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Absolute Rate Expressions for Intramolecular Displacement Reactions of Primary Alkyl Radicals at Sulfur[1]

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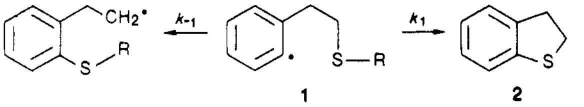
Arrhenius parameters are presented for the intramolecular displacement reactions of 4-(alkylthio)butyl radicals, where alkyl = benzyl, propyl, and *tert*-butyl, giving tetrahydrothiophene and the corresponding alkyl radical (R•). Arrhenius expressions were determined by competition of the rearrangement (displacement) with abstraction of hydrogen from tributylstannane. The Arrhenius parameters for the intramolecular displacement reactions were as follows [R•, log (A/s^{-1}), E_a (kcal/mol), at the 95% confidence interval]: benzyl, 9.92 ± 0.22, 8.63 ± 0.40; *tert*-butyl, 10.77 ± 0.24, 11.36 ± 0.40; *n*-propyl, 10.17 ± 0.56, 12.15 ± 1.16. The 4-(benzylthio)butyl and 4-(propylthio)butyl radicals undergo a competing intramolecular 1,6-hydrogen migration to form the corresponding α-(butylthio)benzyl and (butylthio)propyl radicals. The Arrhenius parameters [log (A/s^{-1}), E_a (kcal/mol), 95% confidence interval], per hydrogen atom abstracted, for these latter two reactions were as follows: 4-(benzylthio)butyl, 9.51 ± 0.28, 8.87 ± 0.44; 4-(propylthio)butyl, 9.10 ± 1.9, 9.98 ± 3.9. The Arrhenius parameters of the intramolecular displacement reaction are consistent with a product-like rate-determining step, as opposed to the formation of an intermediate sulfuranyl radical followed by nonselective ligand loss. INDO calculations predict the SOMO of the trialkylsulfuranyl radicals to be a σ^* orbital with electron density distributed about sulfur and two pseudoapical carbons. The pseudoapical C–S–C angle defined by this SOMO suggests a predominance of exocyclic (axial–axial) displacement over endocyclic (equatorial–axial) displacement for the intramolecular displacement reactions forming a tetrahydrothiophene ring. MM2 calculations of internal rotational barriers of *tert*-butyl, hex-5-en-1-yl, and the 4-(alkylthio)butyl radicals and of the exocyclic ligands of models of the displacement transition structures are presented to aid in the interpretation of displacement *A* factors.

Introduction

Homolytic displacement reactions at sulfur are of particular interest since displacement at sulfide by aryl or alkyl radicals may proceed through a relative energy minium corresponding to a tricoordinate, hypervalent intermediate, in contrast with the analogous hydrogen transfer between carbon centers. Early studies[2,3] of homolytic displacement of alkyl groups of sulfides by carbon-centered radicals or one-electron reduction of sulfonium salts[4] addressed the question of intermediacy of 9-*S*-3 (9 formal valence electrons about tricoordinate sulfur[5]) structures in the displacement reactions. The highly exergonic displacement of radical groups by an aryl radical examined in the first relative rate study[2] exhibited very low selectivities as a function of displaced ligand, leaving the question of intermediacy of aryldialkylsulfuranyl radicals unresolved. However, numerous sulfuranyl radicals possessing one or more electronegative ligands are known.[5,6] The first Arrhenius parameters for unimolecular decomposition of a trialkoxysulfurane have been reported,[7] and examples of persistent 9-S-3 structures have been prepared by Martin et al.[6] Sulfuranyl radicals of σ- or σ^*- and π-type electronic structure have been deduced from ESR proton hyperfine coupling transmitted through the σ (ω coupling) or π bonds of aryl ligands,[5,6] although the assignment of the ground-state electronic structure of several dialkoxysulfuranyl radicals remains controversial.

Thus, while 9-S-3 radicals possessing one or more electronegative ligands exhibit appreciable stability,[5] accumulating experimental evidence suggests low stability for 9-S-3 structures lacking electronegative apical ligands and electropositive, pseudoequatorial ligands.[8] Whether the displacement reactions of alkyl radicals at sulfur involve 9-S-3 intermediates or merely transition structures, the bonding requirements identified for 9-S-3 trivalent sulfur species will be reflected in the stereoelectronic requirements for displacement. The intramolecular displacement reactions of the 2-[2-(alkylthio)ethyl]phenyl radicals[2] revealed exclusive departure of the acyclic ligand (k_1) and the absence of the endocyclic displacement pathway (k_{-1}). This observation was interpreted as evidence that backside attack of the approaching radical was necessary for displacement. Displacement of the alkyl ligand was suggested to proceed through a distorted T-shaped hypervalent structure similar to the general structures postulated[5,6] for arylalkylalkoxysulfuranyl radicals. The very small differences in relative rates of displacement with variation of R (eq 1),[2] suggested either an early transition state for the displacement reactions, a preequilibrium involving a sulfuranyl radical and the starting radical structure, or the formation of a 9-S-3 intermediate in the rate-determining step of the reactions. However, an analysis of the thermochemistry of the displacements (vide infra), coupled with more recent rate data, rules out intermediates of significant stability. Thus, while a preequilibrium involving a 9-S-3 intermediate cannot be strictly ruled out, the low selectivity for displacement of a series of ligands by the aryl radical can most likely be attributed to an early transition state.



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In a related study of electron transfer to sulfonium salts, a reaction which results in cleavage of a ligand to form a sulfide from sulfonium salts possessing at least one aryl group (eq 2), Beak and Sullivan[4] found low selectivity for

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[1] This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC06-76RLO 1830.

