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The Stereochemistry of Free Radical Eliminations on β-Phenylthio Radicals

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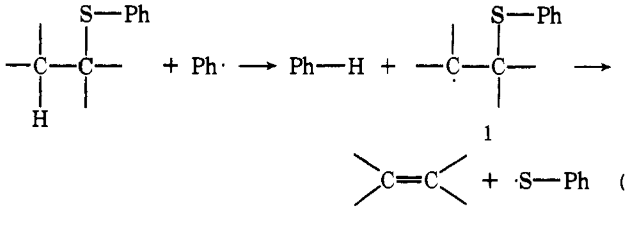
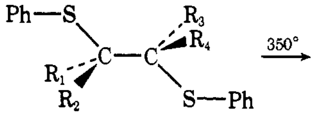
Abstract: Tributyltin radicals have been allowed to react with *erythro-* and *threo*-2-bromo-3-phenylthiobutane (**4a** and **4b**) to generate β-phenylthio radicals (**1**). The intermediate **1** eliminates thiophenoxy radical to form the 2-butenes nonstereospecifically. The lack of stereospecificity coupled with the fact that no 2-phenylthiobutane, the normal reduction product, is formed implies that the barrier to rotation in **1** is <7.2 kcal/mol and that stabilization of the radical by sulfur bridging is unimportant. The relative rates of reaction of **4a** and **4b**, as well as those of *cis-* and *trans*-1-bromo-2-phenylthiocyclohexane (**7a** and **7b**), with tributyltin radicals have been measured. The results of these experiments (k_{4a}/k_{4b} = 1.12 ± 0.13 and k_{7b}/k_{7a} = 1.57 ± 0.28) indicate that anchimeric assistance of bromine abstraction by sulfur is unimportant.

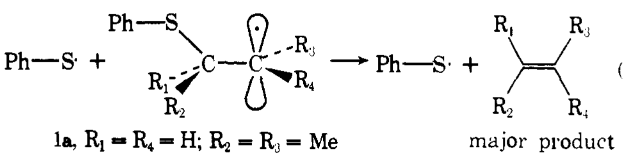
The elimination of a thiophenoxy radical from a β-phenylthio radical, **1**, is well documented in the literature. For example, Kampmeier and coworkers have observed that reaction of phenylthioalkanes with phenyl radicals generates **1**, which subsequently eliminates thiophenoxy radical to form an alkene (eq 1).[1] A similar free radical elimination has been observed when 1,2-bis(phenylthio)ethanes (**2**) are pyrolyzed.[2,3] We have shown that elimination of phenyl disulfide from **2a** and **2b** proceeds with a predominance of anti stereochemistry (eq 2).[3]



(1)



2a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
b, $R_1 = R_3 = H$; $R_2 = R_4 = Me$

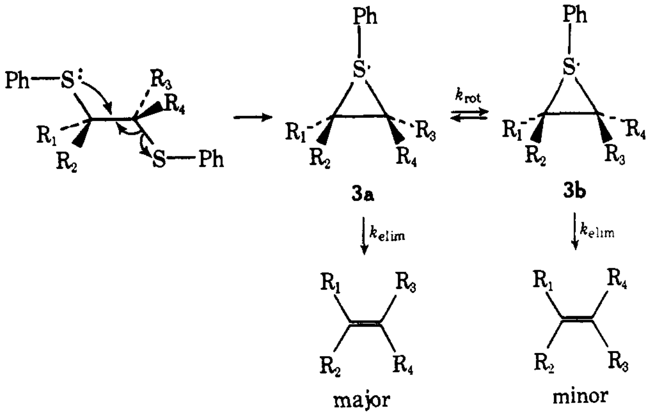


(2)

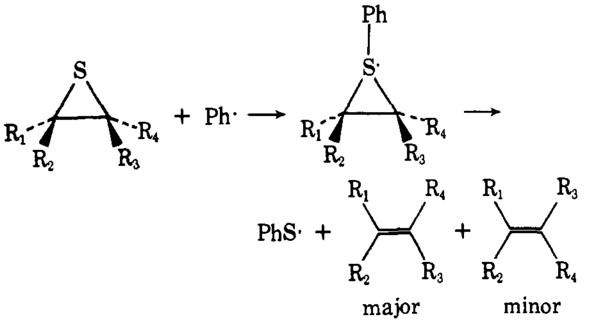
1a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
b, $R_1 = R_3 = H$; $R_2 = R_4 = Me$

major product

The stereochemistry observed in the pyrolysis of **2** indicates that the rate of elimination of the intermediate β-phenylthio radical is more rapid than rotation about the C-C bond. This restricted rotation can be rationalized by proposing that homolysis of the C-S bond is anchimerically assisted by the second sulfur and leads to the sulfur bridged structures **3a** and **3b** rather than to **1a** and **1b**. If sulfur bridging restricts rotation in **3** and causes k_{elim} to be greater than k_{rot}, the observed stereochemistry will result. It has been established that sulfur can assist in the homolysis of aromatic peresters.[4]



We have reported the reaction of phenyl radicals with episulfides[5,6] (eq 3) which should initially generate a species having the geometry of a bridged radical. This reaction results in stereoselective alkene formation with elimination of a thiophenoxy radical. The fact that this reaction is only stereoselective rather than completely stereospecific indicates that the bridged radical either permits some rotation or opens to a species in which rotation is no longer restricted.



