# A Kinetic Study of the Migration of a Phenyl Group from Sulfur to a Carbon Radical Center: Rearrangement of the α-(Phenylthio)benzyl Radical

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**Abstract:** The first rate constants for the neophyl-like 1,2-phenyl migration from sulfur to a carbon-centered radical site are reported. An Arrhenius expression was determined for the neophyl-like 1,2-phenyl migration reaction of the α-(phenylthio)benzyl radical (2) to form the diphenylmethylthio radical (6) in nonane at 160–215 °C: $\log (k/\mathrm{s}^{-1}) = (10.65 \pm 0.74) - (21.4 \pm 1.55)/\theta$, $\theta = 2.3RT$ kcal/mol (errors are 1σ). The rate constants were measured in a competition between the rearrangement of 2 versus hydrogen abstraction from thiophenol in nonane. The basis rate expression for hydrogen abstraction, $\log (k_{\mathrm{abs}}/\mathrm{M}^{-1}$ $\mathrm{s}^{-1}) = (8.60 \pm 0.02) - (6.64 \pm 0.03)/\theta$, was determined by a competition between self-termination ($k_t$) of 2 and abstraction ($k_{\mathrm{abs}}$) from thiophenol from 27 to 220 °C in nonane. The relative rate expression, $\log (k_{\mathrm{abs}}/k_t^{1/2}) = 2.86 - 5.24/\theta$, was converted to the absolute rate expression for abstraction by use of the von Smoluchowski expression for the self-reaction of 2, $\log (k_t^{1/2}) = 5.74 - 1.40/\theta$. Experimental diffusion coefficients of benzyl phenyl sulfide in nonane were determined for comparison with calculated values for modeling the diffusion of 2. MNDO-PM3(RHF) calculations predict that the rearrangement 2 → 6 proceeds through a transitional structure, 10, rather than an intermediate. Substituted thiaspiro[2.5]octadienyl and thiiranylcarbinyl radicals are predicted to exhibit no or low (0.5 kcal/mol) barriers to C–S cleavage, respectively, suggesting that thiiranylcarbinyl radicals are candidates for picosecond radical clocks.

## Introduction

The 1,2-migration of a phenyl group to an adjacent radical site, known as the neophyl rearrangement, has been the subject of extensive study[1] since Wieland's report of the rearrangement of the triphenylmethoxy radical 81 years ago.[2] Many studies of the migration of a phenyl group from carbon to a carbon-centered radical followed the discovery of the rearrangement of the 2-methyl-2-phenylpropyl ("neophyl") radical.[3] Few studies were carried out in a manner allowing the rate constants for the rearrangements to be estimated.[1] Recently, spectroscopic and kinetic studies of the proposed bicyclic intermediates for carbon-to-carbon and carbon-to-oxygen rearrangements have appeared.[4-6] The spiro[2.5]octadienyl radical was detected by nanosecond optical spectroscopy, and unimolecular lifetimes for its ring opening to the 2-phenylethyl radical were measured.[4] Leardini et al.[5] demonstrated that the 2-(9-anthracenyl)ethyl radical cyclizes to form the EPR-detectable 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl radical, which was isolated as its dimer. Falvey, Khambatta, and Schuster[6] detected an intermediate in the rearrangement of 1,1-diphenylethoxy radical that exhibited a visible absorption spectrum characteristic of cyclohexadienyl radicals. The intermediate decayed with a lifetime of 312 ns at room temperature to form the 1-phenyl-1-phenoxyethyl radical. This surprisingly long lifetime implies an Arrhenius activation barrier of >8.8 kcal/mol, much higher than activation barriers for *less* exergonic ring-opening reactions of substituted cyclopropylcarbinyl radicals (see below). Although the formation of the intermediate occurred within a 17-ps laser pulse, abstraction of hydrogen by the alkoxy radical was detected. This suggests that cyclization to form the *spiro* intermediate was reversible, with rate-deter-

mining ring opening to the product radical. In recent years, the determination of absolute rate expressions for the reaction of alkyl radicals with trialkylstannanes made possible the determination of absolute rate expressions for neophyl-like rearrangements: A rate expression for the parent neophyl rearrangement of sufficient accuracy for its employment as a radical "clock" reaction has been measured.[7,8] To this date there remain few examples of neophyl-like rearrangements from carbon to adjacent heteroatoms, or between adjacent heteroatoms, other than carbon-to-oxygen phenyl migrations. Warkentin and co-workers reported the first example of a synthetically useful phenyl migration from nitrogen to an adjacent nitrogen-centered radical.[9] Indirect evidence has been developed for the migration of the phenyl group from sulfur to an adjacent carbon-centered radical.[10] However, no direct observation or kinetic characterization of this rearrangement has been reported. The sulfur-to-carbon neophyl-like rearrangement, and its reverse reaction, may be an important pathway for structural rearrangement in pyrolytic reactions such as the liquefaction of sulfur-containing coal. The presence of sulfur, disulfides, and thiols during the pyrolysis of alkyl-substituted aromatic structures leads to the reversible substitution of the benzylic hydrogen atoms of alkyl aromatic hydrocarbons with aryl groups via sequential 1,2-aryl migrations between sulfur and carbon-centered radicals.[10] In this paper we report the first rate constants of a new neophyl-like rearrangement, the rearrangement of the α-(phenylthio)benzyl radical to the diphenylmethylthio radical in hydrocarbon solvent.

## Results

Rate constants for the rearrangement of the α-(phenylthio)benzyl radical were determined by competition between rearrangement and abstraction of hydrogen from thiophenol. To convert the relative rates of rearrangement vs abstraction to rate

(1) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; pp 161–183. Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; pp 67–113.

(2) Wieland, H. *Chem. Ber.* **1911**, *44*, 2250.

(3) Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438–1440.

(4) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063. The spiro[2.5]octadienyl radical opens to the phenylethyl radical ($\Delta H° = -16$ kcal/mol) with rate constants given by log $(k/\mathrm{s}^{-1}) = (9.2 \pm 1) - (2.8 \pm 0.4)/\theta$. If we assign a conventional A factor, $10^{13}$ s$^{-1}$, to this rearrangement and pivot the Arrhenius expression around the mean temperature of the kinetics, 153 K, an activation barrier of 5.4 kcal/mol results.

(5) Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zunardi, G.; Foresti, E.; Palmieri, P. *J. Am. Chem. Soc.* **1989**, *111*, 7723–7732.

(6) Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056–1059.

(7) Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964. For appropriate basis abstraction rate expressions to combine with relative rates of the neophyl rearrangement vs abstraction from tributylstannane, see ref 8.
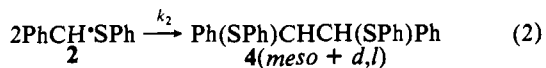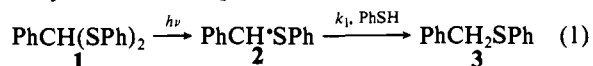
(8) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

(9) Wang, S. F.; Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1988**, *110*, 7235–7236.

(10) (a) Alnajjar, M. S.; Franz, J. A. *Prepr. Div. Fuel Chem., Am. Chem. Soc.* **1986**, *31*, 287–295. (b) The conversion of thioanisole to toluene in steam at 450 °C may be an example of a sulfur-to-carbon neophyl-like rearrangement: Van Buren, R. L.; Baltisberger, R. J.; Woolsey, N. F.; Stenberg, V. I. *J. Org. Chem.* **1982**, *47*, 4107–4110.

constants for rearrangement, a basis rate expression was determined for abstraction of hydrogen atom from thiophenol by the α-(phenylthio)benzyl radical.

