This solution was distributed (1.5-mL aliquots) into tightly capped vials and suspended in an oil bath. In each instance, a control of the respective N^1-oxides (6 and 7) was carried out at the same time. In the case of 2 and 6, the oil bath was maintained at 76 ± 1 °C and in the case of 7 and 8 at 64 ± 1 °C. At regular intervals, vials were removed and chilled in ice, and the UV spectra recorded (Figure 1). Compounds 2 and 8 showed complete degradation in 90 min ($t_{1/2}$ = 27 min) and 8 h ($t_{1/2}$ = 64 min), respectively, whereas 7 showed no observable degradation by UV, and the UV spectrum of 6 remained essentially unchanged except for a slightly diminished intensity.

The stabilities of 6, 7, 10, and 13 were also examined separately at 76 °C (0.02 M) in CD_3OD–D_2O (1:1), monitoring by UV, NMR, and TLC (solvent B). After 90 min, 6 showed ca. 30% degradation (estimated by NMR and verified by TLC which showed the presence of a faster moving spot) even though the UV spectrum was unchanged except for diminished intensity. NMR indicated that total breakdown had occurred after 22 h (TLC showed several spots and the UV spectrum showed a much decreased intensity). After 90 min, 7 showed no degradation by UV or TLC, NMR indicating ca. 1% breakdown, and after 22 h the UV spectrum showed a slightly diminished intensity, but NMR indicated ca. 35% degradation and TLC showed four spots. **13** showed no degradation by NMR after 4 h, and **10** showed no degradation by UV, NMR, or TLC even after 22 h.

In the case of **17**, carried out in H_2O at 81 °C no breakdown could be detected after 4 h by UV, TLC, or NMR, although some slight discoloration of the NMR sample (0.02 M) was evident; **14** showed complete degradation at this point.[16a]

In the case of **3** (X = tosylate or iodide) complete degradation was noted at the first time point (5 min).

Acknowledgment. We thank Dr. S. S. Danyluk for his interest and C. F. Ainsworth for recording the NMR spectra. This work was supported by the U.S. Department of Energy under contract number W-31-109-ENG-38.

Registry No. 1, 362-75-4; 2, 5605-63-0; 5, 5167-12-4; 6, 72525-43-0; 7, 72525-44-1; 8, 30685-66-6; 10, 72525-45-2; 12, 4137-54-6; 13, 34245-48-2; 14, 2627-64-7; 17, 72525-46-3.

Stereochemistry of Free-Radical Eliminations on β-Phenylsulfonyl Radicals

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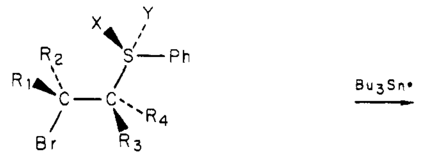
Tributyltin radicals have been allowed to react with *erythro*- and *threo*-2-bromo-3-(phenylsulfonyl)butane (**5a,b**) to generate β-(phenylsulfonyl)-*sec*-butyl radicals **9**. The intermediate **9** eliminates phenylsulfonyl radicals to form 2-butenes in a nonstereospecific manner. The lack of stereospecificity is due to rotation about the C_2–C_3 bond before the loss of the phenylsulfonyl radical can occur and implies that the stabilization of the radical by sulfur bridging is negligible.

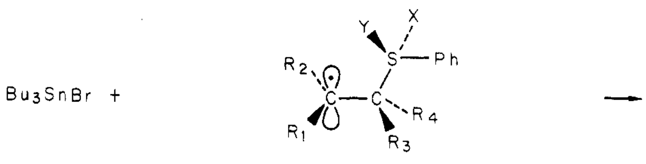
Alkyl radicals, substituted at the β position with a sulfur, often eliminate a sulfur-centered radical to generate an alkene.[1] We have recently investigated the stereochemistry of this elimination when β-phenylthio radicals, **1**,[1a] and β-phenylsulfonyl radicals, **2**,[1b] are generated by reaction of the corresponding bromides with tributyltin radicals (eq 1).