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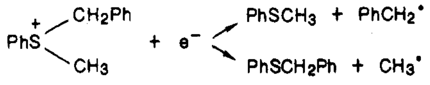

(2)

competitive ligand loss. The loss of benzyl vs. methyl from benzylmethylsulfonium occurred in the ratio of 15:1, corresponding to a difference in free energy of activation of only 1.6 kcal/mol at room temperature. The small free energy difference for different substituents implies a shallow well for the sulfuranyl structures. The failure of simple trialkylsulfonium salts to undergo one-electron reduction was interpreted by Beak and Sullivan[4] to indicate that electron transfer to aryldialkylsulfonium salts occurred to the LUMO of the aromatic ring of the arylsulfonium salts, forming a sulfonium-radical anion species (which is not formally a hypervalent radical[5]). The absence of a relatively low-lying LUMO in the trialkylsulfonium salts appears to preclude electron transfer. Saeva and Morgan[9] have challenged the proposed mechanism of stepwise transfer of an electron to the aromatic group followed by ligand loss suggested by Beak and Sullivan. The results of a cyclic voltammetric study of one-electron transfer to arylmethylalkylsulfonium salts revealed higher peak potentials than those expected in the one-electron reduction of an aryl ring and a high sensitivity of the peak potentials to ligand electronegativity. These observations were cited as evidence for simultaneous or nearly simultaneous transfer of an electron and ligand loss.[9] However, this interpretation does not explain the failure of trialkylsulfonium salts to undergo reductive cleavage. The lack of evidence for trialkyl or arylalkylsulfuranyl radicals of appreciable stability probably reflects a requirement of electronegative apical ligands[6,7] to stabilize the 9-S-3 structure, by analogy to the ligand electronegativity requirements to form stable closed-shell 10-S-4 sulfuranes.[8]

Although the results of Kampmeier,[2,3] Beak,[4] and Saeva[9] suggest that homolytic displacement at sulfide sulfur is not likely to proceed through a sulfuranyl radical of significant stability, existing relative rate data have been measured only for rapid, highly exothermic aryl displacement reactions, and no Arrhenius expressions have been published for displacement at sulfur. Arrhenius parameters for the nearly symmetric alkyl–alkyl displacement reaction should optimize sensitivity to the displaced ligand and provide a better definition of the rate-determining step for displacement. Of importance to the field of coal chemistry, no data pertaining to the energetics of formation and cleavage of the important cyclic sulfur-containing ring systems by thermal radical pathways exist. Finally, the possible synthetic utility of the radical cyclization pathway to thiophene ring formation warrants evaluation.

Thus, we present the first Arrhenius expressions for S_Hi displacement at sulfur.[10] Arrhenius parameters for the cyclic displacement of benzyl, *tert*-butyl, and propyl radicals by a primary radical, and Arrhenius parameters for the competing 1,6-hydrogen migration reactions in the 4-(benzylthio)butyl and 4-(propylthio)butyl radicals are presented and discussed in terms of the structural characteristics of the rate-determining step of the displacement reaction. The structure and bonding of trialkylsulfuranyl radicals predicted by INDO calculations are presented and discussed in terms of the stereoelectronic requirements for alkyl radical displacement at sulfur. MM2 calculations of rotational barriers in the ground and model transition structures of the 4-(alkylthio)butyl radicals are presented for analysis of relative cyclization *A* factors.

Experimental Section

General. ^{1}H FTNMR spectra were determined with a Varian FT-80 instrument. Gas chromatography (GC) was carried out on a Hewlett-Packard 5880A equipped with a 30-m J+W Scientific DB-5 capillary column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Reagents. Isooctane, *tert*-butyl methyl ether, pentane (HPLC grade, Burdick & Jackson), ethyl ether (anhydrous, EM Science), azoisobutyronitrile (AIBN) (Eastman Kodak), benzene (HPLC grade), tetrahydrothiophene, tributylstannane, benzyl mercaptan, 1-propanethiol, butyl disulfide, dodecyl chloride, and *tert*-butyl mercaptan were used as obtained from Aldrich. 4-Chloro-1-butene was obtained from Chemical Procurement Labs. 1-Butene was obtained from Matheson.

Butyl propyl sulfide (3),[11a] benzyl butyl sulfide (4),[11b] phenyl butyl sulfide, phenyl 4-bromobutyl sulfide, butyl *tert*-butyl sulfide (5),[12] propyl 4-chlorobutyl sulfide (6), benzyl 4-chlorobutyl sulfide (7), and *tert*-butyl 4-chlorobutyl sulfide (8) were prepared by a standard procedure, illustrated for 6.

In a quartz reaction cell, 0.89 g of 4-chloro-1-butene was combined with 0.89 g of propanethiol (ca. 1.2 equiv). The solution was purged with argon for 1 min, sealed, and photolyzed at room temperature for 1 h with a 400-W medium-pressure Hg lamp. The reaction was diluted with ether, washed three times with 10% aqueous KOH and once with water, dried over magnesium sulfate, filtered, concentrated, and chromatographed (0–5% ether/pentane on silica gel) to yield 0.98 g of propyl 4-chlorobutyl sulfide (6) as a clear oil (60% yield, 98% purity by GC): ^{1}H NMR (CDCl$_3$) δ 1.0 (t, 3 H), 1.4–2.1 (m, 6 H), 2.1 (m, 4 H), 3.55 (t, 2 H); mass spectrum, *m/z* (relative abundance) 61.00 (37), 89.15 (100), 91.05 (18), 131.15 (10), 166.15 (28, M$^+$), 168.05 (11). This compound and the other chloroalkyl sulfides were stored at −25°C. to prevent formation of cyclic sulfonium salts at above ambient temperatures.

Sulfides 3–5 were prepared as indicated above, although they are commercially available. The NMR spectra and GC traces confirmed the identity and purity of the compounds.

***tert*-Butyl 4-chlorobutyl sulfide (8)** was obtained as a clear oil in 50% yield (97% purity by GC): ^{1}H NMR (CDCl$_3$) δ 1.25 (s, 9 H), 1.5–2.0 (m, 8 H), 2.55 (t, 2 H), 3.55 (t, 2 H); mass spectrum, *m/z* (relative abundance) 57.1 (100), 180.15 (5, M$^+$), 182.15 (1).

Phenyl 4-bromobutyl sulfide[13] was obtained as a colorless oil (21% yield): ^{1}H NMR (CDCl$_3$) δ 1.5–2.2 (m, 4 H), 2.9 (t, 2 H), 3.4 (t, 2 H), 7.3 (brs, 5 H).

Phenyl butyl sulfide[14] was obtained as a clear oil (75 yield): ^{1}H NMR (CDCL$_3$) δ 0.9 (m, 3 H), 1.2–1.8 (m, 4 H), 2.9 (t, 2 H), 7.3 (m, 5 H).

Benzyl 4-chlorobutyl sulfide (7)[15] was obtained as a clear oil in 85% yield (97% purity by GC): ^{1}H NMR (CDCl$_3$) δ 1.5–2.0 (m, 4 H), 2.42 (t, 2 H), 3.48 (t, 2 H), 3.69 (s, 2 H), 7.28 (s, 5 H).