**Measurement of a Basis Rate Expression for Abstraction of Hydrogen from Thiophenol by the α-(Phenylthio)benzyl Radical.** Samples of α,α-bis(phenylthio)toluene (1) and thiophenol in nonane were photolyzed in Pyrex tubes to produce α-(phenylthio)benzyl radical (2) (eq 1):

$$\text{PhCH(SPh)}_2 \xrightarrow{h\nu} \text{PhCH·SPh} \xrightarrow{k_1,\ \text{PhSH}} \text{PhCH}_2\text{SPh} \quad (1)$$
$$\mathbf{1} \qquad\qquad \mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

$$2\text{PhCH·SPh} \xrightarrow{k_2} \text{Ph(SPh)CHCH(SPh)Ph} \quad (2)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{4}(meso + d,l)$$

Abstraction of hydrogen ($k_1$) or self-reaction ($k_2$) by 2 produces benzyl phenyl sulfide (3) or 4, respectively. The dimer, 4, was found to undergo partial (ca. 5%) conversion to cis- and trans-stilbenes 5 under the reaction conditions. This reaction reflects the loss of thiophenoxyl radicals from 4 (eq 3):

$$4 \rightarrow \text{PhCH=CHPh} + 2\text{PhS·} \quad (3)$$
$$\mathbf{5}$$
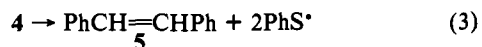
Control experiments revealed that the unimolecular decomposition of 4 was slow on the time scale of the kinetic experiments (≤180 s, 215 °C) in the dark. Conversion of 4 to stilbenes 5 probably reflects radical chain decomposition of 4 involving a radical displacement of SPh from 4 followed by β-scission of PhS· from the intermediate radical or partial direct photolysis of 4. Thus, the modest concentration of stilbenes was added to the concentration of the dimer to obtain the total self-termination product concentration. Under conditions of constant light flux, negligible consumption of optically dilute photoprecursor 1 (<1–2%) and negligible production of light-absorbing products, the concentration of α-(phenylthio)benzyl radical (2) remains constant. A plot of the yield of benzyl phenyl sulfide or [4 + 5] vs photolysis time was linear over the photolysis times employed, confirming that the radical concentrations were constant. Thus, the growth of appreciable concentrations of light-absorbing products, substantially changing the steady-state concentration of 2, was unimportant. The rate of formation of benzyl phenyl sulfide (3) is given by eq 4, and the rate of production of 4 + 5 is given by eq 5.

$$d[3]/dt = k_1[\text{PhSH}]_{av}[2] \quad (4)$$

$$d[4 + 5]/dt = k_2[2]^2 \quad (5)$$

Dividing the integral of eq 4 by the square root of the integral of eq 5 provides eq 6, which relates the rate constant for abstraction, $k_1$, to the termination rate constant, $k_2$, the duration of the photolysis, $\Delta t$ seconds, and product concentrations:

$$k_1 = (k_2)^{1/2}[3]/[\text{PhSH}]_{av}[4 + 5]^{1/2}(\Delta t)^{1/2} \quad (6)$$

The kinetic data exhibited excellent precision over a wide temperature range (27–220 °C) giving log $(k_1/k_2^{1/2}/\text{M}^{-1/2}\ \text{s}^{-1/2})$ = (2.86 ± 0.02) – (5.24 ± 0.03)/θ (errors are 1σ). This expression was converted to an absolute rate expression for abstraction using values of $k_2$ calculated from the von Smoluchowski equation[11–14]

(eq 7), with the diffusion coefficient, $D_{AB}$, given by the Spernol–Wirtz modification[15] of the Debye–Einstein equation (eq 8):

$$2k_2 = (8\pi/1000)\sigma\rho D_{AB}N \quad (7)$$

$$D_{AB}\eta/T = k/6\pi r_A f \quad (8)$$

Experimental values of the diffusion coefficients, $D_{AB}$, of benzyl phenyl sulfide, the model for 2, were determined as a function of temperature in nonane and found to be in excellent agreement with values calculated from eq 8.

**Errors in Abstraction Rate Constants Due to Errors in the Smoluchowski Termination Rate Constants.** Rate constants for self-termination of tert-butyl and benzyl radicals, gathered over a wide range of solvents, viscosity, and temperature, are described by the von Smoluchowski equation with high accuracy.[12] Fischer and co-workers have demonstrated that a variety of alkyl and benzyl radicals exhibit values of σ (the fraction of cage encounter pairs undergoing cage reaction) close to $^1/_4$ in nonassociating solvents.[16] Although photochemically generated singlet pairs may undergo appreciable cage escape,[17] close to 100% of thermally produced singlet encounter pairs appear to react in the cage,[18] as implied by σ = $^1/_4$. Claridge and Fischer[12b] suggest that the largest error in the Smoluchowski relation arises from the estimation of ρ. For benzyl radicals at room temperature in cyclohexane, the ratio $2k_{t,exptl}/2k_{t,calcd}$, where $2k_{t,calcd}$ is the Smoluchowski self-termination rate constant (eq 7), varies from 0.64 to 1.38, with an average of 1.02 ± 0.22. The temperature dependence of the deviation of experimental data vs the Smoluchowski prediction is also modest. For example, the experimental expression for self-termination of benzyl radical in hexane is given by ln $(2k_{t,exptl}/\text{M}^{-1}\ \text{s}^{-1})$ = 25.98 – 1803.6/$RT$[19] compared to the Smoluchowski expression, ln $(2k_{t,calcd}/\text{M}^{-1}\ \text{s}^{-1})$ = 26.53 – 2065.6/$RT$. From these expressions, $2k_{t,exptl}/2k_{t,calcd}$ = 0.89 at 25 °C and 0.75 at 220 °C. These results suggest that absolute errors in the Smoluchowski termination rate constants predicted for 2 in nonane should be no greater than 25% over the temperature range of the kinetics. The temperature dependence of termination constants calculated from the von Smoluchowski equation for self-termination of 2 is represented by ln $(2k_2/\text{M}^{-1}\ \text{s}^{-1})$ = 27.122 – 2.802/θ or log $(k_2^{1/2}/\text{M}^{-1/2}\ \text{s}^{-1/2})$ = 5.74 – 1.40/θ. Combining this expression with the relative rate expression for termination vs abstraction provides an absolute rate expression for the abstraction of hydrogen atom from thiophenol: log $(k_1/\text{M}^{-1}\ \text{s}^{-1})$ = (8.60 ± 0.02) – (6.64 ± 0.03)/θ (errors are 1σ). At the mean temperature of the abstraction kinetics, 398 K, $k_1$ = 0.96$k_2^{1/2}$ = 0.9 × 10⁵ M⁻¹ s⁻¹. Applying a ±25% error to $k_2$ yields a lower limit for $k_1$ of 0.8 × 10⁵ M⁻¹ s⁻¹ and an upper limit for $k_1$ of 1.0 × 10⁵ M⁻¹ s⁻¹. This modest error of ca. 10% in $k_1$ will be propagated linearly into the rearrangement rate constants (see below).

The Arrhenius plot of abstraction data is shown in Figure 1. For comparison, rate expressions for reactions of alkyl and benzyl

**Table I.** Rate Expressions for Reaction of Alkyl and Benzylic Radicals with Thiophenol[a]

| radical | log $(A/\text{M}^{-1}\ \text{s}^{-1})$ | $E_a$, kcal/mol | $k$, 300 K | ref |
|---|---|---|---|---|
| butyl | 9.41 ± 0.13 | 1.74 ± 0.21 | 1.4 × 10⁸ | 20 |
| isopropyl | 9.26 ± 0.19 | 1.70 ± 0.21 | 1.1 × 10⁸ | 20 |
| tert-butyl | 9.26 ± 0.26 | 1.50 ± 0.20 | 1.5 × 10⁸ | 20 |
| benzyl | 8.27 ± 0.14 | 3.79 ± 0.24 | 3.1 × 10⁵ | 19 |
| α-(phenyl-thio)benzyl | 8.60 ± 0.04 | 6.64 ± 0.07 | 5.8 × 10³ | this work |

[a] Errors are 2σ.