Reaction of either **3a** or **3b** with tributyltin radicals generates the same mixture of (*E*)- and (*Z*)-2-butenes, indicating that the barrier to rotation in **1** is less than the barrier to elimination.[1a] In striking contrast, however, reactions of tributyltin radicals with the four diastereomeric bromo sulfoxides **4a–d** produce (*E*)- and (*Z*)-2-butenes stereoselectively.[1b] The 2-butenes generated are those expected from loss of the phenylsulfinyl radical from nonequilibrium conformations of **2**. Thus, the barrier to rotation in **2** is larger than the barrier to elimination. We have rationalized this result by proposing that the greater kinetic stability of the phenylsulfinyl radical, **7**, as compared to the phenylthio radical, **6**,[2,3] lowers the barrier to elimination in **2** relative to **1**.

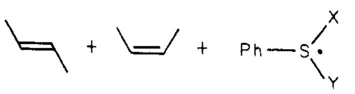
In order to test the hypothesis that the stability of the leaving radical determines the stereochemistry of the elimination, we now report a study of the reaction of the diastereomeric 2-bromo-3-(phenylsulfonyl)butanes (**5a,b**)



3a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = Y = :
3b, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = Y = :
4a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = O; Y = :
4b, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = :; Y = O
4c, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = O; Y = :
4d, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = :; Y = O
5a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = Y = O
5b, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = Y = O



1a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = Y = :
1b, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = Y = :
2a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = O; Y = :
2b, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = :; Y = O
2c, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = O; Y = :
2d, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = :; Y = O
9a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$; X = Y = O
9b, $R_1 = R_3 = Me$; $R_2 = R_4 = H$; X = Y = O



(1)

6, X = Y = :
7, X = :; Y = O
8, X = Y = O

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[1] (a) T. E. Boothe, J. L. Greene, Jr., and P. B. Shevlin, *J. Am. Chem. Soc.*, **98**, 951 (1976); (b) T. E. Boothe, J. L. Greene, Jr., P. B. Shevlin, M. R. Willcott, III, R. R. Inners, and A. Cornelis, *ibid.*, **100**, 3874 (1978); (c) J. T. Hepenstall and J. A. Kampmeier, *ibid.*, **95**, 1904 (1973); (d) J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *ibid.*, **88**, 1257 (1966); (e) A. Schonberg and T. Stolpp, *Justus Liebigs Ann. Chem.*, **483**, 90 (1930); (f) P. B. Shevlin and J. L. Greene, Jr., *J. Am. Chem. Soc.*, **94**, 8447 (1972); (g) B. Lythgoe and I. Waterhose, *Tetrahedron Lett.*, 4223 (1977).

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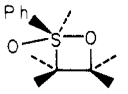
Table I. Stereochemistry of 2-Butene Formation in the Reaction of 2-Bromo-3-(phenylsulfonyl)butanes with Tributyltin Radicals

compd	$[Bu_3SnH]/[5]$[a]	condtns[b]	2-butene yield, %[c]	E/Z[d]
5a	1.0	1 h, 80 °C	48.4	2.18 ± 0.27
5a	5.0	1 h, 80 °C	73.5	2.05 ± 0.13
5a	1.0	$h\nu$, 3 h, −67 °C	17.3	4.94 ± 0.25
5a	1.0	$h\nu$, 3 h, −67 °C	22.6	4.89 ± 0.02
5b	1.0	1 h, 80 °C	55.3	2.21 ± 0.05
5b	5.0	1 h, 80 °C	66.5	1.99 ± 0.07
5b	1.0	$h\nu$, 2 h, −67 °C	33.0	4.50 ± 0.25
5b	1.0	$h\nu$, 3 h, −67 °C	39.3	4.72 ± 0.44

[a] [Bromide] = 0.12 M, AIBN used as initiator. [b] Thermal reactions were complete in 1 h. [c] Traces of 1-butene and butane observed in several cases. [d] Ratio of E to Z isomer for 2-butene.

with tributyltin radicals. Since phenylsulfonyl radicals, **8**, are comparable in stability to PhS· and less stable than PhSO·,[2,3] it is expected that the bromo sulfones **5a** and **5b** will react with tributyltin radicals with stereochemical consequences similar to those observed for **3**.