Benzyl 4-(phenylseleno)butyl sulfide (9), *tert*-butyl 4-(phenylseleno)butyl sulfide (10), and propyl 4-(phenylseleno)butyl sulfide (11) were prepared by the following procedure illustrated for ***tert*-butyl 4-(phenylseleno)butyl sulfide (10)**.

In a flame-dried, 50-mL, three-neck flask under argon were combined 0.74 g of phenyl diselenide and 11 mL of dry isopropyl alcohol. Sodium borohydride was added in small portions until the yellow color of the starting diselenide disappeared. After the mixture was stirred an additional 15 min, 0.81 g of *tert*-butyl 4-chlorobutyl sulfide in 2 mL of isopropyl alcohol was added at once, and the reaction was brought to reflux for 1 h. GC analysis showed the starting chloride to be consumed. The reaction was

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cooled, diluted with ether, and washed four times with water, once with 5% aqueous H_2SO_4, and once with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to yield the crude product in 70% yield. Purification by HPLC (0–10% *tert*-butyl methyl ether/isooctane on silica gel) gave **10** as a clear oil (99% purity by GC): ^1H NMR ($CDCl_3$) δ 1.3 (s, 9 H), 1.5–2.0 (m, 4 H), 2.5 (t, 2 H), 2.8 (t, 2 H), 7.1–7.7 (m, 5 H). Anal. Calcd for $C_{14}H_{22}SSe$: C, 55.80; H, 7.36. Found: C, 56.07; H, 7.35.

Propyl 4-(phenylseleno)butyl sulfide (11) was obtained as a clear oil in 70% yield (98% purity by GC): ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H), 1.3–2.0 (m, 6 H), 2.47 (m, 4 H), 2.91 (t, 2 H), 7.1–7.7 (m, 5 H). Anal. Calcd for $C_{13}H_{20}SSe$: C, 54.34; H, 7.02. Found: C, 54.58; H, 7.23.

Benzyl 4-(phenylseleno)butyl sulfide (9) was obtained as a clear oil in 70% yield (97% pure by GC): ^1H NMR ($CDCl_3$) δ 1.5–2.0 (m, 4 H), 2.39 (t, 2 H), 2.86 (t, 2 H), 3.67 (s, 2 H), 7.2–7.7 (m, 10 H). Anal. Calcd for $C_{17}H_{20}SSe$: C, 60.91; H, 6.01. Found: C, 60.93; H, 5.84.

Kinetic Experiments. Sample Preparation. The stock solutions were prepared as follows and stored in the dark at −20 °C prior to use.

tert-Butyl #1: 2.63 mM **10**, 9.16 mM Bu_3SnH, 0.162 mM *tert*-butylbenzene, and 0.041 mM AIBN (0.45% vs. Bu_3SnH). *tert*-Butyl #2: 3.38 mM **10**, 5.47 mM Bu_3SnH, and 0.204 mM *tert*-butylbenzene.

Propyl #1: 1.64 mM **11**, 1.33 mM Bu_3SnH, 0.167 mM *tert*-butylbenzene. Propyl #2: 3.28 mM **11**, 2.66 mM Bu_3SnH, 0.333 mM *tert*-butylbenzene. Propyl #3: 6.56 mM **11**, 5.33 mM Bu_3SnH, 0.666 mM *tert*-butylbenzene. Propyl #4: 13.1 mM **11**, 10.66 mM Bu_3SnH, 1.33 mM *tert*-butylbenzene.

Benzyl #1: 2.83 mM **9**, 3.95 mM Bu_3SnH, 0.5 mM *tert*-butylbenzene. Benzyl #2: 5.66 mM **9**, 7.91 mM Bu_3SnH, 0.5 mM *tert*-butylbenzene. Benzyl #3: 8.49 mM **9**, 11.86 mM Bu_3SnH, 0.5 mM *tert*-butylbenzene. Benzyl #4: 11.33 mM **9**, 15.82 mM Bu_3SnH, 0.5 mM *tert*-butylbenzene.

Reaction vials were prepared by micropipetting 200 μL of stock solution into 5-mm glass tubes. These tubes were degassed on a high-vacuum line via three freeze–pump–thaw cycles using liquid nitrogen and then flame sealed while frozen. Head space in the reaction vials varied between 300 and 400 μL. Reactions were carried out in thermostated oil baths (±0.3 °C). For experiments at 195 °C and above, an oil bath contained in a 2-L, three-neck flask under argon was used to avoid oil decomposition. At each temperature, trial samples of each stock solution were run to determine the reaction times needed to ensure that appropriately small amounts of Bu_3SnH were consumed. Samples were removed from the oil bath and cooled quickly to quench the reaction. GC analysis was carried out in duplicate on the neat samples immediately after opening.

GC response factors for the products and the internal standard were linear over a range of concentrations (0.023–0.35 mM). Mass balances [(selenide recovered + $\sum$products)/[initial selenide]] averaged 95.9% for **9**, 99.6% for **11**, and 76% for **10**. Because of low material balances for **10**, a second set of reactions were carried out, which gave mass balances of >95% but with larger errors than for **9** and **11**. The overall average mass balance for **10** was 89%. The GC traces were invariably clean for reactions of **10**, product ratios were invariant wth material balance, and 2-methylpropene yields agreed within 15% to yields of tetrahydrothiophene. These observations led us to expect irreproducibility in the GC analysis of **10**. A careful examination of the GC calibration data revealed response factors for the selenides to be occasionally erratic in both splitless and on-column GC modes, while the product ratios (tetrahydrothiophene/RSBu) were invariably accurate to within 1–2%. Absolute yield calculations for reactions taken to short extent of reaction tend to show larger errors from the relation $\sum$products/(selenide$_t$ − selenide$_0$), since composite errors in the denominator approach the magnitude of total products formed. The alternate method of calculation, (selenide$_t$ + $\sum$products)/selenide$_0$, tend to be insensitive at short extents of reaction. Nevertheless, the overall material balances were satisfactory to excellent. A possible side reaction of **10**, which would lead to a reduced yield, is intramolecular abstraction of hydrogen from the *tert*-butyl group and departure of the resulting thiyl radical, producing isobutylene and butyl mercaptan. However, this reaction would have no effect of the kinetic scheme, and only traces of isobutylene were detected in several experiments. Butyl mercaptan was not detected.

