Articles

Mechanism of the Solution-Phase Reaction of Alkyl Sulfides with Atomic Hydrogen. Reduction via a 9-S-3 Radical Intermediate

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The low selectivity of benzyl alkyl sulfide fragmentation subsequent to its reaction with atomic hydrogen is indicative of a reaction that proceeds via an early transition state. The competitive reduction of a series of substituted-benzyl alkyl sulfides was insensitive to the substituent on the aromatic ring ($\rho = -0.13$, $r = 0.99$). The relative rates of fragmentation of a series of the substituted-benzyl alkyl sulfides gave a V-shaped Hammett plot. Both electron-donating and electron-withdrawing groups destabilized the transition state ($\rho = +0.99$, $r = 0.999$; $\rho = -0.82$, $r = 0.992$). Since the relative rates of disappearance of the alkyl benzyl sulfides are not substituent dependent, but the relative rates of fragmentation are, a 9-S-3 intermediate is preferred as the structure leading to products.

Introduction

Homolytic displacement reactions at sulfur have been of mechanistic interest since displacement at sulfur may proceed to products, as does phosphorus[3] or iodine,[4] through a hypervalent intermediate. Previous studies of homolytic displacements of alkyl groups from sulfides by carbon-centered radicals[5−7] addressed the question of the intermediacy of a 9-S-3 hypervalent radical.[8] Displacement of a series of alkyl groups by an aryl radical exhibited very low selectivities as a function of leaving group stability.[5]

The absolute rates of S_Hi displacement at sulfur have been reported, and an analysis of their Arrhenius parameters suggested that displacement proceeds via a trivalent transition state and not a 9-S-3 intermediate. The authors stipulated, however, that a preequilibrium involving a sulfuranyl radical and the starting radical structure could not be ruled out.[7]

A number of sulfuranyl radicals have been generated;[8,9] however, their stability appears to depend upon their substituents having one or more electronegative ligands.

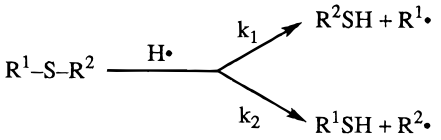
Fragmentation of a series of aryldialkylsulfuranyl radicals generated by the reduction of their sulfonium salts likewise showed low selectivity for competitive ligand loss.[10]

Results obtained from the cyclic voltammetric study of the one-electron transfer reductions of a series of arylmethylalkylsulfonium salts suggested that the fragmentation of the reduced salts was evidence for simultaneous or nearly simultaneous electron transfer fragmentation.[11a]

Although the results of Kampmeier,[5,6] Beak,[10] Saeva,[11b] and Franz[7] suggest that homolytic displacement at sulfide sulfur is not likely to proceed through a sulfuranyl radical of significant stability, the relative rate data that have been measured for displacements by atomic hydrogen at the sulfur center of alkyl disulfides and unsymmetric alkyl sulfides are compatible with reactions of a trivalent intermediate.[12] The displacements on the disulfides and the sulfides show structure−reactivity relationships where displacement on the sulfur of the disulfide occurs at the sterically least hindered sulfur and displacement at sulfur of the sulfide yields a thiol and the most stable radical. Since the displacement by atomic hydrogen at sulfur showed a structure−reactivity relationship, the reduction provided a possible probe for the involvement of a longer lived trivalent sulfuranyl radical.

Results and Discussion

The solution-phase reactions of atomic hydrogen with a series of unsymmetric alkyl sulfides result in the cleavage of an alkyl−sulfur bond with the formation of a thiol and an alkyl radical (eq 1).



(1)

The relative rates of cleavage, k_1/k_2, favor the most stable radical.[12]

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(1) NSERC, Undergraduate Research Fellowship.

(2) Postdoctoral Fellow, University of Alberta, 1994−1996.