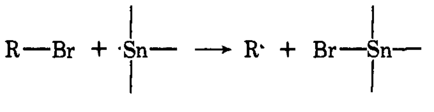
(3)

These studies do not allow evaluation of the importance of bridging in the ground state of the β-phenylthio radical. The homolysis of a C-S bond in **2** is an endothermic reaction in which anchimeric assistance is likely. Hence, the bridging and consequent restricted rotation may simply be a result of the requirement for this assistance and may not play a significant role in stabilizing the ground state of the radical. A more rigorous test for bridging in the ground state of β-phenylthio radicals is the formation of these radicals by an exothermic reaction in which anchimeric assistance is unnecessary. In such an experiment, a $k_{\text{rot}}/k_{\text{elim}} < 1$ would imply that the bridged species is a ground state. Conversely, observation of a $k_{\text{rot}}/k_{\text{elim}} > 1$ would indicate that bridging is unimportant in the ground state of the β-phenylthio radical.

Table I. Stereochemistry of 2-Butene Formation in the Reaction 4a and 4b with Tributyltin Radicals

Diastereomer	$[Bu_3SnH]/[4]$[a]	Conditions[b]	2-Butene yield, %	[*trans*]/[*cis*]
4b	1	1 h, 80°	28	2.13
4b	1	1 h, 80°		2.47
4a	1	1 h, 80°	50.5	2.67
4a	1	1 h, 80°	59.8	2.31
4b	1	3 h, 80°	41.6	2.44
4b	1	4 h, 80°	44.6	1.94
4b	5	1 h, 80°	75.5	2.22
4b	1	*hν*, 2 h, −67°	17.2	5.19
4a	1	*hν*, 2 h, −67°	53.6	5.58
4b	1	*hν*, 2 h, −67°		5.80
4b	2[c]	*hν*, 2 h, −67°[d]	80.2	4.78

[a] [4] = 0.136 M unless otherwise indicated. [b] AIBN used as initiator unless otherwise indicated. [c] [4] = 1.89 M. [d] No AIBN added.



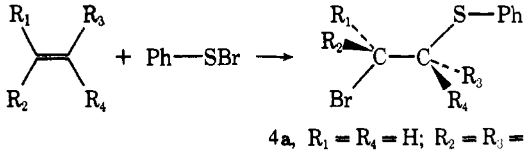
$$\text{R—Br} + \cdot\overset{|}{\underset{|}{\text{Sn}}}\text{—} \longrightarrow \text{R}\cdot + \text{Br—}\overset{|}{\underset{|}{\text{Sn}}}\text{—} \qquad (4)$$

$$\Delta H = -15\ \text{kcal/mol}$$

The reaction of alkyl bromides with trialkyltin radicals is a well-established method of generating free radicals (eq 4).[7] Moreover, a consideration of the strength of a secondary C-Br bond (68 kcal)[8] and that of the Sn-Br bond (83 kcal)[9] indicates that the reaction should be exothermic by ~15 kcal. Thus, reaction of β-phenylthio alkyl bromides with trialkyltin radicals should provide an exothermic pathway to β-phenylthio radicals. It is expected that this exothermicity may lower the activation energy for radical formation to such an extent that anchimeric assistance is not necessary. In order to assess the magnitude of sulfur bridging in radicals generated by this method, we have allowed the diastereomeric 2-bromo-3-phenylthiobutanes to react with tributyltin radicals and examined the stereochemistry of the elimination of thiophenoxy radicals.

Results

Reaction of *erythro*- and *threo*-2-Bromo-3-phenylthiobutane with Tributyltin Radicals. *erythro*- and *threo*-2-bromo-3-phenylthiobutane (**4a** and **4b**) were synthesized by the addition of phenylsulfenyl bromide to (*E*)- and (*Z*)-2-butene, respectively. This reaction has been shown to yield the indicated diastereomer via an anti addition.[10]

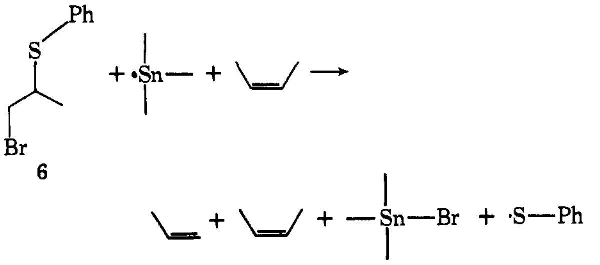


4a, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
b, $R_1 = R_3 = H$; $R_2 = R_4 = Me$

Each diastereomer was allowed to react with tributyltin radicals, generated from AIBN and tributyltin hydride, in benzene at 80°. The resulting 2-butenes were swept from the reaction vessel by a stream of nitrogen, trapped at −196°, and analyzed by gas chromatography and infrared spectroscopy. The results given in Table I show that the butenes are formed nonstereospecifically. Analysis of the reaction mixture by gas chromatography showed that no 2-phenylthiobutane (**5**) was produced.