Alternately, the radical center in **9** may stabilize by interaction with the neighboring sulfonyl groups via the cyclic oxysulfuranyl radical **10**. This type of stabilization would tend to raise the barrier to rotation and hence stereoselectively of elimination of $PhSO_2\cdot$.



10

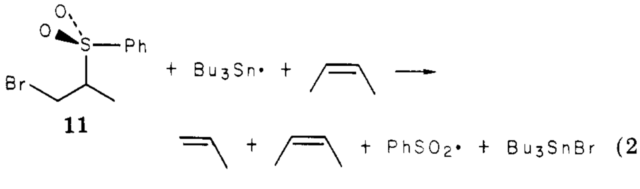
β-Alkylsulfonyl radicals can be generated by the addition of sulfonyl radicals to alkenes,[4] and there is clear evidence that the addition is reversible.[5] The photoinitiated addition of the phenylsulfonyl radical to (E)- and (Z)-2-butene produced the same ratio of products regardless of the starting olefin.[6] The β-alkylsulfonyl radical from sulfolane has been detected by ESR, and other β-alkylsulfonyl radicals have been implicated in the reaction of hydroxyl radicals with dialkyl sulfones.[7] β-Alkylsulfonyl radicals have also been produced by the reaction of tributyltin radicals with β-hydroxy sulfones.[1g] However, the stereochemistry of the elimination itself has not been investigated.

Results and Discussion

Reaction of *erythro*- and *threo*-2-Bromo-3-(phenylsulfonyl)butane with Tributyltin Radicals. *erythro*- and *threo*-2-bromo-3-(phenylsulfonyl)butane[8] (**5a,b**) were prepared by the *m*-chloroperbenzoic acid oxidation of **3a** and **3b**. Each diastereomer was allowed to react with tributyltin radicals, generated from AIBN and tributyltin hydride in benzene at 80 °C. The resulting 2-butenes were swept from the reaction vessel by a stream of nitrogen, trapped at −196 °C, and analyzed by gas chromatography and infrared spectroscopy. The results, given in Table I, show that the (E)- to (Z)-2-butene ratio is independent of the starting sulfone. Although no attempt was made to optimize the yields, alkene formation appeared to be the major course of this reaction. Increasing the reaction times and/or the tributyltin hydride concentration resulted in correspondingly higher butene yields (Table I). After 1 h of reaction, NMR analysis showed the presence of unreacted bromo sulfone and did not reveal products other than those resulting from the loss of the phenylsulfonyl radical from **9**. Analysis of the reaction mixture by gas chromatography showed that no 2-(phenylsulfonyl)butane was produced.

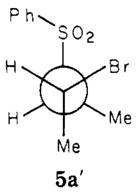
In order to assess the effect of temperature on the stereochemistry of elimination, tributyltin radicals were generated photolytically and allowed to react with **5a** and **5b** at −67 °C in toluene. The 2-butenes produced in the reaction were pumped from the reactor at reduced pressure, trapped at −196 °C, and analyzed as above. The results of these experiments, as shown in Table I, indicate that even at this low temperature the same E/Z ratio is obtained regardless of whether one starts with **5a** or **5b**.

In all cases, attempts were made to carry out appropriate control experiments. It was determined that **5a** and **5b** did not interconvert under either thermal or photolytic reaction conditions. The possibility of isomerization of the butenes before they could be removed from the reaction vessel was excluded by carrying out a reaction of tributyltin radicals with 2-bromo-1-(phenylsulfonyl)propane, **11**, in the presence of (Z)-2-butene (eq 2). The (Z)-2-butene was isomerized to an extent of 2 and 3% at 90 and −67 °C, respectively.

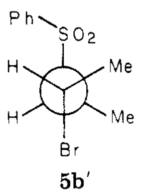


(2)

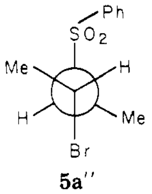
The results obtained from eliminations on β-sulfonyl radicals from **5a** and **5b** demonstrate that rotation about the C_2–C_3 bond in the intermediate radical is more rapid than elimination. A consideration of vicinal coupling constants[9] in **5a** (J = 3.90 Hz) and **5b** (J = 2.55) and the expected steric interactions in these compounds leads to the conclusion that **5a′** and **5b′** are the predominate conformers. If bromine is abstracted from these conformers, a substantial barrier to rotation in **9** would lead to (Z)-2-butene in each case. Alternately, if abstraction from anti conformers **5a″** and **5b′** is preferred, a barrier to rotation in **9** should result in (E)-2-butene from **5a** and (Z)-2-butene from **5b**. Since the experimental results are not in accordance with either of the above predictions, we conclude that rotation about the C_2–C_3 bond in **9** is more rapid than elimination.