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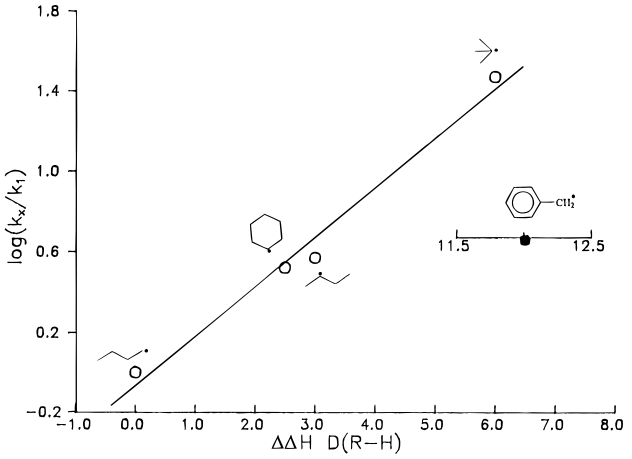
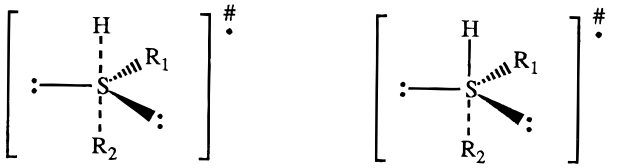


Figure 1. Evans−Polanyi plot of the ratio of rates of fragmentation of R•, $k_{x°}$/the primary alkyl radical, $k_{1°}$, *versus* the difference in *D*(R−H).

The stabilities of the radical products produced in these competitive fragmentations were put on a quantitative scale by applying the Evans−Polanyi relationship[13] to their relative rates of fragmentation. The plot showed a slope of 0.25; see Figure 1.

A reaction series that has an Evans−Polanyi plot with a slope of 0.25 can be interpreted as representing a reaction with a transition state in which the carbon−sulfur bond is 25% broken. The value of the slope is consistent with an early transition state resulting either from direct displacement (i) or from the fragmentation of a trivalent, 9-S-3, intermediate (ii).



(i) (ii)

Previous studies of displacement reactions on sulfur or of the fragmentation of electrochemically generated 9-S-3 intermediates concluded that if a 9-S-3 intermediate was involved it would be extremely short lived.[5−7,10−11] The low selectivity for displacement or fragmentation was proposed to be the result of an early transition state.[5−7,10−12]

The structure−reactivity relationship for displacement can be probed by competitive kinetics since a mechanism that proceeds by a biomolecular direct displacement reaction predicts that a sulfide with two primary alkyl groups would react more rapidly than a sulfide that contained more highly substituted alkyl groups. Presumably, steric effects would inhibit the direct displacement. Competitive rates of disappearance of diprimary sulfides vs more highly substituted sulfides did not confirm this prediction. The order of reactivity (1°,2° > 1°,3° > 2°,2° > 1°,1° >> 3°,3°) showed a reactivity relationship that was a combination of steric interactions and leaving group stability; see Table 1.

Table 1. Relative Rates of the Reactions of Alkyl Sulfides with Atomic Hydrogen at −78 °C in Acetone[a]

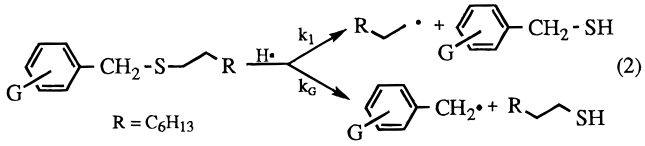
	alkyl sulfide R_1SR_2	$(k/k_o)_{disappearance}$[b]	$(k_1/k_o^1)_{fragmentation}$[c]
1.	$R_1 = R_2 =$ *n*-Hexyl	1	1
2.	$R_1 =$ *n*-C_8H_{17}[d] $R_2 =$ *sec*-C_4H_7	3.48 (±0.4)	3.70 (±0.5)
3.	$R_1 =$ *n*-C_6H_{13}[d] $R_2 =$ *t*-C_4H_9	1.97 (±0.1)	30.10 (±0.7)
4.	$R_1 = R_2 =$ *n*-propyl	1	1
5.	$R_1 = R_2 =$ *i*-C_3H_7	1.10(±0.1)	
6.	$R_1 = R_2 =$ *t*-C_4H_9	*e*	
7.	$R_1 =$ *n*-C_8H_{17} $R_2 = C_6H_5CH_2$	1.68 (±0.03)[f]	4.56 (±0.25)[g]