In order to assess the effect of temperature on the stereochemistry of this free radical elimination, tributyltin radicals were generated photolytically and allowed to react with **4a** and **4b** at −67° in toluene. The 2-butenes produced in this reaction were pumped from the reactor at reduced pressure, trapped at −196°, and analyzed as above. Again the elimination was nonstereospecific as shown in Table I.

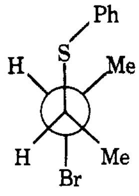
In all cases, attempts were made to carry out appropriate control experiments. In this connection, we observe that **4a** and **4b** do not interconvert under the reaction conditions. The possibility of isomerization of the butenes before they could be removed from the reaction vessel was excluded by carrying out a reaction of tributyltin radicals with 1-bromo-2-phenylthiopropane (**6**) in the presence of (*Z*)-2-butene at −67°. This reaction produced propene, while the (*Z*)-2-butene was recovered without detectable isomerization.



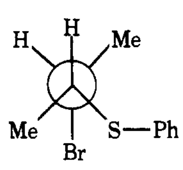
(5)

Another control experiment involved the slow addition of (*Z*)-2-butene to a reacting mixture of **6** and tributyltin radicals at 80°. When this reaction was carried out with equimolar amounts of tributyltin hydride and **6**, the recovered (*Z*)-2-butene was 30% isomerized. This isomerization can be attributed to reversible addition of thiophenoxy radicals to the 2-butene. However, addition of a fivefold excess of tributyltin hydride to trap the thiophenoxy radicals resulted in only 5% isomerization of the (*Z*)-2-butene. Since reaction of **4b** in the presence of a fivefold excess of tributyltin hydride produces essentially the same ratio of *E*:*Z*-2-butene as an equimolar quantity of tributyltin hydride (Table I), the 2-butenes must be formed nonstereospecifically.

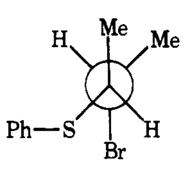
These results demonstrate that the rotation about the C–C bond in the intermediate radical is more rapid than elimination. Of the three conformers of **4b**, conformer A should predominate with smaller amounts of B and C



A



B



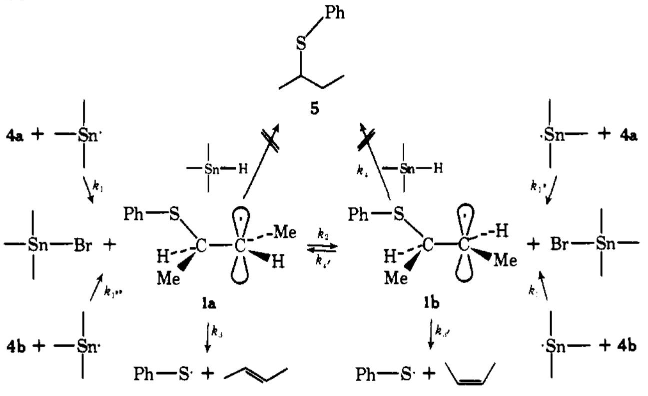
C

present. If there were a substantial barrier to rotation in the intermediate radical, conformer A would produce (*Z*)-2-butene while (*E*)-2-butene is expected from conformers B and C. Hence, a barrier to rotation would result in a preponderance of (*Z*)-2-butene from **4b**. A similar argument leads to the conclusion that a barrier to rotation in the intermediate radical would favor the production of (*E*)-2-butene from **4a**.

A calculation of conformer populations[11] using the coupling constants of the vicinal hydrogens on carbons 2 and 3[10b] of **4a** (J = 6.35 Hz) and of **4b** (J = 3.15 Hz) indicates that the anti conformer constitutes approximately 60% of the mixture in each case. If the rate of elimination were greater than the rate of rotation, the observed results could only be rationalized if the anti conformer of **4b** reacts *slower* than the gauche conformers by a factor of 3.7. At the same time, the anti conformer of **4a** would have to react *faster* than the gauche conformers by a factor of 1.6. This situation would be rather unlikely. Furthermore, experiments with *cis*- and *trans*-1-bromo-2-phenylthiocyclohexane (vide infra) indicate a preferential reaction of the anti conformer.