5a′



5b′



5a″

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Table II. Relative Reactivities of 3, 4, and 5 toward Tributyltin Radicals

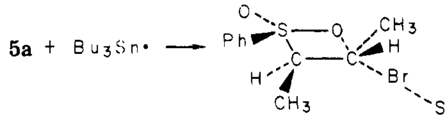
compd	k_{rel}	compd	k_{rel}
3a	1.55 ± 0.08	4c	2.46 ± 0.14
3b	1.38 ± 0.09	4d	1.96 ± 0.16
4a	2.19 ± 0.20	5a	2.09 ± 0.14
4b	1.45 ± 0.11	5b	2.84 ± 0.18

The increase in the ratio of (*E*)- to (*Z*)-2-butene from both **5a** and **5b** at −67 °C as compared to 80 °C is probably a result of a lower relative energy for the transition state leading to (*E*)-2-butene at the lower temperature.

Neighboring-Group Participation in β-Sulfur-Substituted Radicals. In order to evaluate the extent of assistance of bromine abstraction by the neighboring phenylsulfonyl group, we have measured the rate of reaction of **5** as compared to those of **3** and **4**. This was done in a series of experiments in which the indicated diastereomer of **3**, **4**, or **5** and a mixture of 1-bromo-2-(phenylthio)propane and 2-bromo-1-(phenylthio)propane were allowed to compete for tributyltin radicals. Since bromine abstraction is undoubtedly the rate-determining step, the relative rates of bromine abstraction are determined by comparison of the ratios of propene to 2-butenes from **3**, **4**, and **5** and are given in Table II.

An examination of Table II shows that no diastereomer of **3**, **4**, or **5** shows a significant rate enhancement over any of the others. If anchimeric assistance were operative in these systems, it is expected that diastereomers in which steric interactions between methyls are minimized in the transition state for anti abstraction would react significantly faster.

In particular, there is no evidence for assistance by the phenylsulfonyl group in the anti abstraction of bromine from **5**. If such an effect were operative, **5a** should react faster than **5b** as steric interactions between methyls are minimized in the transition state for bromine abstraction (eq 3). The data in Table II show that **5a** and **5b** react at similar rates, with **5b** actually going a bit faster. These facts are inconsistent with any significant neighboring-group participation in the reaction of **5**. We have previously used similar arguments to demonstrate the lack of significant participation by the sulfur-containing group in the reactions of **3** and **4** with tributyltin radicals.[1a,b]

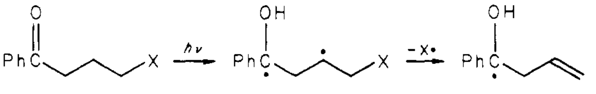


(3)

Table II shows a small average rate increase in going from **3** to **4** to **5**. The ease of radical formation at C_2 seems to parallel the ease of anion formation at this carbon. This observation is rationalized by the work of Kuivila,[10] who has shown that the abstraction of a halide by nucleophilic tin radicals places a partial negative charge on carbon in the transition state.

Conclusion

These experiments demonstrate that the β-phenylsulfonyl radicals **9a** and **9b** are similar to the β-phenylthio radicals **1a** and **1b** in that the barrier to rotation about the C_2–C_3 bond is lower than the barrier for elimination of the sulfur-centered radical. The stereochemical behavior of radicals **1** and **9** is strikingly different from that of the β-phenylsulfonyl radicals **2a–d** in which the barrier to elimination is lower than the barrier to rotation. Wagner, Seden, and Lindstrom have reported[3] that the relative rates of cleavage of $PhS\cdot$, $PhSO\cdot$, and $PhSO_2\cdot$ are in a ratio of 16.1:92.6:1 when the β-substituted radicals are generated by the photolysis shown in eq 4. This report confirms that



(4)

X = PhS, PhSO, $PhSO_2$

$PhSO\cdot$ is eliminated more rapidly than $PhS\cdot$ and $PhSO_2\cdot$ and provides a rationale for our observed stereoselective $PhSO\cdot$ eliminations.