(11) The rate expression for self-reaction of 2 in nonane was calculated according to the method outlined by Fischer, et al. (ref 12) using the following data: radical model, benzyl phenyl sulfide, mp 317 K, bp 588 K; ρ = 7.0 × 10⁻⁸ cm (average of GD (ref 13), van der Waals (ref 14), and Spernol–Wirtz (ref 15) reaction diameters); solvent, nonane, MW 128.3, mp 220 K, bp 424 K; Andrade viscosity of nonane, ln (η, cp) = –4.207 + 2246.44/$RT$; benzyl phenyl sulfide, density = 1.3738 – (9.431 × 10⁻⁴ × T,K); nonane density = 0.9724 – (8.636 × 10⁻⁴ × T,K). The Spernol–Wirtz microfriction factor is given by $f$ = (0.16 + 0.4$r_A/r_B$)(0.9 + 0.4$T_A^r$ – 0.25$T_B^r$). Reduced temperatures are given by $T_X^r$ = $(T – T_X^f)/(T_X^b – T_X^f)$, where $T_X^f$ and $T_X^b$ are the freezing and boiling points of species X = A, benzyl phenyl sulfide the model of 2, or X = B, nonane. The radii in the microfriction factor term are given by $r_X$ = $(3V_X(\chi)/4\pi N)^{1/3}$, where $\chi$ = 0.74, the volume fraction for cubic closest-packed spheres, and $V_X$ values are density molar volumes. The resulting expression for self-termination of 2 is ln $(2k_2/\text{M}^{-1}\ \text{s}^{-1})$ = 27.122 – 2801.7/$RT$ or log $(k_2^{1/2}/\text{M}^{-1/2}\ \text{s}^{-1/2})$ = 5.74 – 1.40/θ.
(12) (a) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130. (b) Claridge, R. F. C.; Fischer, H. *J. Chem. Phys.* **1983**, *87*, 1960–1967.
(13) Gorell, J. H., Jr.; Dubois, J. T. *Trans. Faraday Soc.* **1978**, *63*, 347.
(14) Edward, J. T. *J. Chem. Educ.* **1970**, *47*(4), 261–270.
(15) Spernol, A.; Wirtz, K. *Z. Naturforsch.* **1953**, *8a*, 522–532.
(16) Saltiel, J.; Atwater, B. W. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley-Interscience: New York, 1989; Vol. 14, pp 1–99.
(17) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393–1396.
(18) Koenig, T.; Scott, T. W.; Franz, J. A. In *Bonding Energetics in Organometallic Compounds*; Marks, T., Ed.; ACS Symp. Ser. **1990**, *428*, 113–132.
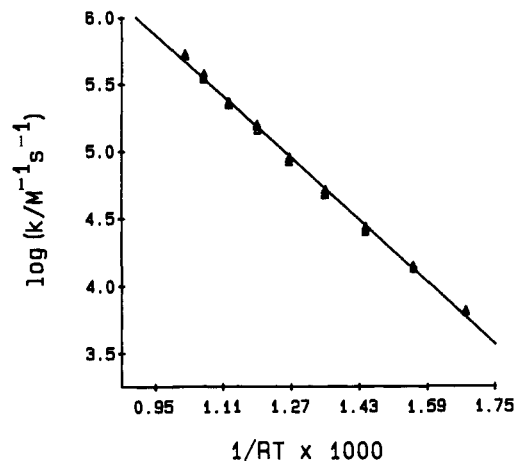(19) Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19.
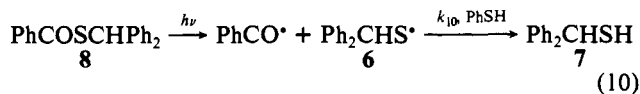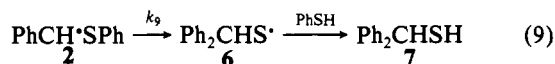
**Figure 1.** Arrhenius plot for the abstraction of hydrogen by the α-(phenylthio)benzyl radical from thiophenol in nonane, 27–220 °C.

radicals with thiophenol[19,20] are also presented in Table I. The rate constant for reaction of **2** with thiophenol is a factor of 53 lower at ambient temperature than that of benzyl radical, reflecting the additional stabilization imparted by the α-benzylthio substituent. The $A$ factor lies within the range expected for bimolecular hydrogen atom abstraction reactions, log $(A/M^{-1} s^{-1})$ = 8.5 ± 1.0.[21]

**Measurement of Rate Constants for 1,2-Phenyl Migration of the α-(Phenylthio)benzyl Radical (2).** Rate constants for the rearrangement of **2** were measured by the competition of rearrangement $(k_9)$ with hydrogen abstraction $(k_1)$ from thiophenol. **2** was produced by photolysis of the thioketal precursor **1** in the presence of thiophenol in nonane. Under the conditions of short

$$PhCH^{\cdot}SPh \xrightarrow{k_9} Ph_2CHS^{\cdot} \xrightarrow{PhSH} Ph_2CHSH \quad (9)$$
$$\quad \mathbf{2} \qquad\qquad \mathbf{6} \qquad\qquad\qquad \mathbf{7}$$

$$PhCOSCHPh_2 \xrightarrow{h\nu} PhCO^{\cdot} + Ph_2CHS^{\cdot} \xrightarrow{k_{10}, PhSH} Ph_2CHSH$$
$$\quad \mathbf{8} \qquad\qquad \mathbf{6} \qquad\qquad\qquad\qquad \mathbf{7}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (10)$$

extent of conversion of radical precursor (<2%) and donor thiophenol (<5%), the relative rate of rearrangement $(k_9)$ to abstraction $(k_1)$ is given by eq 11, which is appropriate for an irreversible rearrangement:

$$k_9/k_1 = [3]/[7][PhSH]_{av} \quad (11)$$

The product thio radical **6** will be efficiently scavenged by thiophenol. In a separate study, we have determined rate constants for reaction of octylthio radical with thiophenol: $k_{10}$ = 2.6 × 10$^5$ M$^{-1}$ s$^{-1}$ at room temperature.[22] By analogy with carbon-to-oxygen neophyl-like rearrangements and from thermochemical and semiempirical theoretical predictions, we expected the rearrangement to proceed in the opposite direction (e.g., **6** → **2**), and several attempts were carried out to observe the rearrangement of **6** to **2**. The thioester, **8**, was photolyzed to produce **6** at temperatures up to 220 °C in nonane in the presence and absence of donor thiophenol. Only the unrearranged product, diphenylmethanethiol, could be detected. No products (**3**, **4**, or **5**) from the reverse rearrangement were detected. Bis(diphenylmethyl) sulfide and bis(diphenylmethyl) disulfide were also photolyzed
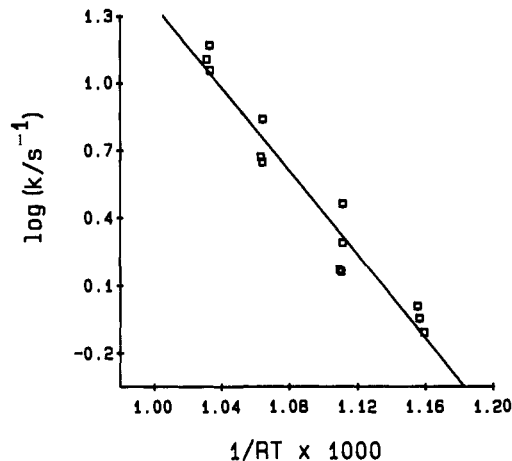
(20) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.

(21) (a) Benson, S. W. *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley-Interscience: New York, 1976. (b) Benson, S. W. *Chem. Rev.* **1978**, *1*, 23. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 453. (d) Gutman, D. *Acc. Chem. Res.* **1990**, *23*, 375–380 and references therein. (e) Wayner, D. D. M.; Griller, D. D. In *Advances in Free Radical Chemistry*; Tanner, D. D., Ed.; JAI Press, Inc.: Greenwich, CT, 1990; Vol. 1, pp 159–192.

(22) Alnajjar, M. S.; Garrossian, M.; Autrey, T.; Ferris, K. F.; Franz, J. A. *J. Org. Chem.*, manuscript in preparation.