[a] The reactions were carried out with a hydrogen flow rate of 4 mL/min (4 Torr) using He as a makeup gas using a nonreactive internal standard, 1 chloroheptane. [b] *n*-Hexyl sulfide was used as a reference substrate (k_o) for entries 2, 3, and 7 and *n*-propyl sulfide was used for entries 5 and 6 (1:1 mixture of alkyl sulfides, 0.01−0.05 M). [c] The fragmentation ratio for unsymmetric sulfides were obtained by product analysis. k_o^1 Represents the cleavage of the primary alkyl−sulfur bond. [d] An experiment performed with a 1:1 mixture of *n*-octyl *sec*-butyl sulfide and *n*-hexyl *tert*-butyl sulfide (0.05 M) gave a relative rate of disappearance of (k_{sec}/k_{tert}) 1.60. The calculated relative rate using entries 2 and 3 was 1.76. [e] This compound did not show any appreciable reaction with hydrogen atoms when reacted in a 1:1 mixture of *n*-propyl sulfide in which *n*-propyl sulfide showed a 30.0% conversion. [f] The mole fraction of *n*-hexyl sulfide was varied from 0.25−0.75. [g] A value of 2.72 (±0.1) was obtained at −42 °C ΔE_a ($E_a(1°) - E_a$(benzyl)) = 1.27 kcal/mol.

In order to remove the importance of these steric interactions, the reaction kinetics of a series of benzyl and *meta*- and *para*-substituted benzyl alkyl sulfides were investigated; see Table 2.

As expected, the relative rates of disappearance of the substituted benzyl alkyl sulfides were relatively insensitive to the aromatic substituents, electron withdrawing or electron donating. A linear free energy treatment of the data showed a Hammett $\rho\sigma$ correlation of $\rho = -0.13$ (σ^+, $r = 0.99$); see Figure 2.

Since the competitive rates of disappearance of the substituted-benzyl alkyl sulfides did not appear to be appreciably effected by substituents and the relative rates of fragmentation of the dialkyl sulfides did show a structure−reactivity relationship, the relative rates of fragmentation (see eq 2) of the series of *m*- and *p*-substituted benzyl alkyl sulfides were examined; see Table 3.



(2)

Although the benzyl group of the benzyl alkyl sulfide fragmented much more slowly than expected, Table 1 (Figure 1), the relative rate of disappearance, k/k_o, was only marginally slower than the 3°/1° sulfide. Since it had been suggested that a low selectivity for displacement might be due to a pre-equilibrium between the substrate and a 9-S-3 intermediate[7] (Scheme 1, eqs 3−5), the competitive reduction was investigated at several concentrations of the di-primary-alkyl sulfide.

When the mole fraction of R_1SR_1 was varied from 0.25 to 0.75, the relative rates of disappearance were unchanged 1.68 (±0.03).

(10) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 4450−4457.
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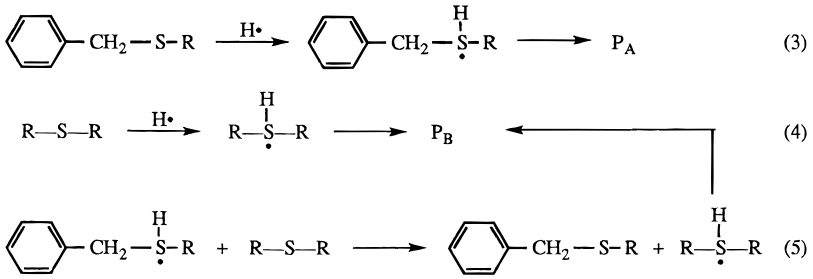
Scheme 1