The reactions which take place are outlined in Scheme I. The two conformers of the 3-phenylthio-2-butyl radical, **1a** and **1b**, are produced by bromine abstraction. Conformer **1a** predominates initially when **4a** is reacted, while **1b** is the major initial conformer of the radical when bromine is abstracted from **4b**. The fact that (*E*)-2-butene predominates

Scheme I



in each case indicates that the rate of rotation in **1a** and **1b** is more rapid than the rate of elimination ($k_2 > k_3$ and $k_2' > k_3'$). The increase in the ratio of *E*:*Z* 2-butene from both **4a** and **4b** at −67° as compared to 80° is probably the result of a lower relative energy for the transition leading to (*E*)-2-butene at the lower temperature. If it is assumed that $k_1'[\mathbf{4a}] = k_1''[\mathbf{4b}]$ (Scheme I), steady state expressions for **1a** and **1b** yield eq 6 and 7. In these expressions, *M* is the

$$(k_2/k_3)M + M = (k_2'/k_3') \quad (6)$$

$$(k_2/k_3)N - 1 = (k_2'/k_3') \quad (7)$$

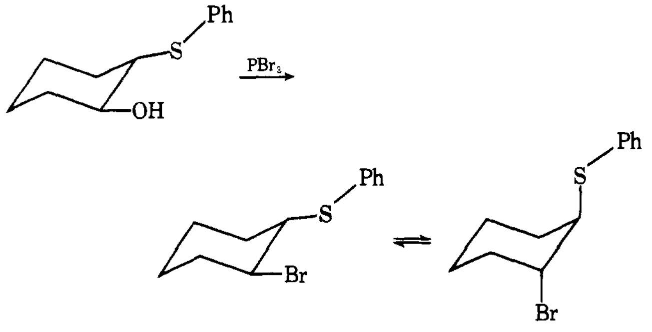
ratio of *E*:*Z* 2-butene from **4b**, and *N* is the *E*:*Z* ratio from **4a**. If the 2-butenes are formed stereoselectively, eq 6 and 7 may be solved for k_2/k_3 and k_2'/k_3'.[3] However, in the present case, no stereoselectively is observed and only lower limits for k_2/k_3 and k_2'/k_3' can be calculated. If it is assumed that at 80° $M < N$ by no more than the experimental error of the measurements (here taken as twice the standard deviation), values of $k_2/k_3 \geq 6.4$ and $k_2'/k_3' \geq 15.3$ are calculated.

The fact that 2-phenylthiobutane (**5**), the normal reduction product, is not detected in this reaction allows an estimate of the upper limit for the barrier to rotation in **1b**. The rate constant for abstraction of hydrogen from tributyltin hydride by a secondary radical has been measured.[12] If we assume that this value (1.2×10^6 M^{-1} sec^{-1} at 25°) is a reasonable estimate of k_4 in Scheme I at 80°, we can calculate that $k_3' > 8.2 \times 10^5$ sec^{-1}. Since we actually could have detected **5** at levels corresponding to 5% of the butene yields, $k_3' > 1.6 \times 10^7$ sec^{-1}. This approach yields a $k_2' \geq 2.5 \times 10^8$ sec^{-1} and value of 7.2 kcal/mol for the upper limit of the free energy barrier to rotation in **1b**.

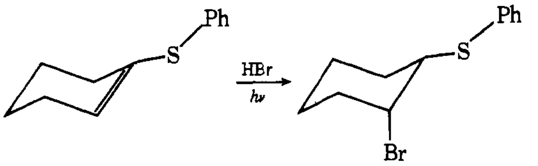
Relative Reactivity of Diastereomeric 1-Bromo-2-phenylthio Compounds. In order to assess the importance of anchimerically assisted bromine abstraction in the present study, we have measured the relative rates of reaction of **4a** and **4b** with tributyltin radicals. Assistance by sulfur should produce initially **3a** from **4a** and **3b** from **4b**. If this is the case, abstraction from **4a** may be more rapid than from **4b** as **3a** has trans methyl groups while the methyls in **3b** are cis.

The relative reactivities of **4a** and **4b** toward tributyltin radicals were measured by allowing each diastereomer to react with tributyltin hydride in the presence of **6** (eq 5). The ratio of butenes to propene from each diastereomer under these conditions gives the relative reactivities. The experiment yields $k_{4a}/k_{4b} = 1.12 \pm 0.13$, indicating essentially no difference in the relative reactivity of the diastereomers. However, since the energies of **3a** and **3b** may be quite similar, this experiment does not provide a conclusive test of the importance of anti abstraction.

A better assessment of the necessity for anti abstraction may be obtained by comparing the relative rates of *cis*- and *trans*-1-bromo-2-phenylthiocyclohexane (**7a** and **7b**) with tributyltin radicals. Since *cis*-1-bromo-2-phenylthiocyclohexane (**7a**) cannot assume an anti arrangement of bromine and sulfur, its rate of reaction with tributyltin radicals as compared to that of *trans*-1-bromo-2-phenylthiocyclohexane (**7b**) should be a measure of the importance of anti abstraction. The trans isomer **7b** was most conveniently synthesized by the addition of phosphorus tribromide to 2-phenylthiocyclohexanol. The cis compound **7a** was prepared by the photolytic addition of hydrogen bromide to 1-phenylthiocyclohexene.



