work was taken in part from the Ph.D. thesis of R. L. Caret, The University of New Hampshire, Durham, N.H., 1974.
(3) Postdoctoral research associate, 1972–1973. Recipient of a Fulbright-Hays travel grant.
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(20) We initially attempted to isolate **10** and **11** as the sulfonium bromides. The instability of these salts was shown to be due to nucleophilic attack of the bromide anion on **10** and **11** to give **4**.
(21) Pure 1-thiachroman (**5**) was obtained by low-temperature (−78°) recrystallizations (heptane) of fractions enriched in **5** by careful fractional distillation: bp 82–87° (1 mm) [lit.[8] bp 85–89° (0.2 mm)]; nmr ($CDCl_3$) δ 1.92 (m, 2, $CH_2CH_2CH_2$), 2.65 (t, J = 6.5 Hz, 2, $ArCH_2$), 2.85 (m, 2, SO_2CH_2), 7.0 (m, 4, ArH); ir (neat) ν_{max} 3055 (m), 3000 (m), 2930 (s), 2845 (m), 1580 (m), 1560 (m), 1465 (s), 1425 (s), 1280 (m), 1265 (m), 1120 (m), 1070 (m), 1045 (m), 930 (m), 775 (m), 740 (s) cm^{-1}.
(22) Based on the two first-order reactions (eq i and ii), the following linear

$$11 + py \xrightarrow{k_{11}} 4 + pyCH_3^+BF_4^- \quad \text{(i)}$$

$$10 + py \xrightarrow{k_{10}} 4 + pyCH_3^+BF_4^- \quad \text{(ii)}$$

eq iii was used.

$$\ln (C_{\infty 11} - C_{11}) = k_{11}/k_{10} \ln (C_{\infty 10} - C_{10}) + \text{constant} \quad \text{(iii)}$$

Isotopic Scrambling Processes in the Acetolysis of Labeled *exo*-Dehydro-2-norbornyl Brosylate

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Abstract: Acetolysis of *exo*-dehydro-2-norbornyl-*3-exo-t* brosylate (**1**-*3-exo-t*-OBs) at 24, 45, or 65° gave in each case about 50% rearrangement of the label from C-2,3 to C-1,4,5,6,7 in the product, **1**-*x-t*-OAc, in agreement with the results from **1**-*3-exo-d*-OBs obtained by Cristol and coworkers. Degradation of the **1**-*x-t*-OAc, however, showed that the distribution of the T label was approximately 12, 38, 38, and 12%, respectively, at C-2, C-3, C-1,4,7, and C-5,6, not a 50:50 split over C-3 and C-7 as was previously assumed. It is suggested that the overall T distribution is the net result of a number of contributing processes, including (1) formation of product from an equilibrating mixture of the Wagner–Meerwein related homoallylic dehydronorbornyl cations **2a** and **2b**, (2) elimination to norbornadiene followed by addition of HOAc to give scrambled **1**-*x-t*-OAc, and (3) the occurrence of 3,2 hydrogen shift before product formation. A possible rationalization of the discrepancies reported by previous workers is discussed.

Discrepancies in the extents of isotopic scrambling observed in the *exo*-dehydro-2-norbornyl acetate obtained from acetolysis of ^{14}C- or D-labeled *exo*-dehydro-2-norbornyl brosylate have been reported by two groups of workers.[1,2] In 1955, Roberts, *et al.*,[1] found that in the acetolysis of *exo*-dehydro-2-norbornyl-*2,3*-$^{14}C_2$ brosylate (**1**-*2,3*-^{14}C-OBs) at 45° in the presence of KOAc, 38% of the ^{14}C label was rearranged from the C-2,3 positions to the rest of the carbon skeleton in the resulting *exo*-dehydro-2-norbornyl-*x*-^{14}C acetate (**1**-*x*-^{14}C-OAc). On the other hand, Cristol and coworkers[2] reported in 1966 that the acetolysis of *exo*-dehydro-2-norbornyl-*3-exo-d* brosylate (**1**-*3-exo-d*-OBs) at 24° in the presence of NaOAc gave a **1**-*x-d*-OAc product, the mass spectral analysis[3] of which showed an essentially 50% rearrangement of the D label from C-2,3 to C-1,4,5,6,7. These differences prompted Lee and Hahn[4] to study the reaction once more, using **1**-2-*endo-d*-OBs as the labeled reactant. It was found that both the results of Roberts[1] and of Cristol[2] were essentially correct, and it was thought that differences in reaction temperature might have played a role in giving rise to the different extents of rearrangement. Recently, however, Cristol and Beimborn[5] reinvestigated the acetolysis of **1**-*3-exo-d*-OBs under various experimental conditions including the different temperatures used by Lee and Hahn. Again about 50% rearrangement was observed in all cases. Professor Cristol also indicated that he has examined the data from the thesis of Hahn, found no errors in the calculations, and was unable to rationalize the difference between their results and those of Lee and Hahn.[4] Since the mass spectral analysis of the **1**-*x-d*-OAc from either **1**-*3-exo-d*-OBS or **1**-*2-endo-d*-OBs gave only the overall rearrangement of the D label from C-2,3 to C-1,4,5,6,7 based on fragmentation by the retrograde Diels–Alder reaction,[3] we have decided to repeat the investigation using **1**-*3-exo-t*-OBs and degrade the **1**-*x-t*-OAc product in order to obtain more detailed information which may help to explain the apparent discrepancies in the published results.

In the acetolysis of **1**-*2,3*-^{14}C-OBs,[1] reaction *via* a rapidly equilibrating pair of enantiomeric homoallylic ions **2a** and **2b**, or the intervention of a symmetrical ion such as **3**, would give rise to 50% rearrangement of the label from C-2,3 to C-1,7 in the resulting **1**-*x*-^{14}C-OAc. Since less than 50% rearrangement was observed,[1] a relatively slow equili-