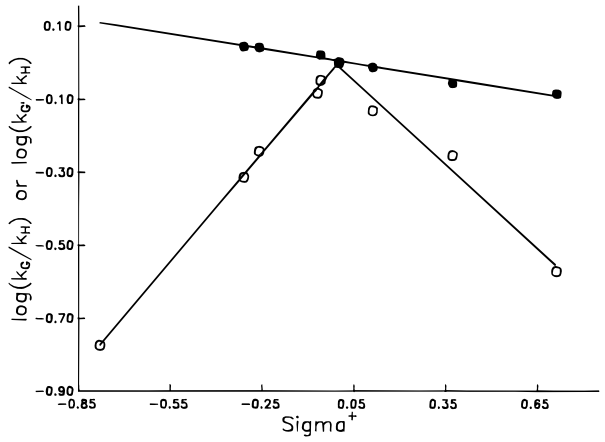


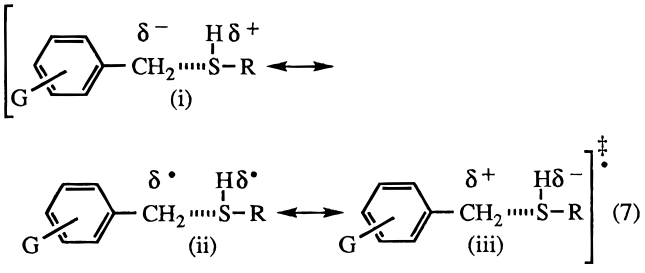
Figure 2. Hammett plot of the log of the relative rates of reaction of a series of alkyl benzyl sulfides *vs* σ^+: ●, relative rates of disappearance (k_G/k_H); ○, relative rates of fragmentation ($k_{G'}/k_{1^\circ}$)/(k_H/k_{1°).

Assuming that k_1 is not appreciably effected by the substituent, the relative rates of fragmentation (eq 6) can be presented on the same Hammett plot used for the competitive intermolecular reactions; see Figure 2.

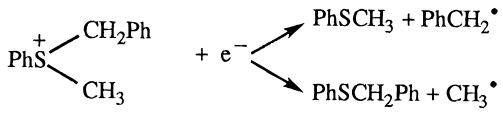
$$\ell n((P_{G'}/P_1)/(P_H/P_1)) = \rho\sigma^+ \qquad (6)$$

$$\ell n((k_{G'}/k_1)/(k_H/k_1)) = \ell n(k_{G'}/k_H) = \rho\sigma^+$$

It is apparent that all of the substituents, electron withdrawing or electron donating, decrease the rate of fragmentation of the benzyl groups compared to the reference octyl groups. The substituent effects can be rationalized if one considers the transition state for the fragmentation of an 9-S-3 intermediate, eq 7.



When the value k_{benzyl}/k_1 (4.56) was added to the Evans−Polanyi plot, it was apparent that the benzyl radical was formed much more slowly then expected; see Figure 1. Its rate of formation reflects a diminished dependence on the resonance stabilization of the benzyl radical, as expected for a transition state where the radical is only partially (~25%) formed. With so little demand for resonance stabilization it is not surprising that the substituents do not have the expected effect, but in fact promote a polarity that destabilizes the transition state. The transition-state structure is summarized by the three contributing cannonical forms (i−iii), eq 7. The carbon−sulfur bond, usually polarized toward the more electronegative sulfur, has an electropositive hydrogen atom attached. The nonpolarized structure, ii, is now the most important contributing form. Any added polarity, due to aromatic substitution, appears to destabilize the transition state. The decreased selectivity for benzyl vs octyl radical fragmentation and its low activation energy ($\Delta\Delta E_a$ = 1.27 kcal/mol) is entirely consistent with the observed relative fragmentation rates of k_{benzyl}/k_{CH_3} (15/1, $\Delta\Delta E_a$ = 1.6 kcal/mol) reported by Beak[10] for the reduction of the phenylbenzylmethylsulfonium salt (eq 8).



(8)

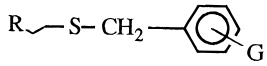
Conclusion

Subsequent to their reaction with atomic hydrogen, the relative rates of fragmentation of unsymmetric sulfides show a structure−reactivity relationship that is consistent with an $S_{RN}2$ or a 9-S-3 fragmentation. The mechanistic results suggest that the displacement proceeds by an early transition state that is sensitive to steric deactivation. In order to remove the importance of these steric interactions, a series of substituted-benzyl alkyl sulfides was treated with the hydrogen atom plasma. Competitive rates of reaction of the substituted- and unsubstituted-benzyl alkyl sulfides were relatively insensitive to substituents, $\rho = -0.13$, while the relative rates of fragmentation of the series of substituted-benzyl alkyl sulfides were strongly influenced by the substituents. Since the relative rates of disappearance of the alkyl benzyl sulfides are not substituent dependent, but the relative rates of fragmentation are, a 9-S-3 intermediate is preferred as the structure leading to products.