**Figure 2.** Arrhenius plot for the neophyl-like rearrangement of the α-(phenylthio)benzyl radical in nonane, 160–215 °C.

at temperatures up to 220 °C in nonane, with no rearrangement products being detected. By contrast, photolysis of **1** in the absence of thiophenol in nonane produced extensive rearrangement at 215 °C. Trapping of **6** by hydrogen atom abstraction from thiophenol is clearly much faster than the reverse rearrangement, **6** → **2**. Thus, the products of the rearrangement **2** → **6** were satisfactorily demonstrated to be formed with kinetic control of product ratios under the conditions of the kinetic experiments, and relative rate kinetics were determined by photolysis of **1** in solutions of PhSH in nonane from 160 to 215 °C. The upper bound of this range was imposed by the limit of thermal stability of the product diphenylmethanethiol (**7**). The lower bound of the range was dictated by the necessity of using thiophenol as the donor at sufficiently high concentrations to maintain constant concentrations of thiophenol, prevent consumption of **7**, and render negligible the small amount of thiophenol produced as a side product of the photolysis. The relatively high concentrations of thiophenol, combined with a high rearrangement barrier, result in negligible rearrangement below ca. 150 °C and, hence, the relatively narrow temperature range. The resulting Arrhenius expression for rearrangement versus abstraction was found to be log $(k_9/k_1/M)$ = (2.05 ± 0.74) − (14.8 ± 1.55)/θ. Combining this relative rate expression with the rate of abstraction by **2** from thiophenol provides the rate expression for rearrangement, log $(k_9/s^{-1})$ = (10.65 ± 0.74) − (21.4 ± 1.55)/θ, where the errors are 1σ and reflect only errors in the rearrangement competition. As mentioned above, values of $k_9$ may include a linearly propagated error of up to ca. 10% of $k_9$ associated with errors in the Smoluchowski estimate of termination rate constants. An Arrhenius plot of the rearrangement rate data is shown in Figure 2.
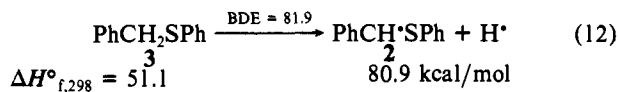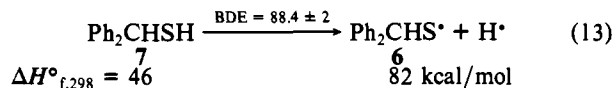
**Discussion**

The Arrhenius expression for rearrangement of **2**, log $(k_9/s^{-1})$ = (10.65 ± 0.74) − (21.4 ± 1.55)/θ, reveals an activation barrier much higher than barriers previously reported for exergonic all-carbon neophyl-like rearrangements.[1,7] For example, the parent neophyl rearrangement $(\Delta H° = -6$ kcal/mol) is represented by the Arrhenius expression, log $(k/s^{-1})$ = (11.55 ± 0.24) − (11.8 ± 0.48)/θ.[7] All-carbon neophyl rearrangements exhibit $A$ factors around 10$^{11.5-11.8}$.[1] Thus, the Arrhenius parameters for $k_9$ may be slightly low. Pivoting the Arrhenius expression around the mean temperature of the kinetics, $T_m$ = 460 K with $A_9$ = 10$^{11.7}$, would give $E_9$ = 23.6 kcal/mol, which lies within the 2σ error limit. In order to compare the rearrangement of **2** with all-carbon neophyl rearrangements of comparable exergonicity and to estimate the depth of the potential well, if any, for the intermediate in the rearrangement **2** → **6**, we examine the thermochemistry of the reactant, product, and intermediate in the rearrangement.

**Thermochemistry of the Rearrangement of 2.** The bond dissociation energy of benzyl phenyl sulfide has been found to be 81.9 ± 2 kcal/mol,[23–25] compared with 88 kcal/mol for toluene or 85.5 for ethylbenzene:[21c]

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$$PhCH_2SPh \xrightarrow{BDE = 81.9} PhCH\cdot SPh + H\cdot \qquad (12)$$

$$\underset{\mathbf{3}}{\phantom{PhCH_2SPh}} \qquad\qquad \underset{\mathbf{2}}{\phantom{PhCH\cdot SPh}}$$

$$\Delta H^\circ_{f,298} = 51.1 \qquad\qquad 80.9 \text{ kcal/mol}$$

Although reliable heats of formation can be estimated for **2** and **3**,[26] thermochemical data are less well-developed for branched aryl-substituted sulfur-containing structures.[27]

To construct $\Delta H^\circ_{f,298}$ for **7**, we estimate the group additivity parameter for diaryl-substituted sulfide carbon, $C(C_B)_2(S)(H)$, to be $-2.7$ kcal/mol.[28] This yields $\Delta H^\circ_{f,298} = 46$ kcal/mol for $Ph_2CHSH$. From S–H bond dissociation energies of alkanethiols, $(88.4 \pm 2 \text{ kcal/mol}^{29})$, the heat of formation of diphenylmethylthio radical is estimated to be $82 \pm$ ca. 2 kcal/mol:

$$Ph_2CHSH \xrightarrow{BDE = 88.4 \pm 2} Ph_2CHS\cdot + H\cdot \qquad (13)$$

$$\underset{\mathbf{7}}{\phantom{Ph_2CHSH}} \qquad\qquad \underset{\mathbf{6}}{\phantom{Ph_2CHS\cdot}}$$

$$\Delta H^\circ_{f,298} = 46 \qquad\qquad 82 \text{ kcal/mol}$$

The enthalpy change for the rearrangement is predicted to be approximately thermoneutral: $\Delta H^\circ = 1 \pm$ ca. 4 kcal/mol. Although the reaction was near-thermoneutral, only rearrangement in the direction **2 → 6** was observed. In a separate study, we have determined the rate expression for reaction of an alkylthio radical with thiophenol in alkane solvent: $\log (k_{abs}/M^{-1} s^{-1}) = 8.5 - 4.2/\theta$.[22] Assuming $k_{-9} \approx k_9$, then $k_{abs}[PhSH]/k_{-9} = 170$ at 460 K and $1.5 \times 10^{-4}$ M [PhSH]. Clearly, the rate of trapping of **6** is much faster than the reverse rearrangement, $k_{-9}$. By contrast, for the forward rearrangement, $k_1[PhSH]/k_9 = 14$ at 460 K, allowing about 7% rearrangement.

No measurements of Arrhenius parameters have been reported for examples of thermoneutral all-carbon neophyl rearrangements for comparison with the near-thermoneutral reaction **2 → 6**. Beckwith and Ingold cite the unpublished work of Griller in which $E_{14}$ is estimated to be $>19$ kcal/mol. From the estimated barrier for ring opening of the spiro[2.5]octadienyl radical, 5.4 kcal/mol,[4] and $\Delta H^\circ = 16$ kcal/mol for intermediate formation, we estimate $E_{14}$ to be 21 kcal/mol:

$$PhCH_2CD_2\cdot \rightarrow PhCD_2CH_2\cdot \qquad (14)$$

(Early studies of the [1-$^{14}$C]-1,1,2-triphenylethyl[30] and [2-$^{14}$C]-2-phenylethyl radical rearrangements[31] do not provide reliable kinetic data due to uncertainties in the identity and concentrations of hydrogen atom donors.) Thus, the barrier for rearrangement of **2**, 21.4 kcal/mol (or the adjusted value with an assigned $A$ factor of $10^{11.7}$ s$^{-1}$, 23.6 kcal/mol), is comparable to or slightly higher than the estimate for a representative thermoneutral all-carbon neophyl rearrangement.