Example of Kinetic Determination. In a typical experiment, a 200-μL sample of *tert*-butyl #1 stock solution was heated at 80 °C for 30 min. GC analysis showed 10% Bu_3SnH consumption. Therefore, $[Bu_3SnH]_{av,T} = 0.95 \times 9.16$ mM × density correction = 8.14 mM. GC analysis revealed 0.0196 mM tetrahydrothiophene and 0.157 mM *tert*-butyl butyl sulfide, a molar ratio of 0.1248. Multiplication of this ratio by $[Bu_3SnH]_{av,T}$ and by the value of k_5 at 80 °C (6.63×10^5 M^{-1} s^{-1}) gives $k_6 = 5.72 \times 10^3$ s^{-1}.

Attempted Cyclization of Phenyl 4-Bromobutyl Sulfide. In a round-bottom flask under argon were combined 6.3 mg (2.1 mM) of starting bromide, 12.4 mL of 3.12 mM Bu_3SnH in benzene, and a catalytic amount of AIBN. After the mixture was refluxed overnight, GC analysis showed only phenyl butyl sulfide and no tetrahydrothiophene (based on a detection limit for tetrahydrothiophene of 0.1% of the reduced product, and $[Bu_3SnH]_{av} = 2$ mM, $k_6 < 0.1/99.9(6.3 \times 10^6)0.002 = 13$ s^{-1}.

Determination of Relative Reactivity of $Bu_3Sn\cdot$ with Dodecyl Chloride vs. Benzyl Butyl Sulfide. A stock solution of 19.5 mg of bibenzyl (GC standard), 17 mg of dodecyl chloride (9.6 mM), 17.8 mg of benzyl butyl sulfide (9.9 mM), 21 μL of Bu_3SnH (7.9 mM), and AIBN (0.4mM) in 10 mL of benzene was prepared, and freeze–thaw degassed, sealed in Pyrex tubes, and heated at 80 °C for 40, 85, 130, and 270 min. The relative rate for reaction with the sulfide compared to the chloride is given by the expression[16]

$$k_s/k_{Cl} = \ln([C_{12}H_{25}Cl]_0/[C_{12}H_{25}Cl]_t)/\ln([\text{sulfide}]_0/[\text{sulfide}]_t)$$

An average value of $k_s/k_{Cl} = 1.16 \pm 0.16$ was obtained. From the known relative rates of abstraction of PhSe vs. Cl from a variety of structures,[16c] the selenide group will react with $Bu_3Sn^\bullet$ at a rate >100-fold faster than displacement of the alkyl groups substituted at sulfur. Thus, it can be safely concluded that the product 4-(alkylthio)butanes will not be lost in secondary reactions in the presence of excess selenide starting material.

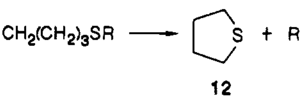
Results

The reaction of *tert*-butyl 4-(phenylseleno)butyl sulfide and Bu_3SnH proceeds through the sequence of reactions depicted in eq (3 and 4), R = $C(CH_3)_3$, which include selective abstraction of SePh by $Bu_3Sn^\bullet$, followed by abstraction (k_5, eq 5) or displacement (k_6, eq 6). For a negligible change in [Bu_3SnH], k_6 can be written as in eq. 7. Average values of [Bu_3SnH] were used in the calculations, with corrections for density variation as a function of temperature, d_f: $[Bu_3SnH]_{av} = d_f([Bu_3SnH]_{init} + [Bu_3SnH]_{final})/2$. The temperature dependence of the benzene solvent density was calculated by the method of Gunn and Yamada,[17] from which the density correction expression

$$Bu_3SnH + R_i^\bullet(AIBN) \longrightarrow Bu_3Sn^\bullet \quad (3)$$

$$Bu_3Sn^\bullet + PhSe(CH_2)_4SR \longrightarrow {}^\bullet CH_2(CH_2)_3SR + Bu_3SnSePh \quad (4)$$

$$^\bullet CH_2(CH_2)_3SR + Bu_3SnH \longrightarrow \underset{\mathbf{3}}{CH_3(CH_2)_3SR} + Bu_3Sn^\bullet \quad (5)$$


(6)

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$$k_6 = k_5[Bu_3SnH]([\mathbf{12}]/[\mathbf{3}]) \quad (7)$$

$$d_f = [1.188 - (1.045 \times 10^{-3})/T \text{ (in K)}]/0.8759$$

was constructed. The values of k_5 were estimated from

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Table I. Arrhenius Expressions for Intramolecular Displacement and Intramolecular 1,6-Hydrogen Migration of 4-(Alkylthio)butyl Radicals[a]

$R^{\bullet}$	log A, s^{-1} (ΔS^*, eu)[b]	E_a, kcal/mol (ΔH^*, kcal/mol)[b]	k, s^{-1} (298 K)	T_m, K[b]
Intramolecular Displacement Reactions (k_6)				
benzyl	9.92 ± 0.22 (−15.71)	8.63 ± 0.40 (7.84)	3.91×10^3	405.5
tert-butyl	10.77 ± 0.24 (−11.66)	11.36 ± 0.40 (10.63)	2.74×10^2	370.5
n-propyl	10.17 ± 0.56 (−14.81)	12.15 ± 1.16 (11.26)	18.2	455.5
Intramolecular 1,6-Hydrogen Migration Reactions (k_8)				
benzyl	9.51 ± 0.28 (−17.59)	8.87 ± 0.22 (8.08)	2.2×10^3	405.5
n-propyl	9.1 ± 1.9 (−19.7)	9.98 ± 3.93 (9.09)	40.2	455.5

[a] Errors are at the 95% confidence interval (2σ). [b] Arrhenius parameters are converted to absolute rate expressions using the relations $\Delta H^* = -R(\Delta \ln (k/T)/\Delta(1/T)) = E_a - RT_m$, where T_m is the mean temperature of the kinetics, and $\Delta S^* = R(\ln (k_{T_m}/T_m) - \ln (k_b/h) + \Delta H^*/RT_m) = R \ln (hA/ek_bT_m)$, where k_b is Boltzmann's constant, h is Planck's constant, and k_{T_m} is the rate constant from the Arrhenius expression at mean temperature.