7b



7a

The reactivities of **7a** and **7b** toward tributyltin radicals were measured relative to that of bromocyclohexane. These experiments show that $k_{7b}/k_{7a} = 1.57 \pm 0.28$. An anti abstraction appears to be only slightly favored in this system. It is interesting to note that the trans isomer reacts approximately four times as fast as bromocyclohexane while the cis reacts 2.6 times as fast.

Discussion

We interpret the results of the present study to indicate that in the ground state of the β-phenylthio radical there is a rather low barrier to rotation and that bridging is unimportant. Further, there appears to be little requirement for the sulfur to assist in the abstraction of bromine by tributyltin radicals.

It is interesting to compare the elimination of thiophenoxy radical with that of a bromine atom from a β-bromo radical (**8**). A study of the reaction of *meso*- and *dl*-2,3-dibromobutane with tributyltin radicals shows that bromine elimination from **8** is highly stereoselective (eq 8).[13] Similar stereochemical results are obtained in reductive eliminations on the diastereomeric 2,3-dibromobutanes by chromium(II), a reaction which has been shown to proceed via a free radical mechanism.[14] The stereospecificity of these reactions has been taken as evidence for bromine bridging in **8**. Anchimeric assistance by bromine of bromine abstraction appears to be important as *trans*-1,2-dibromocyclohexane reacts with chromium(II) ~150 times as fast as *cis*-1,2-dibromocyclohexane at 20°.[15] These results, which are in striking contrast to those reported here, serve to point up the differences between a neighboring bromine and a neighboring sulfur in stabilizing a radical center.

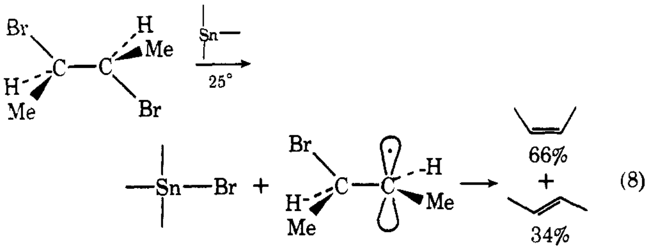


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Table II. Values of $k_{\text{rot}}/k_{\text{elim}}$ for β-Phenylthio Radical Produced in Various Reactions

	$k_{\text{rot}}/k_{\text{elim}}$	
Radical forming reaction	Cis radical	Trans radical
2,3-Bis(phenylthio)butanes at 360°[3]	0.65	0.39
2,3-Bis(phenylthio)butanes + $h\nu$[3]	6.8	3.2
2-Butene episulfides + phenyl radical[5]	0.46	0.32
2-Bromo-3-phenylthiobutanes + tributyltin radical	>15.3	>6.4

Table II summarizes values of $k_{\text{rot}}/k_{\text{elim}}$, calculated using eq 6 and 7, from this work and previous studies. A striking feature of this table is the dependence of $k_{\text{rot}}/k_{\text{elim}}$ on the method by which the β-phenylthio radical is produced. These data are interpreted to indicate that the nature of the radical is dependent upon the energetics of its formation. When there is sufficient exothermicity for the radical to form without anchimeric assistance, as in the reaction of **4** with tributyltin radicals, the nonbridged ground state radical results. The photolytic production of **1** from an excited electronic state of **2** (Table II) is another example of exothermic radical formation which results in a nonbridged structure and nonstereospecific elimination.

However, the endothermic formation of a β-phenylthio radical by thermolysis of a carbon-sulfur bond in **2** requires assistance by the second sulfur and results in the kinetically favored bridged radical **3**. Since it has been shown that a bridged intermediate is involved in the addition of thiyl radicals to alkenes,[16] the principle of microscopic reversibility requires that such an intermediate lie on the reaction coordinate for elimination. The reaction of a phenyl radical with an episulfide (eq 3) results in a species which initially has a bridged geometry and $k_{\text{rot}}/k_{\text{elim}} < 1$ (Table II). Alternatively, the stereoselectivity of the episulfide reaction may result from opening to a β-phenylthio radical which initially is in the proper conformation for elimination and therefore stereoselective.

These studies lead to the conclusion that bridging can act to stabilize the transition state leading to β-phenylthio radicals but does not provide appreciable stabilization in the ground state of the radical. ESR studies[17,18] of β-thiyl radicals have shown that the ground state is not a symmetrically bridged species. Estimates of rotational barriers from the temperature dependence of the ESR spectra[17,19] indicate that these barriers are all less than the 7 kcal calculated here as the upper limit to the rotational barrier in **1b**. We are currently attempting to investigate the energy surfaces involved in these reactions using semiempirical molecular orbital calculations.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 621; NMR spectra were measured with a Varian A-60 and are reported in ppm (δ) downfield from 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% dimethylsulfolane on firebrick column at room temperature using a Carle microdetector. Solution compositions were determined by gas chromatography on a Perkin-Elmer 990 or an Aerograph A-350-B using either a 15 ft or 12 ft × 0.25 in. 20% SE-30 on 60-80 Chromosorb W column.