An increased barrier to rotation in **2** as compared to **1** and **9** would also rationalize the observed stereochemistry. This would imply that the interaction between sulfur and the radical center is greater in **2** than in **1** or **9**. If this were the case, it is expected that this effect would manifest itself in the transition state leading to the radical. Since the rate of bromine abstraction is similar for all diastereomers of **3**, **4**, and **5**, an increased interaction with the phenylsulfinyl group appears unlikely. Although nonstrained sulfuranyl and sulfuranyloxy radicals have been observed by ESR,[11] bridged sulfur radicals are not involved to a significant extent in the reactions reported here.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 621 spectrometer. ^1H NMR spectra were measured with a Varian A-60 or Varian EM-390 spectrometer and are reported in ppm (δ) downfield from internal Me_4Si standard. Carbon-13 magnetic resonance spectra were obtained with a Varian CFT-20 and are reported in parts per million downfield from internal Me_4Si.

Gaseous products were identified by infrared spectroscopy, and product distributions were determined by gas chromatography on a 20 ft × 0.25 in., 20% dimethyl sulfolane on firebrick column at room temperature using a Carle microdetector. Solution compositions were determined by gas chromatography on a Perkin-Elmer 990 or Aerograph A-350-B using either a 15 or 12 ft × 0.25 in., 20% SE-30 on 60–80 mesh Chromosorb W column.

The 2-butenes and propene were used as received from the Matheson Co. Tri-*n*-butyltin hydride was prepared by the procedure of Kuivila and Beumel[12] or used as received from Eastman Kodak Co. The benzene and toluene used for reactions were dried and stored over molecular sieves. *m*-Chloroperbenzoic acid (MCPBA, 85%) and tri-*n*-butyltin chloride (96%) were obtained from Aldrich. Azobis(isobutyronitrile) (AIBN) was used as received from Baker Chemical Co.

***erythro*-2-Bromo-3-(phenylsulfonyl)butane,[8] 5a.** Into a 500-mL three-necked flask equipped with a 500-mL addition funnel and low-temperature thermometer was placed **3a**[8,13] (10.0 g, 0.041 mol) in 175 mL of chloroform. In the addition funnel was placed MCPBA (16.7 g, 0.082 mol) dissolved in 350 mL of chloroform. The flask and contents were cooled to −15 °C with a dry/ice–CCl_4 bath. The MCPBA solution was added dropwise over a 50-min period, keeping the temperature below 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The solution was filtered and washed first with 200 and then with 100 mL of saturated sodium bicarbonate. The aqueous layers were washed with 150 mL of chloroform. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator. The residue

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[10] H. G. Kuivila, *Acc. Chem. Res.*, 1, 299 (1968).

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solidified and was recrystallized from 10:1 ethanol–hexane to give 8.15 g (71.8%) of **5a** and again from ethanol to give 6.27 g (55.2%): mp 66.8–67.9 °C (lit.[8] mp 59–61 °C); ^{1}H NMR (CCl_4) δ 1.36 (d, 3 H), 1.82 (d, 3 H), 3.11 (qd, *J* = 3.90, 1 H), 4.65 (qd, *J* = 3.90, 1 H), 7.63 (m, 3 H), 7.79 (m, 2 HO; ^{13}C NMR ($DCCl_3$) δ 11.46, 25.72, 44.90, 65.86, 129.23, 129.35, 134.08; IR (CCl_4) 3070, 2990, 2945, 1449, 1385, 1315 (SO_2), 1250, 1219, 1150 (SO_2), 1090, 1072, 994, 700, 690 cm^{-1}.