**Heat of Formation of the Intermediate (or Transitional) Structure 10.** We estimate the heat of formation of **10** to be 100.3 $\pm$ 3 kcal/mol. The error in this estimate may be as great as $\pm 3$ kcal/mol, from uncertainty introduced by substitution of two



C5-S7-C8 ANGLE (DEGREES)

**Figure 3.** MNDO-PM3(RHF) potential surface for the rearrangement **2 → 6**. The inflection on the potential surface corresponding to the structure of **10** is apparent in the vicinity of angle C5–S7–C8 = 48° (see Figure 4c).

additivity parameters[32] and estimation of ring corrections for the thiaspiro[2.5]octadiene system[33] and the C–H bond dissociation energy of **9**.[34,35]



$$\Delta H^\circ_{f,298} = 79.4 \qquad\qquad 100.3 \text{ kcal/mol}$$

$$\underset{\mathbf{9}}{\phantom{xxxx}} \qquad\qquad\qquad \underset{\mathbf{10}}{\phantom{xxxx}}$$

Thus, $\Delta H^\circ(\mathbf{2 → 10})$ is estimated to be 19.4 $\pm$ ca. 3 kcal/mol. This is consistent with the observed activation enthalpy, 20.5 $\pm$ 3 kcal/mol, and permits a small barrier for ring opening within the error limits. Unfortunately, the combined errors in $\Delta H^\circ(\mathbf{2 → 10})$ and $\Delta H^\ddagger_9$ are too large for meaningful estimation of the potential well for C–C cleavage of **10**.[36]

**Ring-Opening Reactions of Spiro[2.5]octadienyl Radicals.** Kinetic data for ring-opening reactions of the spiro[2.5]octadienyl[4]

(23) The α-CH BDE of benzyl phenyl sulfide (81.9 $\pm$ 2 kcal/mol) was determined by laser photoacoustic calorimetry (ref 24): unpublished work of M. S. Alnajjar and D. Griller.

(24) Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

(25) Janousek, B. K.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125.

(26) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1988**, Suppl *1*, *17*, 1. An estimate of the gas-phase heat of formation of **3**, 46.0 kcal/mol, from the average of PhSSPh (58.0 kcal/mol) and PhCH$_2$CH$_2$Ph (34.2 kcal/mol) was reported. We prefer to combine PhSPh (55 kcal/mol) and PhCH$_2$SCH$_2$Ph (46 kcal/mol), which gives an estimate of 50.5 kcal/mol, in good agreement with the group additivity value, 51.1 kcal/mol.
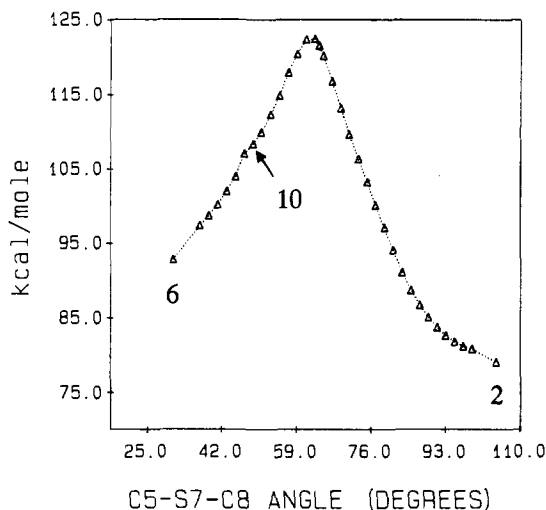
(27) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic & Organometallic Compounds*; Academic Press: New York, 1970.

(28) From $\Delta H^\circ_{f,298} = 39$ kcal/mol for Ph$_2$CH$_2$ (ref 28), the parameter $C(C_B)_2(H)_2$ is estimated to be $-5$ kcal/mol. Thus, $C(C_B)_2(S)(H) = C(C)_2$-$(S)(H) + (C(C_B)_2(H)_2 - C(C)_2(H)_2) = -2.64 + (-5 - (-4.93)) = -2.7$.

(29) Griller, D.; Simões, J. A. M.; Wayner, D. D. M. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990; pp 37–52.
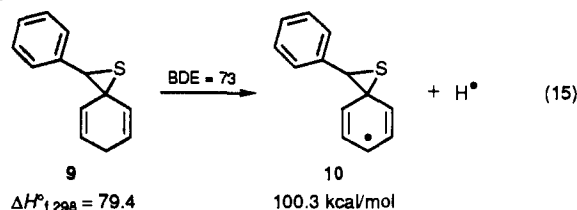
(30) Bonner, W. A.; Mango, F. D. *J. Org. Chem.* **1964**, *29*, 29.

(31) Slaugh, I. H. *J. Am. Chem. Soc.* **1959**, *81*, 2262.

(32) Estimation of the $\Delta H^\circ_{f,298}$ value of diene **9** requires two additivity parameters, $C(C_B)(C)(S)(H)$ and $C(C_d)_2(C)(S)$. Substitution of C(C)-(C)(S)(H) and C(C)(C)(C)(S) for these parameters and addition of a steric correction of 0.8 kcal/mol for the phenyl–cyclohexadiene interaction results in $\Delta H^\circ_{f,298} = 79.4$ kcal/mol for **9**. The errors associated with these parameters are probably not greater than 1 and 2 kcal/mol, respectively, on the basis of trends in carbon, oxygen, and sulfur secondary and tertiary additivity elements (ref 21a).

(33) The ring correction of thiirane, 17.7 kcal/mol, is retained for thiaspiro[2.5]octadiene systems, because only very minor bond angle and bond length changes occur at the juncture of the thiirane and cyclohexadiene rings. For thiaspiro[2.5]octa-4,7-diene, PM3(RHF) calculations predict a C4–C3–C8 angle (spanning the juncture of the two rings) of 115.3°, compared to 113.6° for the C1–C6–C5 angle of cyclohexa-1,3-dien-5-yl radical (C6 is the methylene of cyclohexadienyl radical). If the 115.3° C1–C6–C5 angle is imposed on cyclohexadienyl radical, the heat of formation increases by only 0.05 kcal/mol. Bond lengths about the quaternary center change by less than 0.02 Å.

(34) The tread of resonance energies for radicals, allyl, 11.5, pentadienyl, 17.8, and heptatrienyl, 21.0 kcal/mol, suggests that *additional* pseudoallylic stabilization by the cyclopropyl ring of the pentadienyl radical will be no more than 3 kcal/mol: Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119. Since the cyclopropyl ring stabilizes a primary alkyl radical by only 2 kcal/mol (see ref 35), no additional stabilization of the cyclohexadienyl radical is expected.

(35) A stabilization energy of 1.8 kcal/mol is suggested for the cyclopropylcarbinyl radical: Radom, L.; Paviot, J.; Pople, J. A.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1974**, 58–60. Delbecq, F. *THEOCHEM* **1986**, *136*, 67–75. An experimental determination of $\Delta H_f^\circ = 51.1$ kcal/mol was reported for a bond dissociation energy of cyclopropylmethane of 97.4 $\pm$ 1.6 kcal/mol for a stabilization energy of 3.1 kcal/mol: McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3(4)*, 359. In selecting a stabilization energy of 1.8 kcal/mol, $\Delta H_f^\circ = 52.2$ kcal/mol for cyclopropylcarbinyl. For 3-butenyl radical, $\Delta H_f^\circ = 48.3$ kcal/mol, giving $\Delta H^\circ = -3.9$ kcal/mol for the cyclopropylcarbinyl rearrangement.

A.

B.



D.