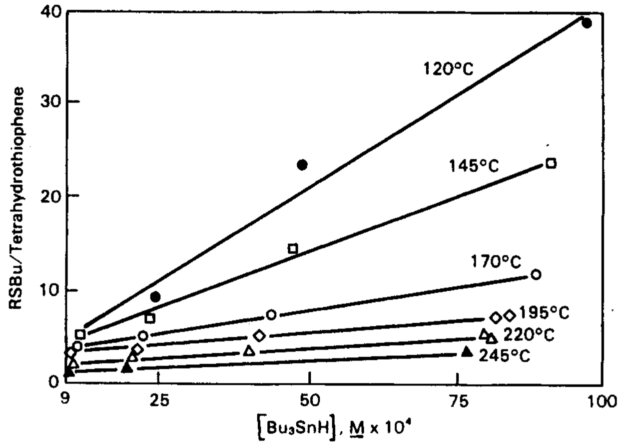


Figure 1. Plot of the ratio of reduced (RSBu, benzyl butyl sulfide) to cyclized (tetrahydrothiophene) products as a function of [Bu_3SnH] and temperature.

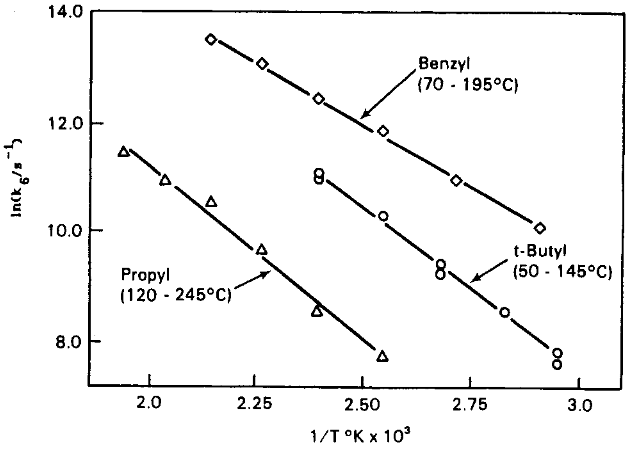
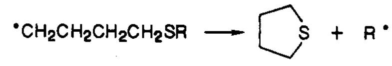


Figure 2. Arrhenius plots for the intramolecular displacement reactions of 4-(alkylthio)butyl radicals, alkyl = benzyl, propyl, *tert*-butyl.

Table II. Enthalpies of Reaction for Intramolecular Displacement Reactions of 4-(Alkylthio)butyl Radicals[a]



$R^{\bullet}$	E_a, kcal/mol	$\Delta H°$, kcal/mol	rel rates at 25 °C	rel rates at 107.5 °C
benzyl	8.6	−4.6	214	59
tert-butyl	11.4	−2.2	16	11
n-propyl	12.2	2.1	(1)	(1)

[a] Reference 34.

the average Arrhenius expressions for the reactions of butyl and ethyl radicals with Bu_3SnH[18] and were used in eq 7 to calculate k_6.

For R = propyl and benzyl, intramolecular 1,6-hydrogen transfer competes with abstraction and intramolecular displacement (eq 8 and 9). Thus, for R′ = ethyl and

$$^{\bullet}CH_2(CH_2)_3SCH_2R' \rightarrow CH_3(CH_2)_3SC(^{\bullet})HR' \quad (8)$$

$$R' = C_2H_5, Ph$$

$$CH_3(CH_2)_3SC(^{\bullet})HR' + Bu_3SnH \rightarrow \underset{\mathbf{3}}{CH_3(CH_2)_3SR} \quad (9)$$

phenyl in eq 8, eq 10 obtains, where $2k_8$ is the total rate constant for intramolecular hydrogen transfer, and k_8 is the rate constant per abstractable hydrogen. Plots of [**3**]/[**12**] vs. [Bu_3SnH] provide k_5/k_6 as the slope, which is combined with values of k_5[18] to evaluate k_6. Multiplying the intercept by k_6 provides $2k_8$, the rate constant for 1,6-hydrogen transfer. Arrhenius parameters for the intramolecular displacement reactions are given in Table I, along with Arrhenius expressions for the competing intramolecular 1,6-hydrogen-transfer reactions.

Figure 1 depicts the dependence of the ratio of reduced to cyclized product as a function of Bu_3SnH concentration. The Arrhenius plots for the intramolecular displacement reactions are depicted in Figure 2.

Discussion

Arrhenius Parameters. The observed selectivity and activation barriers for the displacement reactions of 4-(alkylthio)butyl radicals are consistent with a rate-determining step which involves significant evolution of radical character in the leaving ligand, in constrast to rate-determining formation of a sulfuranyl radical intermediate. Either formation of an intermediate 9-S-3 radical in the rate-determining step of the displacement or the occurrence of an early transition state, as for aryl displacements of alkyl groups, would result in low selectivity. For the present study in which the displacement reactions are close to thermoneutral (Table II), enthalpic effects associated with formation of the product radical are readily apparent. Although an analysis of the A factors is complicated by their proximity and by opposing ground- and transition-state effects, careful analysis reveals characteristics best summarized by a transition structure, rather than a genuine intermediate.

The entropy changes in the displacement reactions can be discussed in two stages. The first stage is the cyclization to form the tetrahydrothiophene portion of the transition structure. The second stage is ejection of the product radical. Rate-determining formation of a sulfuranyl radical followed by nonselective ligand loss will not reveal the entropy changes associated with product radical formation. The differences in A factors associated with the first stage of the displacement reaction, whether involving a 9-S-3 intermediate or merely a transition state, are due to var-

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(18) Chatgilialglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742. For abstraction of hydrogen by the 4-(alkylthio)butyl radicals, the expression log k_5 (M^{-1} s^{-1}) = $(9.07 - 3.69)/\theta$, θ = $2.303RT$ (kcal/mol) was used.