***threo*-2-Bromo-3-(phenylsulfonyl)butane,[8] 5b.** **5b** was prepared from **3b** by the same procedure as for **5a**. Removal of the solvent gave 9.55 g (84.1%) of a viscous oil, 4.0 g of which was purified by dry-column chromatography on silica gel, eluting with 4:1 hexane–acetone. The portion with R_f 0.25–0.40 was used: ^{1}H NMR (CCl_4) δ 1.40 (d, 3 H), 1.81 (d, 3 H), 3.44 (qd, *J* = 2.55, 1 H), 4.88 (qd, *J* = 2.55, 1 H), 7.58 (m, 3 H), 7.88 (m, 2 H); ^{13}C NMR ($DCCl_3$) δ 8.05, 20.79, 44.33, 65.88, 128.61, 129.44, 134.13; IR (neat) 3065, 2995, 2940, 1720, 1583, 1446, 1383, 1307 (SO_2), 1302, 1251, 1148 (SO_2), 112, 1081, 1048, 950, 821, 760, 726, 697, 640, 583, 545 cm^{-1}.

Thermally Initiated Reactions of 5a and 5b with Tributyltin Hydride. In a typical run, the appropriate diastereomeric bromo sulfone (100 mg, 0.361 mmol) and AIBN (59.3 mg, 0.361 mmol) in benzene (2.0 mL) were placed in a Pyrex tube and flushed with a stream of nitrogen. Tributyltin hydride (105.1 mg, 0.361 mmol) in benzene (1.0 mL) was added, and the mixture was heated at 80 °C. The gaseous products were continuously swept from the reactor through a water-cooled spiral condenser into a trap at −196 °C by a stream of nitrogen. The contents of the trap were distilled under vacuum from −78 to −196 °C. The distillate was analyzed by IR spectroscopy and gas chromatography. Gas chromatographic analysis of the benzene solution showed no detectable 2-(phenylsulfonyl)butane. Heating the sulfones under these reaction conditions did not result in interconversion of the diastereomers as determined by ^{1}H NMR.

Photolytically Initiated Reaction of 5a and 5b with Tributyltin Hydride. In a typical run, the appropriate diastereomer (100 mg, 0.361 mmol) and AIBN (59.3 mg, 0.361 mmol) were placed in a 1.2 × 20 cm Pyrex tube with toluene (2.0 mL). Tri-*n*-butyltin hydride (105.1 mg, 0.361 mmol) in 1.0 mL of toluene was added. The sample was photolyzed for 120 min at −67 °C in an ethanol–dry ice bath (the reaction temperature was determined with an iron–constantan thermocouple) with a Hanovia 645A36 medium-pressure Hg lamp placed adjacent to the reaction tube. The gaseous products were continuously removed under vacuum (0.2 mm) and trapped at −196 °C. Subsequent treatment was the same as that in thermal reactions. No interconversion of the diastereomers occurred under these conditions.

2-(Phenylsulfonyl)butane.[16] The oxidation of 2-(phenylthio)butane to the sulfone was accomplished according to the above procedure given for **5a**. Removal of the solvent gave a viscous oil which was recrystallized from ethanol at −78 °C and filtered on a funnel cooled to 0 °C to give white crystals which melted to a clear, colorless liquid at room temperature. A total of 1.15 g (60.5%) was obtained which was shown to consist of one product by GLC: ^{1}H NMR (CCl_4) δ 0.95 (t, 3 H), 1.19 (d, 3 H), 1.40 (m, 1 H), 1.95 (m, 1 H), 2.86 (m, 1 H), 7.45 (m, 3 H), 7.80 (m, 2 H).

Preparation of a Mixture of 1-Bromo-2-(phenylthio)propane, 12a, and 2-Bromo-1-(phenylthio)propane, 12b. Into a 1000-mL three-necked flask fitted with a mechanical stirrer, thermometer, and funnel with a drying tube attached was placed PBr_3 (45 g). Dry pyridine (9 g) was added over a 39-min period, followed by 45 mL of benzene. The mixture was cooled to −5 °C with an ice–salt bath. A mixture of 2-(phenylthio)-1-propanol[15] (81.0 g, 0.48 mol) and pyridine (3 g) was added slowly from the funnel over a 2-h period. The reaction mixture was stirred for an additional 48 h. Benzene (400 mL) was added, the solution filtered, and the benzene removed on a rotary evaporator. The residue was distilled to give 59.5 g (54.0%) of a clear liquid, bp 110–112 °C (0.9–1.2 mm). A ^{1}H NMR analysis revealed that the clear liquid contained a 75:25 mixture of **12b** and **12a**. A similar mixture has been reported in the reaction of 2-[(methylsulfonyl)oxy]-1-(phenylthio)propane with lithium bromide;[16] bp 76 °C (0.01 mm). Spectra of product obtained in this work were identical with that reported: ^{1}H NMR (CCl_4) δ 1.43 (d, 0.8 H), 1.77 (d, 2.2 H), 3.33 (m, 2.2 H), 4.05 (m, 0.8 H), 7.21 (m, 5 H).