The 2-butenes, propene, and hydrogen bromide were used as received from the Matheson Co. Cyclohexene, from Eastman Kodak Co., was distilled from NaOH before use. Tri-*n*-butyltin hydride was prepared by the procedure of Kuivila and Beumel[20] or used as received from Eastman Kodak Co. Bromocyclohexane (Aldrich, 95%) was distilled before use.

***threo*-2-Bromo-3-phenylthiobutane (4a).** The general procedure of Trost and Ziman[10a] was used for the preparation of both **4a** and **4b.** Diphenyl disulfide (23.4 g, 0.107 mol) was dissolved in dichloromethane (350 ml) and placed in a 1-l. three-necked flask equipped with an addition funnel, dry ice-acetone condenser, and thermometer. The flask was wrapped in aluminum foil, placed in a CCl_4-dry ice bath, and cooled to −20°. Bromine (16 g, 0.1 mol) in dichloromethane (100 ml) was added to the stirred solution over an 80-min period. The temperature was allowed to rise at −12°, and the mixture was stirred for 60 min. An excess of (*Z*)-2-butene (11.9 g, 0.212 mol) was bubbled through the red solution while maintaining the temperature below −12°. The clear reaction mixture was then stirred for 120 min at −15°. The dichloromethane was removed on a rotary evaporator. Distillation of the residue gave two products: 2,3-dibromobutane (2.5 g, 5.7%, confirmed by its NMR spectrum), bp 48-52° (0.35-0.50 mm), and **4a,** 22.7 g (46.4%), bp 102-108 (0.6 mm); NMR (CCl_4) δ 1.42 (d, 3 H), 1.71 (d, 3 H), 3.68 (qd, 1 H), 4.27, (qd, 1 H), 7.31 (m, 5 H). The product was sealed under N_2 and stored at 5°.

***erythro*-2-Bromo-3-phenylthiobutane (4b).** Diphenyl disulfide (30.0 g, 0.138 mol) was dissolved in dichloromethane (400 ml) and placed in a 1-l. three-necked flask equipped as in the preparation of **4a.** After cooling to −20°, bromine (21.6 g, 0.135 ml) in dichloromethane (110 ml) was added over a period of 65 min. After stirring for 90 min at −20°, (*E*)-2-butene (25.1 g, 0.448 mol) was bubbled through the mixture and the solution was stirred for an additional 180 min. After removal of the dichloromethane, the residue was distilled and the fraction with bp 100-118° (0.08-0.15 mm) was collected. Redistillation gave 12.3 g (18.3%) of **4b:** bp 86.6-90.0° (0.10-0.15 mm); NMR (CCl_4) δ 1.46 (d, 3 H), 1.71 (d, 3 H), 3.19 (dq, 1 H), 4.10 (dq, 1 H), 7.38 (bm, 5 H). The product was sealed under N_2 and stored at 5°.

Thermally Initiated Reactions of 4a and 4b with Tributyltin Hydride. In a typical run, **4a** or **4b** (100 mg, 0.408 mmol) and AIBN (67 mg, 0.408 mmol) in benzene (2.0 ml) were placed in a Pyrex tube and flushed with a stream of nitrogen. Tributyltin hydride (119 mg, 0.408 mmol) in benzene (1.0 ml) was added and the mixture was heated at 80° for 60 min. The gaseous products were continuously swept from the reactor through a water-cooled spiral condenser into a trap at −196° by a stream of nitrogen. The contents were distilled under vacuum from −78 to −196°. The distillate was analyzed by ir spectroscopy and gas chromatography. Product distributions are given in Table I. Gas chromatographic analysis of the benzene solution showed no detectable 2-phenylthiobutane. An NMR analysis of a solution of **4a** and **4b** in benzene showed that the diastereomers did not interconvert at 80°.

Photolytically Initiated Reaction of 4a and 4b with Tributyltin Hydride. In a typical run, **4a** or **4b** (100 mg, 0.408 mmol) and AIBN (0.408 mmol; the reaction was found to proceed equally well without AIBN) were placed in a 1.2 × 20 cm tube with toluene (2.0 ml). Tri-*n*-butyltin hydride (0.408 mmol) in 1.0 ml of toluene was added. The sample was photolyzed for 120 min at −67° in an ethanol-dry ice bath (the reaction temperature was determined with an iron-constantan thermocouple) with a Hanovia 654A36 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°. Subsequent treatment was the same as in thermal reactions. Results are given in Table I.

Reaction of 6 with Tributyltin Hydride in the Presence of (*Z*)-2-Butene at −67°. To a solution of **5** (0.408 mmol), tributyltin hydride (0.408 mmol), and AIBN (0.408 mmol) in toluene (3.0 ml), on a vacuum line, was added (*Z*)-2-butene (0.092 mmol). This mixture was photolyzed at −67° under vacuum. After 5 min of photolysis, the system was opened to a −196° trap under a pressure of 0.2 mm. The photolysis was continued for 2 hr under these conditions. Analysis of volatile products by gas chromatography showed no isomerism of the (*Z*)-2-butene and an 83% yield of propene.