C.
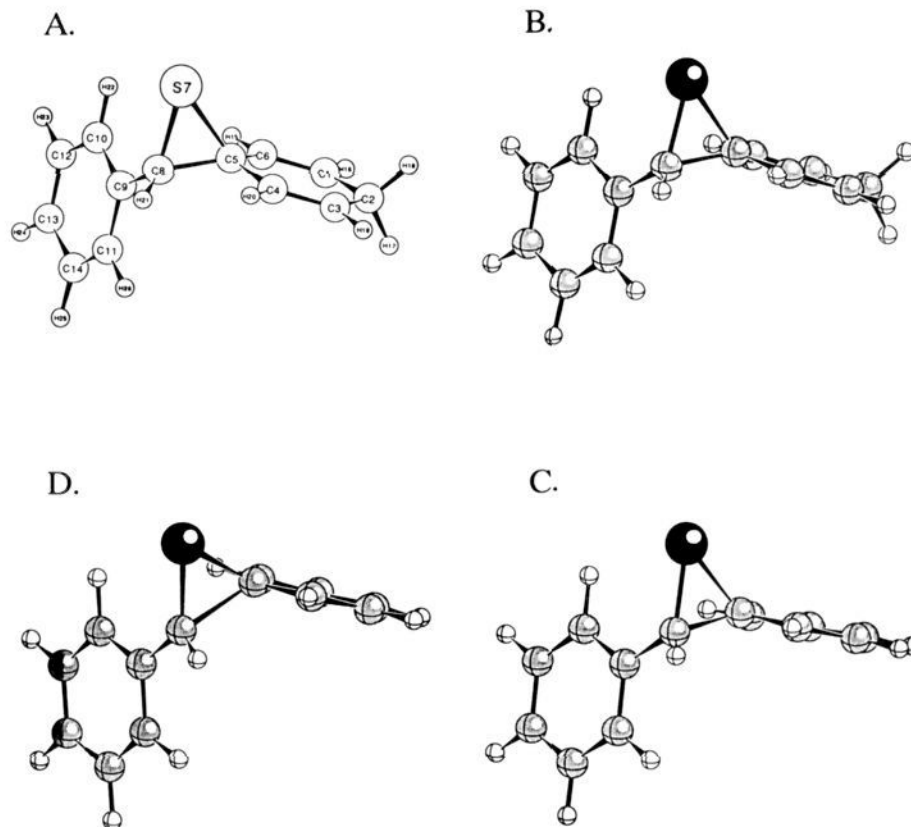


**Figure 4.** (a) Atom numbering for Figure 4b–d. (b) MNDO-PM3 structure of **9**. (c) Structure of **10** calculated by retaining the C8–S7–C5 bond angle of **9**, 48.1°. (d) Transition-state structure. Bond lengths: C5–S7, 1.83 Å; C8–C5, 1.86 Å; S7–C5, 1.78 Å. Dihedral angles: S7–C5–C6–C1, −162.5°; C8–C5–C6–C1, 132°.

and 2-phenyl-2-methyloxaspiro[2.5]octadienyl[6] radicals suggest that spiro[2.5]octadienyl radicals will exhibit significantly higher barriers to opening than substituted cyclopropylcarbinyl radicals. A barrier of >8.8 kcal/mol is estimated for the 2-phenyl-2-methyloxaspiro[2.5]octadienyl radical (for C–C cleavage, $\Delta H°$ ≈ −20 kcal/mol), much higher than the barrier for ring opening of the rearrangement of the *trans*-(2-phenylcyclopropyl)methyl radical to the 4-phenylbuten-4-yl radical ($\Delta H° = -17$ kcal/mol)[37] of 3.25 kcal/mol, although the incipient radical center should be stabilized by a phenyl group in both systems. The activation barrier for ring opening of the spiro[2.5]octadienyl radical, $E_a$ = 5.4 kcal/mol[4] ($\Delta H° = -16$ kcal/mol), is also appreciably higher than the value predicted from an Evans–Polanyi correlation of Arrhenius activation barriers with enthalpy change for substituted cyclopropylcarbinyl radicals, $E_a$ = 2–3 kcal/mol: activation barriers for cyclopropylcarbinyl rearrangements vary from 3.25 kcal/mol[37] for the *trans*-(2-phenylcyclopropyl)methyl radical to 7.05 kcal/mol for the cyclopropylcarbinyl radical ($\Delta H°$ = −3.9 kcal/mol).[38,39] While the existing data for ring opening of spiro[2.5]octadienyl systems[4,6] is very limited, activation barriers for C–C cleavage as high as 8–9 kcal/mol are possible for systems such as **10**, even though C–C cleavage is highly exothermic ($\Delta H°$(**10** → **2**) = −19 kcal/mol). Semiempirical calculations predict that barriers to ring opening via C–C cleavage of thiira-

nylcarbinyl and thiaspiro[2.5]octadienyl radicals will be higher than either the oxygen or all-carbon analogues.[40] Higher ring-opening barriers for spiro[2.5]octadienyl radical systems may result from the distortion of the cyclopropyl ring system necessary to achieve optimal overlap with the cyclohexadienyl π-system and the C–C bond undergoing cleavage in the transition state. Roberts and Walton[41,42] have found that rates of formation and ring-opening reactions of radicals adjacent to cyclopropyl rings in spiro[2.n]- and bicyclo[n.1.0]alkanes are sensitive to the dihedral angle between the adjacent C–H bond (or, for the radical, the singly occupied orbital) and the cyclopropane C–C bond of the parent hydrocarbon or product radical. The high barrier for rearrangement of the bicyclo[2.1.0]pentyl radical ($\Delta H°$ ≈ −30 kcal/mol, $E_a$ = 5.2 kcal/mol) is due to the near-orthogonality between the radical SOMO and the central cyclopropane bond undergoing scission.[43]

(38) Newcomb, M.; Glenn, A. *J. Am. Chem. Soc.* **1989**, *111*, 275–277.
(39) For a recent study of fast radical clocks and a review of cyclopropylcarbinyl rearrangements, see: Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.*, in press.
(40) We have performed semiempirical calculations of the potential surfaces of oxygen, sulfur, and all-carbon analogues of cyclopropylcarbinyl and spiro[2.5]octadienyl radical ring-opening reactions. The calculations predict C–C cleavage barriers of 22.2, 18.2, and 18.0 kcal/mol for thiiranyl-, oxiranyl-, and cyclopropylcarbinyl radicals. PM3(RHF) calculations predict C–C cleavage barriers of 18.2, 10.1, and 10.2 kcal/mol for thiaspiro-, oxaspiro-, and spiro[2.5]octadienyl radicals. Since the thiaspiro[2.5]octadienyl radical is not a stable intermediate, the heat of formation was estimated by retaining the internal C–S–C angle of the thiirane ring of the parent hydrocarbon, thiaspiro[2.5]octa-4,7-diene.
(41) Roberts, C.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, *(16)*, 1109–1111; *J. Chem. Soc., Perkin Trans. 2* **1985**, *2*, 841–846.
(42) For a review of C–H reactivity in bicyclo- and spirocyclopropylalkanes, see: Ingold, K. U.; Walton, J. C. *Acc. Chem. Res.* **1986**, *19*, 72–77.
(43) Arrhenius parameters for rearrangement of the *trans*-(2-phenylcyclopropyl)methyl radical: Newcomb, M.; Manek, B. M.; Glenn, A. *J. Am. Chem. Soc.* **1991**, *113*, 949–958.

(36) Comparing the upper limit of the experimental value (2σ error, 3.1 kcal/mol) of $\Delta H^{\ddagger}_9$, 23.5 kcal/mol with the estimated lower limit of $\Delta H°$(**2** → **10**), 16 kcal/mol, yields an upper limit for the barrier to C–C cleavage of **10** → **6** of 8 kcal/mol.
(37) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662. The reported data yield an Arrhenius expression: log ($k$/s⁻¹) = 13.75 − 3.25/θ. The $A$ factor is slightly high in this expression, probably due to a small error in the basis competitive rate expression (hydrogen abstraction from phenylselenol). Since $\Delta S^{\ddagger}$ must be ≤0 eu for this rearrangement, log ($A$/s⁻¹) will be slightly less than 13. Thus, $E_a$ may be as low as 2.3 kcal/mol.