Experimental Section

General Procedure for the Atomic Hydrogen Reaction.[12] An aliquot solution was placed in the U-shaped reactor. The reactor was cooled to the desired temperature, and a stream of hydrogen or deuterium was passed into the system at a flow rate of 4 mL/min. The reaction system pressure was controlled at 3−4 Torr by a make-up gas (helium). The microwave generator was activated and the reaction allowed to proceed for the desired time. After the reaction, the product mixture was analyzed by GC. For each reaction, the products were identified by comparison of their GC retention times, GC/

Table 2. Product Distribution in Acetone of the Reaction of Atomic Hydrogen with Organic Sulfides of the Type[a,b]



Substituent G	Time (min)	Temp. (°C)	Conc. (mol^{-1})	RC_2H_5	R-CH=CH_2				R-SH	R-SS-R
p-OCH_3	15-30(2)	-78	0.013	1.23	0.05	-	0.25	0.24	1.26	-
p-CH_3	5-15(3)	-78	0.025	0.73	0.09	0.40	1.17	0.23	1.99	0.09
p-$C(CH_3)_3$	5-10(2)	-78	0.05	4.86	0.15	2.48	tr.	1.19	15.7	0.56
p-F	15(2)	-78	0.05	2.89	0.12	0.77	3.60	1.03	14.3	-
m-CH_3	5(2)	-78	0.05	1.43	0.15	0.80	1.65	0.36	7.39	0.07
H	3-5(3)	-78	0.05	1.26	0.06	0.52	2.09	0.67	9.52	-
p-Cl	5(2)	-78	0.05	1.84	0.15	0.25	2.11	0.37	6.33	0.36
m-Cl	5-10(2)	-78	0.05	4.51	-	3.83	2.17	0.50	10.1	0.82
p-CN	5-17(3)	-78	0.025	0.86	0.11	-	0.23	0.44	2.00	-
H	5	-42	0.50	2.50	0.09	0.95	1.67	0.11	7.41	
H	5	-42	0.25	0.65	0.04	0.30	0.98	0.06	2.07	
H	4	-42	0.10	1.02	0.06	0.36	1.33	0.16	3.56	
H	3	-42	0.05	0.30	0.02	0.15	0.33	0.05	0.93	

[a] R = C_6H_{13}, R′ = C_8H_{17}. [b] The hydrogen flow rate was kept at 6 mL/min for all reactions. The reaction volume was 10 mL for reactions at −78 °C and 5 mL for reaction at −42 °C. Substituted benzyl thiols were detected as products, but these appeared to react under the reaction conditions. 1-Chloroheptane was used as an internal standard.

Table 3. Relative Rates of Disappearance and Fragmentation of Alkyl Aromatic Substituted-Benzyl Sulfides with Atomic Hydrogen in Acetone at −78 °C

substituent G	$(k_G/k_H)_{disappearance}$[a]	$(k_{G'}/k_H)_{fragmentation}$[b]
p-OCH_3		0.168 (±0.02)
p-CH_3	1.107 (±0.001)	0.485 (±0.04)
p-$C(CH_3)_3$	1.101 (±0.001)	0.572 (±0.03)
p-F		0.825 (±0.10)
m-CH_3	1.050 (±0.01)	0.895 (±0.04)
H	1	1
p-Cl	0.971 (±0.04)	0.739 (±0.04)
m-Cl	0.879 (±0.03)	0.557 (±0.04)
p-CN	0.822 (±0.01)	0.268 (±0.04)

[a] The reactions were carried out in a 1:1 mixture of (0.01−0.05 M) substituted- and unsubstituted-benzyl alkyl sulfides in the presence of chloroheptane as an internal standard. [b] The relative rates of fragmentation between primary alkyl and aromatic substituted-benzyl fragments were determined by their product distribution and were normalized by the relative rate of fragmentation of the unsubstituted analog; see Table 2.