Reaction of 6 with Tributyltin Hydride in the Presence of (*Z*)-2-Butene at 80°. A stream of nitrogen was swept through a vessel containing 0.22 mmol of (*Z*)-2-butene at 0° and into a solution of **6** (0.408 mmol), AIBN (0.408 mmol), and tributyltin hydride (2.04 mmol) in 3 ml of benzene at 80°. The gases were swept from the reactor and analyzed as before. Under these conditions, 37% of the (*Z*)-2-butene was swept through the reactor. The recovered (*Z*)-2-butene was 5% isomerized to the *E* isomer.

***trans*-2-Bromocyclohexanol (9).**[21] *N*-Bromosuccinimide (Fisher reagent grade, 89.0 g, 0.5 mol) and water (400 ml) were placed in a 1-l. three-necked flask equipped with a thermometer, condenser, and addition funnel. The solution was stirred magnetically and cooled in an ice-water bath. Cyclohexene (65.2 g, 0.794 mol) was added dropwise, and the reaction mixture was stirred for 12 h at room temperature. The solution was then extracted with ether and dried over $MgSO_4$. The ether was removed on a rotary evaporator and the residue distilled to give 70.6 g (79%) of **9**: bp 47.6-49.8° (0.7 mm) [lit.[22] bp 85.5-86.5° (10 mm)].

***trans*-2-Phenylthiocyclohexanol (10).** Metallic sodium (6.43 g, 0.28 g-atom) was dissolved in 280 ml of absolute ethyl alcohol contained in a 1-l. three-necked flask equipped with a thermometer, addition funnel, and condenser. After the solution had returned to room temperature, thiophenol (31 g 0.28 mol) was added and the solution again allowed to return to room temperature. To the stirred solution, **9** (50 g, 0.28 mol) was added over a period of 30 min. After stirring for 12 h, the solution was heated to 65° for about 5 min at which time sodium bromide began to precipitate. The reaction mixture was then stirred at room temperature for 84 h. The NaBr was removed by filtration and the remaining solution refluxed for 30 min. After cooling, benzene (100 ml) and 4% HCl (50 ml) were added. The organic layer was separated and the aqueous layer washed with benzene (50 ml). The combined benzene layers were washed with water (30 ml) and dried over $MgSO_4$. The benzene was removed and the residue distilled to give 36.5 g (62.3%) of **10:** bp 120-125° (0.7-0.9 mm) [lit.[23] 130-132° (1 mm)]; NMR (CCl_4) δ 1.67 (complex m, 8 H), 3.05 (complex m, 3 H), 7.48 (m, 5 H).

***trans*-1-Bromo-2-phenylthiocyclohexane (7b).**[24] Phosphorus tribromide (6.0 g, 22 mmol) was placed in a 100-ml, three-necked flask equipped with a thermometer, addition funnel, and $CaSO_4$ drying tube. After the flask was cooled in an ice-salt bath, pentane (2 ml) was added, the mixture stirred, and a solution of **10** (4.4 g, 21 mmol) in pentane (0.5 ml) added over a 30-min period. The bath was allowed to warm to room temperature, and the reaction mixture was stirred for 67 h. Water was added and the mixture extracted with ether. The extracts were dried over $MgSO_4$ and the solvents removed on a rotary evaporator. Elution of 2.32 g of residue on silica gel with hexane led to decomposition. The remaining reaction mixture was recrystallized from absolute ethanol at −78° to yield a substance that melted to a pale yellow liquid below room temperature: NMR (CCl_4) δ 1.67 (complex m, 6 H), 2.30 (complex m, 2 H), 3.56 (qd 2 H), 4.34 (qd 2 H), 7.34 (complex m, 5 H).

1-Phenylthiocyclohexane (11).[25] Thiophenol (110 g, 1.0 mol), cyclohexanone (117.8 g, 1.2 mol), *p*-toluenesulfonic acid (3.0 g), and toluene (1 l.) were placed in a 2-l. flask. The flask was equipped with an air condenser, water trap, and water-cooled condenser. The mixture was refluxed for 5 hr (the time required for a stoichiometric amount of water to be collected). The toluene was removed on a rotary evaporator. Benzene was added to the remaining oil, and the solution was washed successively with saturated sodium carbonate and water and dried over $MgSO_4$. The benzene was removed on a rotary evaporator and the residue distilled to give **11:** 82.8 g (43%), bp 78.7-80.0° (0.05 mm) [lit.[25] bp 107-115° (0.1 mm)]; NMR (CCl_4), δ 1.68 (m, 4 H), 2.16 (m, 4 H), 6.16 (m, 1 H), 7.39 (m, 5 H).