*Rearrangement of the α-(Phenylthio)benzyl Radical*

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**Potential Energy Surface for the Rearrangement 2 → 6.** MNDO-PM3(RHF)[44] semiempirical calculations of the potential energy surfaces for the rearrangement 2 → 6 and for rearrangements of the thiaspiro[2.5]octadienyl and thiiranylcarbinyl radicals were carried out. The potential energy surface for the rearrangement 2 → 6 is shown in Figure 3. PM3 structures of 9, 10, and the transition-state structure are shown in Figure 4. The calculations predict that 10 is *not* an intermediate on the potential surface, but undergoes barrierless C5–S7 cleavage or rearrangement (C5–C8 cleavage). An inflection is apparent on the surface in the vicinity of angle C8–S7–C5 = 48°. This is near the C8–S7–C5 angle, 48.1°, of the parent hydrocarbon, 9, and predicts that the energy requirements for C5–S7 bond extension in 10 are more than compensated by synchronous release of the strain energy of the thiiranyl ring system and other contributions. The transition state occurs at a C8–S7–C5 angle of 62.13°[45] and corresponds to C8–C5 bond formation. PM3(RHF) thermodynamic calculations predict log $(A_9/s^{-1}) \approx 12.3$,[45] close to the rough estimate suggested for $A_9$ above of log $(A_9/s^{-1}) = 11.7$. A comparison of 10 (Figure 4c) with the transition-state structure (Figure 4d) shows the approach of the sulfur atom to the plane of the cyclohexadienyl ring. The dihedral angle S7–C5–C4–C3 increases from 135.8 in 10 to 162.9° in the transition structure, while the C8–C5–C4–C3 dihedral angle closes from 151.3 in 10 to 132°. The C5–C8 bond distance increases from 1.51 in 10 to 1.86 Å in the transition structure. The PM3 heat of formation of 6 is overestimated by about 11 kcal/mol, a systematic error associated with the diarylmethane structure, and the heat of formation of the transition-state structure, 122.4 kcal/mol, is overestimated by about 20 kcal/mol.[46] While absolute magnitudes of activation barriers for β-scission reactions of radicals are typically overestimated by PM3 and AM1 calculations by as much 20 kcal/mol, the *relative* barriers of similar reactions can be in quite satisfactory agreement with experiment.[47] It is encouraging for the present purposes that PM3 accurately predicts activation barriers for the formation and cleavage of carbon–sulfur bonds in radical addition/β-scission reactions. For example, the addition of methylthio radical to ethylene exhibits a barrier of 1.7 kcal/mol ($\Delta H° = -12$ kcal/mol)[48] compared with the PM3 prediction of 1.8 kcal/mol. PM3 correctly predicts low barriers for addition of alkylthio

radicals to aromatic systems and for scission of thio radicals from mercaptocyclohexadienyl radicals.[49] The rearrangement $PhCH_2S^\bullet$ → $PhSCH_2^\bullet$, like the rearrangement 2 → 6, is predicted by PM3 to proceed via a transitional, rather than intermediate, thiaspiro[2.5]octadienyl radical. The transition state corresponds to C–C bond formation, similar to the rearrangement 2 → 6.[50] Finally, the rearrangement of allylthio radical to the (vinylthio)methyl radical is predicted by PM3(RHF) to proceed through the intermediate thiiranylcarbinyl radical, which undergoes C–S cleavage with a barrier of only 0.5 kcal/mol but C–C cleavage with barrier of 22.2 kcal/mol.[51] The satisfactory prediction of activation barriers for addition of thio radicals to olefins and rapid, reversible addition to aromatic systems by PM3 provides greater confidence in the prediction that C–S cleavage is a near-barrierless process for thiaspiro[2.5]octadienyl radicals. If correct, thiiranylcarbinyl radicals may provide examples of radical clocks for application in picosecond time regimes. Work in this laboratory is underway to determine the lifetimes of thiaspiro[2.5]octadienyl and thiiranylcarbinyl radicals.

## Summary

A rate expression for the abstraction of hydrogen from thiophenol by the α-(phenylthio)benzyl radical has been determined, providing with previous work[19,20] a selection of rate expressions for use in competitive kinetic studies of reactions of alkyl, benzyl, and substituted benzylic radicals with thiophenol. The first rate expression for the neophyl-like 1,2-phenyl migration from sulfur to a carbon-centered radical has been presented. Thermochemical estimates predict that the intermediate (if any) will undergo C–C cleavage with a barrier no greater than ca. 8 kcal/mol. The need for thermochemical data for spiro[2.n]octadienes is underscored by this study. Semiempirical MNDO-PM3(RHF) calculations predict near-zero barriers to ring opening of thiiranylcarbinyl and thiaspiro[2.5]octadienyl radicals via C–S cleavage. Barriers to ring opening via C–C cleavage of thiiranyl radicals systems are predicted to be greater than the all-carbon analogues. The 1,2-phenyl migration from sulfur to a carbon-centered radical and the reverse reaction are key pathways for the formation and cleavage of strong bonds during the liquefaction of high sulfur-containing coal.[10]

## Experimental Section

**Reagents.** Benzyl phenyl sulfide, *cis*- and *trans*-stilbenes, and benzaldehyde (Aldrich) were used as received. Benzenethiocarboxylic acid, *S*-diphenylmethyl ester (8) was prepared from diphenylmethanethiol, benzoyl chloride, and triethylamine in anhydrous ether: mp, 93–95 °C; $^{13}$C NMR (Varian VXR-300) ($\delta$, $CDCl_3$) 190.1, 140.8, 136.5, 133.5, 128.4, 127.3, 51.9 ppm; $^1$H NMR 7.98 (d, 2 H), 7.65–7.2 (m, 13 H), 6.16 (s, 1 H). Anal. Calcd for $C_{20}H_{15}SO$: C, 78.91; H, 5.30; S, 10.51. Found: C, 79.07; H, 5.36; S, 10.48. Diphenylmethanethiol,[52] benzaldehyde diphenyl mercaptal,[53] and 1,2-bis(phenylthio)-1,2-diphenyl-

(44) PM3 calculations were carried out using the MOPAC Molecular Orbital Program Package, QCPE 455 (version 6.0), Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, IN. (a) Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209–220 and 221–264. (b) Dewar, M. J. S. *J. Comp. Chem.* **1990**, *11*, 541–542. (c) Stewart, J. J. P. *J. Comp. Chem.* **1990**, *11*, 543–544.

(45) The transition-state structure was refined by the method of nonlinear least-squares minimization of the gradient to a final value of gradient norm = 0.23 kcal/mol. A normal coordinate vibrational force calculation revealed a single imaginary frequency, −927.5 cm⁻¹, corresponding to C5–C8 motion. The PM3(RHF) heat of formation of the transition structure was 122.54 kcal/mol at 300 K and 128.12 kcal/mol at 400 K; the entropy ($\sigma = 2$) was 106.8 eu at 300 K and 122.76 eu at 400 K. The PM3(RHF) heat of formation of ground state 2 was 79.58 kcal/mol at 300 K and 84.72 kcal/mol at 400 K; the entropy of the ground state ($\sigma = 4$) was found to be 110.9 eu at 300 K and 127.04 eu at 400 K. In the latter force and thermodynamics calculation, the essentially free Ph–S rotation is left as a low-frequency vibrational mode. Neglecting this, PM3 estimates $\Delta S^\ddagger(300) = -4.1$ eu for an estimate of the Arrhenius $A$ factor of log $(A_9/s^{-1}) = 12.3$, from the relation $A = (ekT/h)(\exp(\Delta S^\ddagger/R))$.

(46) The heat of formation of 9 is predicted to be 88 kcal/mol by PM3. The heat of formation predicted by PM3 for 10 is 109 kcal/mol, corresponding to a C–H bond dissociation energy of 73 kcal/mol. Both of these values are about 9 kcal/mol higher than the thermochemical estimates for 9 and 10 and reflect characteristic systematic errors in PM3 associated with the thiirane and cyclohexadiene ring systems and steric congestion. The method overestimates the heat of formation of thiirane by +10.9 kcal/mol, of 1,4-cyclohexadiene by −6.9 kcal/mol, and of derivatives of diphenylmethane by an average of +7.8 kcal/mol (PM3 errors for $Ph_2CH_2$, $Ph_2CHOH$, and $Ph_2CHSH$ are ca. 4.6, 7.7, and 11.1 kcal/mol). If these errors are assumed to contribute to a composite systematic error of 10.9 − 6.9 + 7.8 = 11.8 kcal/mol, then the "corrected" PM3 heats of formation of 9 and 10 are 78 and 97 kcal/mol, compared to the group additivity estimates, 79 and 100 kcal/mol.