Table III. MM2 Rotational Barriers in 4-(Alkylthio)butyl, Hex-5-en-1-yl, *tert*-Butyl, and Sulfuranyl Radical Structures

barrier, kcal/mol

$^{\bullet}CH_2\underset{0.5}{\text{—}}CH_2\underset{5.4}{\text{—}}CH_2\underset{4.7}{\text{—}}CH_2\underset{1.4}{\text{—}}CH{=}CH_2$

$^{\bullet}CH_2\underset{0.5}{\text{—}}CH_2\underset{4.4}{\text{—}}CH_2\underset{5.8}{\text{—}}CH_2\underset{3.4}{\text{—}}S\underset{2.8}{\text{—}}CH_2\underset{2.7}{\text{—}}Ph$

$^{\bullet}CH_2\underset{0.5}{\text{—}}CH_2\underset{4.4}{\text{—}}CH_2\underset{5.8}{\text{—}}CH_2\underset{3.4}{\text{—}}S\underset{2.8}{\text{—}}CH_2\text{—}CH_2\text{—}CH_3$

$^{\bullet}CH_2\underset{0.5}{\text{—}}CH_2\underset{4.4}{\text{—}}CH_2\underset{5.9}{\text{—}}CH_2\underset{9.3}{\text{—}}S\underset{2.2}{\text{—}}C(CH_3)_2\underset{4.45}{\text{—}}CH_3$

$\overline{CH_2CH_2CH_2CH_2S}(^{\bullet})\underset{1.2}{\text{—}}C(CH_3)_3$

$(CH_3)_2C(^{\bullet})\underset{1.4}{\text{—}}CH_3$

$\overline{CH_2CH_2CH_2CH_2S}(^{\bullet})\underset{1.6}{\text{—}}CH_2CH_2CH_3$

$\overline{CH_2CH_2CH_2CH_2S}(^{\bullet})\underset{4.8}{\text{—}}CH_2\underset{2.8}{\text{—}}Ph$

iation in S–C and C–C ground-state rotational barriers in the *n*-butyl groups as a function of R. Steric congestion in the cyclized tricoordinate structure may lead to an increase in S–R rotational barriers of the departing groups.

To examine the relative ground- and transition-state rotational entropy changes for cyclization of a the 4-(alkylthio)butyl systems, MM2 calculations were carried out to determine the rotational barriers of the ground-state radicals and the cyclized sulfuranyl radicals (Table III). The MM2 program of N. L. Allinger,[19] with input files generated by the MODEL program of Stills et al.,[20] was applied to generate rotational energy profiles. Primary radical parameters of H. D. Beckhaus[21] were installed in the MM2 force-field program. The tricoordinate sulfur radical center was modeled in the MM2 program by fixing the three S–R bond lengths and their corresponding angles at values determined from INDO/1 calculations (vide infra). The rotational barriers of the butyl fragment of the (alkylthio)butyl radical are very similar with the exception of the S–C_4 barrier of 4-(*tert*-butylthio)butyl, 9.3 kcal/mol. The higher cyclization *A* factor from this ground-state effect is *not* compensated by a corresponding increase in the S---Bu-*t* rotational barrier of the cyclized species. Although increased steric compression on cyclization raises the total strain energy of the molecule, compensating effects of adding the second group lowers the rotational barrier of the *tert*-butyl group relative to the ground-state radical. For propyl, the propyl–*S* rotational barrier also decreases slightly on cyclization. Of the three systems, only the benzyl rotational barrier increases on cyclization from 2.8 to 4.8 kcal/mol. For simplicity we have discussed only the highest barrier in each system. A shortcoming of this analysis is that the theoretical sulfuranyl structures used here to model the transition structure have somewhat shorter S–C bonds than those of the actual transition structures. Thus, the rotational barriers in the actual transition structures may be slightly lower.

The second stage of the displacement reaction, formation of the ejected radical, should lead to a distinctive variation in *A* factors. Thus, formation of benzyl radical in the rate-determining step will increase the barrier to phenyl–CH_2 rotation from 2.7 up to 13 kcal/mol, the experimental value of the benzyl barrier,[22] corresponding to the resonance stabilization energy of the benzyl radical, 10 ± 2 kcal/mol[23] leading to a reduced *A* factor compared to propyl and *tert*-butyl. For *tert*-butyl, conversion to a planar structure will lead to a reduction in three methyl rotational barriers from 4.5 to 1.4 kcal/mol, reminiscent of the entropy component of the Thorpe–Ingold effect.[24] However, it is likely that the *tert*-butyl or propyl radicals will be substantially pyramidal in the transition state of displacement, and the methyl rotors of the *tert*-butyl group will exhibit barriers not reduced by more than about 1–2 kcal/mol. The argument for this rests on analogy with hydrogen abstraction reactions between primary carbon radical centers, in which the attacking radical undergoes a major geometry change from planar to nearly tetrahedral, while the evolving product radical has flattened only a few degrees from tetrahedral geometry.[25] To the extent that *tert*-butyl becomes relatively more planar, it will exhibit a higher *A* factor than expected for displacement of propyl and benzyl. Displacement of the propyl group can be expected to exhibit the "normal" *A* factor, since this ligand lacks the steric crowding of *tert*-butyl and the resonance effect of benzyl. In conclusion, the higher *A* factor for *tert*-butyl is a consequence of the ground-state effect and some contribution from the entropy gain on planarization. The benzyl group shows the lowest *A* factor, mainly due to freezing the phenyl rotation, offset somewhat by steric congestion on cyclization. Finally, *n*-propyl exhibits an intermediate *A* factor value. Although the *A* factors overlap at the 95% confidence level, the overall trend exhibits a degree of selectivity based on *A* factors, which suggests a product-like rate-determining step. The overall selectivity clearly rules out rate-determining formation of a 9-S-3 radical.

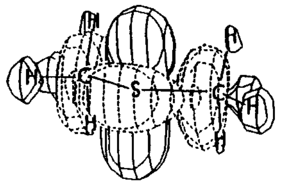

Figure 3. Orbital amplitude plot of the S–C σ^* LUMO of dimethyl sulfide (MO 11) (INDO/1).

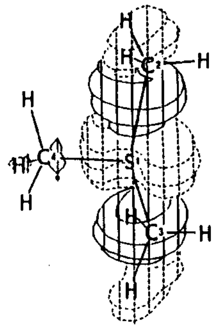

Figure 4. Orbital amplitude plot of the SOMO (MO 14) of trimethylsulfuranyl from INDO/1 calculations. The antibonding SOMO is distributed primarily about the sulfur and the pseudoapical C2 and C3 carbon ligands.

Theoretical Calculations of Trialkylsulfuranyl Radicals. We have performed SFC–MO calculations

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(19) Allinger, N. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(20) We thank Professor K. Stelious, University of Montreal, for providing us with version 2.7 of MODEL.