***cis*-1-Bromo-2-phenylthiocyclohexane (7a).** In a typical reaction, a solution of **11** (2.5 g, 13.1 mmol) in pentane (60 ml) was placed in a 2.3 × 17.0 cm Vycor tube. Hydrogen bromide (4 g) was passed in and the solution irradiated for 150 min with a Hanovia 654A36 medium-pressure Hg lamp placed 7.5 cm from the reaction tube. The reaction mixture was washed with saturated $NaHCO_3$ and water. The pentane layer was dried over $MgSO_4$, the solution filtered, and the solvent removed on a rotary evaporator. The product of three separate reactions was combined to give 9.5 g of crude material. This material (5.6 g) was chromatographed on 175 g of silica gel eluted with hexane. The solvent was removed from the appropriate fractions to give a pale yellow liquid which crystallized on standing. Recrystallization from pentane gave a white solid which was dried at room temperature under vacuum: mp 43.2-44.6°; NMR (CCl_4) δ 1.78 (complex m, 9 H), 3.12 (m, 1 H), 4.48 (m, 1 H), 7.36 (complex m, 5 H); ir (CCl_4) 3045, 2922, 2845, 1465, 1436, 1430, 1288, 1180, 1080, 1055, 980, 890, 682, and 648 cm^{-1}; mass spectrum *m/e* (rel intensity, %) 65 (16), 66 (6), 67 (7), 69 (5), 77 (9), 79 (13), 80 (8), 81 (100), 82 (9), 109 (28), 110 (68), 111 (9), 123 (11), 149 (7), 188 (16), 190 (17), 191 (12), 270 (32), 271 (5), 272 (32), and 273 (5).

Competitive Reactions of 4a and 4b with 1-Bromo-2-phenylthiopropane (6). The appropriate isomer (**4a** or **4b**, 0.408 mmol), **6** (0.408 mmol), AIBN (0.0408 mmol), and tributyltin hydride (0.0409 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 by gas chromatography.

Competitive Reactions of 7a and 7b with Bromocyclohexane. Each reaction was run in a sealed vial containing **7a** or **7b** (0.369 mmol), bromocyclohexane (0.369 mmol), AIBN (0.0369 mmol), and tri-*n*-butyltin hydride (0.0369 mmol) in 1.0 ml of toluene at 80° for 2 hr. The reaction mixture was cooled, placed in a flask, and vacuum transferred at room temperature to a trap at −196°. The distillate was subjected to GLC analysis to determine product composition and distribution.

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Conformational Analysis. XXXI. Conformational Equilibria of 1,3-Dioxanes with Polar Substituents at C-5[1]

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Abstract: The positions of equilibrium, established by acid catalysis, between epimeric 2-isopropyl-5-X-1,3-dioxanes in which X is CH_2OCH_3, $OCOCH_3$, $COCH_3$, $COOCH_3$, COO^-, SCH_3, $S(CH_3)_2^+$, $SOCH_3$, SO_2CH_3, NO_2, NH_3^+, $NH(CH_3)_2^+$, $N(CH_3)_3^+$ are reported and compared with previously published data for X = Me,[2] F, Cl, Br, CN,[3] CH_3O, C_2H_5O,[4] CH_2OH, and OH.[5] In a number of these cases the axial (cis) isomers are favored at equilibrium, even though either steric or dipolar considerations would have led to the opposite prediction. Explanations based on "internal solvation", orbital interaction, and charge attractions are considered; it appears that charge attraction offers the only consistent interpretation for the axial preference of the sulfinyl, sulfonyl, sulfonium, and ammonium and probably also the nitro, CH_2OR, and acetate groups. The mechanism of reaction of methyl mercaptide with diethyl chloromalonate is discussed.

It is one of the basic tenets of conformational analysis[6,7] that axial substituents in six-membered rings are less stable than equatorial ones. We are aware of only one or two exceptions in a monosubstituted cyclohexane: the axial conformation is preferred in cyclohexylmercuric acetate and chloride.[8] Exceptions have long been known, however, in systems where dipolar interactions are dominating; for example, in *trans*-1,2-dibromocyclohexane the diaxial isomer predominates, at least in nonpolar solvents,[9] and in glycosides the axial conformation of the aglycone is preferred because of the operation of the "anomeric effect".[10] We wish to report here several cases of axial predominance of substituents at C-5 in 1,3-dioxanes (cf. Scheme I), even though on both steric and dipolar grounds equatorial preference might have been anticipated.[11,12]

For 2-isopropyl-5-methyl-1,3-dioxane itself (cf. Scheme I, X = Me), the equatorial (trans) isomer is preferred,[2,5] though only by 0.9 kcal/mol (the value is virtually independent of solvent[5]). The difference between this value and the 1.7 kcal/mol preference for the equatorial conformation in methylcyclohexane[13] was explained by the small "effective size" of the unshared pairs on oxygen compared to the syn-axial hydrogen atoms in cyclohexane; however, there is presumably a residual nonbonded repulsion between the carbon and hydrogens of the axial methyl group and the ring oxygen atoms.