(47) For example, see: Autrey, S. T.; Alnajjar, M. S.; Nelson, D. A.; Franz, J. A. *J. Org. Chem.* **1991**, *56*, 2197–2202.

(48) Kerr, J. A.; Moss, S. J. *Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press, Inc.: Boca Raton, FL, 1981; Vol. II, p 156.

(49) PM3(RHF) predicts a barrier of 7.6 kcal/mol for the addition of HS to the ipso position of toluene. Scission of HS from 1-mercapto-1-methyl-cyclohexadienyl radical is predicted to exhibit a barrier of 12 kcal/mol by PM3(RHF). Thus, PM3 successfully predicts the rapid and readily reversible addition of thio radicals to aromatic rings. A barrier of 33.5 kcal/mol is predicted for scission of $CH_3$ from 1-mercapto-1-methylcyclohexadienyl radical, illustrating the trend of PM3 to systematically overestimate C–C scission barriers, in this case by ca. 10 kcal/mol.

(50) PM3(RHF) heats of formation for $PhSCH_2^\bullet$, $PhCH_2S^\bullet$, and thiaspiro[2.5]octadienyl radicals are 64.0, 58.5, and 79.8 kcal/mol, in excellent agreement with thermochemical estimates of 63.5, 59.2, and 74–77 kcal/mol. The transition state occurs at the thiiranyl C–S–C angle of 64°, 98.0 kcal/mol. An inflection is apparent on the potential surface in the vicinity of angle C–S–C of 47–48° (78–80 kcal/mol). Barrierless C–S cleavage occurs from this point on the surface. As in the case of 10, the thiaspiro[2.5]octadienyl radical is not a stable structure.

(51) PM3 heats of formation for allylthio, (vinylthio)methyl, and thiiranylcarbinyl radicals are 49.8, 52.5, and 60.2 kcal/mol, in good agreement with the thermochemical estimates of 49.3, 56, and 56 kcal/mol for these species. The transition state for C3–S1 cleavage (numbering: C2–S1–C3–C4') occurs on extension of the S1–C3 bond from 1.86 to 2.02 Å (heat of formation, 60.74 kcal/mol). The transition state for C2–C3 cleavage occurs on extension of the C2–C3 bond from 1.50 to 2.08 Å (heat of formation, 82.2 kcal/mol).

(52) Klenk, M.; Suter, C.; Archer, S. *J. Am. Chem. Soc.* **1948**, *70*, 3846.

(53) Sondheimer, F.; Rosenthal, D. *J. Am. Chem. Soc.* **1958**, *80*, 3995.

ethane[54] (1:1 mixture of meso and d,l isomers) were prepared according to literature methods.

**Kinetic Experiments.** Stock solutions of photoprecursors and thiophenol in nonane were sealed in Pyrex tubes and degassed with three freeze–thaw cycles on a high-vacuum line. Variable-temperature photolysis of reaction samples with light from a defocused 450-W xenon lamp (Hanovia L-5179-000) were carried out in a thermostated octadecane bath equipped with quartz windows and purged with argon. For reactions of the α-(phenylthio)benzyl radical, optically dilute (above 330 nm) solutions of α,α-bis(phenylthio)toluene (**1**, 0.01 M) were photolyzed for 15–120 s in the presence of $3 \times 10^{-3}$ M thiophenol from 27 to 220 °C. In a typical case, photolysis of the stock solution for 60 s at 299.8 K produced $2.204 \times 10^{-5}$ M **3**, $6.07 \times 10^{-5}$ M **4**, $1.519 \times 10^{-6}$ M *cis*-stilbene, and $4.426 \times 10^{-7}$ M *trans*-stilbene at [PhSH] = $2.912 \times 10^{-3}$ M, giving, using eq 6, $k_1 = (2.719 \times 10^9)^{1/2}(2.204 \times 10^{-5})/(6.266 \times 10^{-5})^{1/2}(60)^{1/2}(2.912 \times 10^{-3}) = 6.428 \times 10^3$ M$^{-1}$ s$^{-1}$. A full tabulation of kinetic data can be found in the supplementary material.

Rearrangement kinetics were determined over the range 160–215 °C. In the rearrangement study, the concentration of thiophenol was reduced to $1.5 \times 10^{-4}$ M. The concentration of thiophenol was chosen to insure that the small amount of photolytically produced thiophenol remained an insignificant (<5%) fraction of the initial donor concentration and that **7** was protected from consumption by an excess of thiophenol. In a typical case, photolysis of **I** at 434 K produced **3** ($4.445 \times 10^{-6}$ M) and **7** ($1.548 \times 10^{-7}$ M) and consumed 3.15% of the thiophenol for an average, density-corrected [PhSH]$_{av,dc}$ of $1.202 \times 10^{-4}$ M. Using $k_1 = 1.849 \times 10^5$ M$^{-1}$ s$^{-1}$ at 434 K, $k_9 = (1.849 \times 10^5)(1.202 \times 10^{-4})(1.548 \times 10^{-7})/(4.445 \times 10^{-6}) = 7.739 \times 10^{-1}$ s$^{-1}$. All product and donor concentrations were corrected for changes in solvent density with temperature. Careful analyses of sealed but unphotolyzed samples were carried out as control experiments. Products of kinetic experiments were analyzed using a Hewlett-Packard Model 5890 gas chromatograph equipped with a 30-m J & W Scientific DB-17 or a 10-m DB-5 column with direct on-column injection. The 10-m column was required for the analyses of *meso*- and *d,l*-**4**.

**Irreversibility of the Rearrangement 2 → 6.** Solutions of **8** (0.01 M) in nonane without added PhSH or with $1.5 \times 10^{-4}$ M PhSH were photolyzed at 215 °C. No products (stilbenes or benzyl phenyl sulfide) from the rearrangement **6 → 2** were detected. Only diphenylmethanethiol (**7**) was found. Similar experiments using bis(diphenylmethyl) sulfide and bis(diphenylmethyl) disulfide as photolytic precursors to **6** also failed to give any rearrangement products.

**Diffusion Coefficients.** The diffusion coefficients of benzyl phenyl sulfide in nonane were determined using the Taylor method[55] over the range 313–393 K. The apparatus consisted of a Water's liquid chromatography pump attached to a 30-cm silica column to dampen pressure fluctuations, an injector, and a 33.22-m (length), 0.0398-cm (inside diameter) stainless steel column immersed in a Braun Thermomix constant-temperature oil bath. Analysis of the effluent was carried out with a Water's Model R401 refractometer. The variance ($\sigma^2$) of the benzyl phenyl sulfide peak was determined from the chromatography trace by averaging the measurement of the peak width at half-height Γ, where Γ = $2.345\sigma$, and the measurement taken from the half-width (= $\sigma$) at 60.65% of peak height. The relationship between the internal radius of the coiled tube, $r$, the retention volume $t$, $\sigma^2$, and the diffusion coefficient $D$ is given by $D = r^2 t / 24\sigma^2$. The experimental diffusion coefficients were found to agree with less than 4% error with the Debye/Einstein/Spernol–Wirtz calculated values: (temp K, exptl, and calcd values of $D$ in units of $10^{-5}$ cm$^2$ s$^{-1}$): 313, 2.60, 2.50; 333, 3.33, 3.27; 353, 4.27, 4.16; 373, 5.32, 5.166; 393, 6.53, 6.28.

**Supplementary Material Available:** Tables of complete kinetic data including product yields, temperatures, reaction times, and sample calculations of rate constants for the abstraction of hydrogen by **2** from thiophenol vs self-termination and for rearrangement of **2** vs abstraction of hydrogen atom from thiophenol (3 pages). Ordering information is given on any current masthead page.

(54) Kaufmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13(5)*, 291.

(55) (a) Taylor, G. *Proc. R. Soc. London, Ser. A* **1954**, 235, 473. (b) Pratt, K. C.; Wakeham, N. A. *Proc. R. Soc. London, Ser. A* **1974**, *336*, 393. (c) Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467.