Competitive Reactions of 5a and 5b with 12a and 12b. The appropriate diastereomeric bromo sulfone (100 mg, 0.361 mmol), the 3:1 mixture of **12b** and **12a** (83.4 mg, 0.361 mmol), AIBN (6.0 mg, 0.0361 mmol), and tributyltin hydride (10.5 mg, 0.361 mmol) were treated as previously described for the thermally initiated reactions. The relative reactivity was determined by comparing the amounts of 2-butenes and propene produced as determined by gas chromatography.

2-Bromo-1-(phenylsulfonyl)propane, 11. Into a flask were placed **12a** and **12b** (10.0 g, 0.043 mmol) and 80 mL of glacial acetic acid. To this was added H_2O_2 (9.8 g, 0.086 mmol, 30%), and the contents were heated over a water bath at 85–90 °C for 9 h. The reaction mixture was poured into 600 mL of ice–water, and the solid residue was filtered. The solid was recrystallized from ethanol to give 1.41 g (12.4%) of **11**: mp 42.3–43.3 °C; ^{1}H NMR (CCl_4) δ 1.91 (d, 3 H), 3.60 (m, 2 H), 4.48 (m, 1 H), 7.62 (m, 3 H), 7.97 (m, 2 H).

Reaction of 11 with Tributyltin Hydride in the Presence of (*Z*)-2-Butene at 80 °C. A stream of nitrogen was swept through a vessel containing 0.21 mmol of (*Z*)-2-butene at 9 °C and into solution of **11** (94.9 mg, 0.361 mmol), AIBN (59.3 mg, 0.361 mmol), and tributyltin hydride (524.3 mg, 1.81 mmol) in 3 mL of benzene at 80 °C. The gases were swept from the reactor and analyzed as before. Under these conditions, 54% of the (*Z*)-2-butene was swept through the reactor. The recovered (*Z*)-2-butene was 2% isomerized to the *E* isomer. A 78% yield of propene was also produced.

Reaction of 11 with Tributyltin Hydride in the Presence of (*Z*)-2-Butene at −67 °C. To (*Z*)-2-butene (0.105 mmol) were added **11** (94.9 mg, 0.361 mmol), AIBN (59.3 mg, 0.361 mmol), and tributyltin hydride (105.1 mg, 0.361 mmol) in 3.0 mL of toluene. This mixture was photolyzed at −67 °C under vacuum. After 10 min of photolysis the system was opened to a −196 °C trap under a pressure of 0.25 mm. The photolysis was continued for 2 h. Analysis of the volatile products by GC showed 3% isomerization of the (*Z*)-2-butene and an 11.7% yield of propene.

Registry No. 1a, 58620-22-7; **2a**, 72347-33-2; **2b**, 72347-34-3; **3a**, 37434-63-2; **3b**, 37434-62-1; **4a**, 67456-47-7; **4b**, 67504-54-5; **4c**, 67504-55-6; **4d**, 67504-56-7; **5a**, 37434-65-4; **5b**, 37434-64-3; **9a**, 72347-35-4; **11**, 72347-36-5; **12a**, 38307-66-3; **12b**, 13012-62-9; tributyltin hydride, 688-73-3; 2-(phenylsulfonyl)butane, 34009-06-8; 2-(phenylthio)butane, 14905-79-4; 2-(phenylthio)-1-propanol, 32300-49-5; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1.

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[15] M. S. Khan and L. N. Owen, *J. Chem. Soc. C*, 1448 (1971).

[16] M. S. Khan and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 2067 (1972).