(21) We thank Prof. A. L. J. Beckwith for providing the MM2 radical parameters of H. D. Beckhaus (Department of Chemistry, University of Freiburg, Freiburg i. B., Federal Republic of Germany).

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(25) Rayez-Meaume, M. T.; Dannenberg, J. J.; Whitten, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 747.

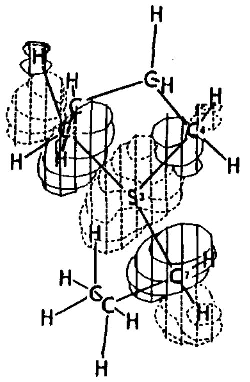

Figure 5. Orbital amplitude plot of SOMO of propyl-1,4-butylidenesulfruanyl (MO 25) from INDO/1 calculations. Spin density is distributed predominately over the C2–S–C7 centers. The orientation of the SOMO about pseudoapical C2 and C7 carbons defines an axial–axial geometric relationship between entering and departing radical centers which precludes endocyclic (axial–equatorial) displacement.

(INDO/1)[26,27] on sulfuranyl radicals to predict the geometry and bonding characteristics in these species. Orbital amplitude plots[28] have been generated to visualize the geometric relationship between the SOMO and entering and leaving groups of the displacement reactions. Interaction of the SOMO of the attacking radical with the LUMO of the sulfide, shown by INDO/1 calculations to be a C–S σ^* orbital (Figure 3), forms the sulfuranyl LUMO. The approximately antibonding SOMO of σ^* symmetry for the radicals are depicted in Figures 4 and 5. The trimethylsulfuranyl radical is intermediate in structure between a pyramidal sulfonium structure and a T-shaped structure, with a C–S–C angle of 146° (compared to the O–S–C pseudoapical angle of 140.7° predicted from MINDO/3-UHF calculations reported by Perkins et al. for an arylalkylalkoxysulfuranyl radical[5]). Substituents that can delocalize the unpaired spin density of the SOMO will clearly stabilize the 9-S-3 transition structure, resulting in a reduced activation barrier for displacement which directly reflects the enthalpy change of the reaction.

Table IV. INDO Structure of Trimethylsulfuranyl[a]

		bond length, Å	
bond	atoms	with d orbitals	without d
C–S	2-1	1.752	1.783
C–S	3-1	1.751	1.783
C–S	4-1	1.725	1.784
		angle, deg	
angle	atoms	with d orbitals	without d
C–S–C	2-1-3	146.28	99.93
C–S–C	2-1-4	102.43	96.94
C–S–C	3-1-4	99.56	98.14

[a] See Figure 4 for atom numbering.

Table V. INDO Structure of Propyl-1,4-butylidenesulfuranyl

bond	atoms	bond length, Å (with d orbitals)
C–S	2-3	1.745
C–S	4-3	1.740
C–S	7-3	1.779
angle	atoms	angle, deg (with d orbitals)
C–S–C	2-3-4	111.51
C–S–C	4-3-7	94.42
C–S–C	2-3-7	148.74

[a] See Figure 5 for atom numbering.

INDO/1 calculations were carried out for the trialkylsulfuranyl radicals both with and without d orbitals on sulfur. The bonding characteristics of 10-S-4 and 9-S-3 species have often been discussed in terms of a qualitative bonding scheme invoking sulfur 3p orbitals.[8] While no definitive statements can be made regarding the role of d orbitals from results at the INDO level, it is of interest to determine the consequence of choice of basis set on the radical geometries, since the geometry of the radical and arguments regarding the relationship between entering and leaving groups may be critically dependent on the MO scheme. Ab initio calculations at the minimal STO-3G basis set level have shown that d orbital polarization functions are necessary for proper prediction of molecular properties of hypervalent third-row elements.[29] Higher level calculations on SF_6 (double ζ + d polarization) have shown that inclusion of d orbitals is essential for an accurate description of this closed-shell species.[30] Such questions are not resolved in general, and we are currently performing an extended basis set calculation utilizing the many-body perturbation theory/coupled cluster method (MBPT/CCM) developed by Bartlett et al.[31] on trimethylsulfuranyl to obtain a definitive structure, $S–CH_3$ bond dissociation energy, and energy profile for the methyl + dimethyl sulfide displacement reaction. For present purposes, we note that the sulfur bond angles changed dramatically with the inclusion of d orbitals, and C–S bond lengths were shortened. (The inclusion of sulfur d orbitals in INDO calculations effected the O–S–O bond lengths but not the O–S–O bond angles in 10-S-4 structures. 9-S-3 O–S–O and O–S–C bond angles are substantially altered with the inclusion of d orbitals.[32]) Table IV presents the INDO geometry predicted for trimethylsulfuranyl, and Table V presents the predicted structure of the sulfuranyl radical formed from 4-(propylthio)butyl radical.

The angle between entering and departing radical groups predicted by INDO is 149°. The SOMOs for trimethylsulfuranyl and propyl-(1,4-butylidene)sulfuranyl radicals shown in Figures 4 and 5 suggest the stereochemical requirement for the displacement, that of axial–axial displacement, assuming that the sulfuranyl radical is a good

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(26) The INDO/1 calculations were carried out using the program ZINDO, version 010183: Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589–599 and references therein.

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(31) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359–401.

(32) INDO/1 predicts an O–S–O bond angles of 168.4° and 170.5° with and without d orbitals for dimethyldihydroxysulfurane (DMDHS). For methyldihydroxysulfuranyl (MDHS), the O–S–O angles are 166.2° without d orbitals and 142.6° with d orbitals. For dimethylhydroxysulfuranyl (M2HS), the pseudoapical O–S–C angles are 142.8° and 128° with and without d orbitals. The O–S bond lengths are about 0.2 Å longer without d orbitals. The O–S and C–S bond lengths with d orbitals are about 0.04 Å too short, due in part to the lack of inclusion of CI in the INDO/1 geometry optimization. Inclusion of d orbitals decreases the charge polarization of the X–S–X bond in all cases. The pseudoapical X–S–X bond angles of dimethyldihydroxysulfurane, predicted without d orbitals, are consistent with qualitative expectations for the structures with highly polarized S–X bonds. For the open-shell species, no clear trend is apparent, and we make the conventional assumption, for purposes of the stereochemical discussion, that inclusion of d orbitals will produce a better structure. It remains to be seen (from extended basis set MBPT/CCM calculations) if INDO/1 geometries are credible for trialkylsulfuranyl radicals; see ref 8a and: Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54–68. Complete INDO/1 geometries for all of these species are given in the supplementary material.

Table VI. Enthalpies of Reaction, Arrhenius Parameters and Relative Rates for Displacement Reactions of 2-[2-(Alkylthio)ethyl]phenyl Radicals

displaced radical	$\Delta H°$, kcal/mol	rel rate (at 107.5 °C)	log A, s^{-1}	E_a
phenyl	2.3[a]	(1)[b]	11[c]	5.4[c]
methyl	−9.5[a]	1.4,[b] (1.4)[d]	11[d]	4.8[d]
benzyl	−24.0[a]	7,[b] 8.2[d]	10.8[d]	3.12[d]

[a] Reference 34. [b] Results of ref 2, Table III, 0.1 M Bu$_3$SnH. [c] Relative rate calculated from results of ref 2. Calculated by using an integrated rate equation accounting for changing donor concentration (ref 16) assuming 10% consumption of Bu$_3$SnH and the rate constant for abstraction of hydrogen by phenyl from Bu$_3$SnH at 107.5 °C, 1.06×10^9 M^{-1} s^{-1} (ref 33). The A factor was assigned by comparison with methyl displacement, resulting in the assigned E_a value. [d] Results of Beckwith (ref 10).

model for the transition structure. The failure to observe endocyclic (axial–equatorial) displacement reactions at sulfur in Kampmeier's study[2] is probably a direct consequence of the axial–axial geometry of the comparable SOMO of the sulfuranyl resulting from the cyclization of 1 (eq 1).

We have used structures of sulfuranyl radicals to infer the geometric relationship between entering and departing radicals in displacement reactions. A theoretical study of the reaction pathway is required to properly address the stereoelectronic requirements for interaction of the SOMO of the attacking radical with the LUMO of the sulfide. An ab initio study carried out at a suitable level of accuracy to provide a predictive basis for the stereochemistry of intra- and intermolecular displacements at sulfur is under way.

Comparison of Primary Alkyl with Aryl Displacement Reactions at Sulfur. The earlier relative rates of displacement vs. abstraction of the 2-[2-(alkylthio)ethyl]phenyl from Bu$_3$SnH in the Kampmeier study[2] can be converted to rates of cyclization for comparison with the present study using the absolute rate expression for reaction of phenyl radical with Bu$_3$SnH,[33] log k_H (in M^{-1} s^{-1}) = $(10.0–1.7)/\theta$, $\theta = 2.303RT$ kcal/mol. The possibility of intramolecular 1,6-hydrogen transfer was not considered in this earlier study and would result in apparent rate constants for displacement lower than the actual values. The rate constants cited in Table VI assume that 10% of Bu$_3$SnH was consumed for purposes of application of a standard integrated rate expression[16] correcting for changing donor concentration to calculate the relative rate of cyclization to abstraction. (If 90% of the Bu$_3$SnH had been consumed, the rates of cyclization would be lower by a factor of 2.) An A factor for the cyclization of the 2-[2-(phenylthio)ethyl]phenyl radical in Kampmeier's study has been assigned by comparison with recent unpublished results of Beckwith,[10] who has determined Arrhenius expressions for two of the three systems (alkyl = benzyl, methyl) studied earlier by Kampmeier (Table VI).

Comparison of the results of the 4-(alkylthio)butyl radical reactions with the 2-[2-(alkylthio)ethyl]phenyl results (Table VI) reveals much greater selectivity for the 4-(alkylthio)butyl radicals, along with much higher activation barriers. The low barrier we estimate for phenyl displacement by the aryl radical (5.4 kcal/mol, (Table VI) is remarkable when compared to that for the displacement of propyl by a primary radical (12.2 kcal/mol, Table I), since both reactions have enthalpies of reaction of about 2 kcal/mol.[34] The high barrier for primary radical displacement of propyl undoubtedly results from the necessity of converting the planar primary alkyl radical to the tetrahedral geometry of the evolving S–C bond, by contrast with the σ aryl radical, which needs no rehybridization upon C–S bond formation. The highly exergonic displacements of methyl and benzyl and the attending low selectivities certainly reflect an early transition state for these displacement reactions. Finally, from the enthalpy change for phenyl displacement, 2.3 kcal/mol, and the estimated activation barrier for aryl displacement of phenyl radical (5.4 kcal/mol) (Table VI) we conclude that the diarylalkylsulfuranyl radical intermediate can lie in a well of no more than 3.1 kcal/mol.

Synthetic Utility of Radical Cyclizations for Tetrahydrothiophene Formation. As indicated in Table I, rate constants for 1,6-hydrogen transfer per abstractable hydrogen atom are comparable or greater than displacement rates at ambient temperature. As a result, displacement of these ligands would be inefficient synthetic routes to the tetrahydrothiophene ring structure. However, displacement of *tert*-butyl (no intramolecular side reaction), results in conversion of the starting selenide to tetrahydrothiophene in 88% yield, with 12% formation of the reduction product at 65 °C and 5.5×10^{-3} M Bu$_3$SnH. Thus, the judicious choice of radical precursor, displaced radical, and tributylstannane concentration can provide a synthetically useful procedure. Utilizing lower Bu$_3$SnH concentration or switching to a less active hydride donor such as Bu$_3$GeH[35] and choosing a good radical leaving group incapable of α-hydrogen donation (e.g., cumyl, PhC(CH$_3$)$_2$) would be anticipated to give excellent yields.

Summary. The Arrhenius parameters for the displacement reactions are consistent with a transition state involving product radical structure formation. INDO calculations indicate that the trialkylsulfuranyl radicals, which may exist as intermediates in a well of probably not more than 2–3 kcal/mol, will have a distorted T-shaped geometry, with electron density of the SOMO distributed over the sulfur and the two pseudapical carbon ligands. Relative enthalpies of activation for displacement of radicals of varying S–C bond strength are suggested to reflect the ability of displaced ligands to stabilize the sulfuranyl SOMO.

Acknowledgment. We thank Prof. A. L. J. Beckwith for providing data of ref 10 prior to publication.

Supplementary Material Available: Kinetic data (five tables) and structures from INDO/1 calculations (20 pages). Ordering information is given on any current masthead page.

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