MS, and GC/IR with those of authentic samples. ^{2}H NMR spectra were also obtained for products of the reactions with deuterium.

Materials. Commercially available *tert*-butyl sulfide (98%), 1-octanethiol (97+%) *n*-hexyl sulfide, and *n*-octane (99%) (Aldrich Chemical Co.) and *n*-propyl sulfide (99.99%) and isopropyl sulfide (99.99%) (American Petroleum Institute Standards) were checked for purity by GC and used as received. ***tert*-Butyl *n*-hexyl sulfide** was identical to the material previously reported.[12] The substituted toluenes were identified by a comparison of their GC/IR, GC/MS, and GC retention times with those of the authentic samples (Aldrich Chemical Co.).

***sec*-Butyl *n*-octyl sulfide** was prepared using the standard procedure[14] using 1-bromooctane (0.15 mol) and *sec*-butanethiol (0.15 mol) in 87% yield (0.13 mol, 26.2 g): bp 120−124 °C/15 mmHg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.70−1.75 (m, 23H), 2.45 (t, 2H, J = 7.5 Hz), 2.65 (t, 1H, J = 7.5 Hz); IR (vapor phase) ν 2934, 2869, 1460, 1381, 1296, 1225, 1140, 1005 cm^{-1}; EI$^+$ m/z 201.9 (M^+), 172.9, 144.9, 69.0, 57.0, 40.9. Anal. Calcd for $C_{12}H_{26}S$: C, 71.22; H, 12.94. Found: C, 71.48 H, 12.87.

Synthesis of *n*-Octyl Substituted-Benzyl Sulfides. These sulfides were prepared using a procedure similar to the one used for dialkyl sulfides.[14] *n*-Octanethiol (7.3 g, 0.05 mol) was heated to reflux with the substituted-benzyl bromides or chlorides (0.05 mol) in the presence of sodium hydroxide (2 g, 0.05 mol) in ethanol (50 mL) for 1 h. The cooled reaction mixture was poured into ice−water (200 mL) and extracted with diethyl ether. The sulfides were obtained as light yellow oils after the column chromatography on silica gel. (Solvents 3:1 mixture of hexane:dichloromethane, yields 50−85%.) A white solid was obtained in the case of *p*-cyano analog, and it was recrystallized from ethanol.

***n*-Octylbenzyl sulfide**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7 Hz), 1.15−1.70 (m, 12H), 2.45 (t, 2H, J = 8.3 Hz) 3.75 (s, 2H), 7.10−7.45 (m, 5H); IR (vapor phase) ν 3071, 2933, 2865, 1601, 1455, 1236, 1029, 701 cm^{-1}; E$^+$ m/z 236.0 (M^+), 145.1, 124.0, 91.1, 69.0, 55.1; bp 153−155 °C/4 mmHg. Anal. Calcd for $C_{15}H_{24}S$: C, 76.21; H, 10.22; S, 13.56. Found: C, 75.98; H, 10.31; S, 13.35.

***n*-Octyl *p*-cyanobenzyl sulfide**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7 Hz), 1.10−1.80 (m, 12H), 2.40 (t, 2H, J = 8.3 Hz), 3.75 (s, 2H), 7.35−7.65 (dd, 4H, J = 40 Hz); IR (vapor phase) ν 2934, 2866, 2234, 1608, 1508, 1235, 1022, 831 cm^{-1}; E$^+$ m/z 261.1 (M^+), 150.0, 145.2, 116.1, 89.1, 69.1, 55.1; mp 34-35 °C. Anal. Calcd for $C_{16}H_{23}SN$: C, 73.51; H, 8.86; S, 12.27; N, 5.38. Found: C, 73.12; H, 9.13; S, 12.29; N, 5.12.

***n*-Octyl *p*-chlorobenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7 Hz), 1.15−1.40 (m, 12H), 2.40 (t, 2H, J = 8.0 Hz), 3.65 (s, 2H), 7.10−7.30 (m, 4H); IR (vapor phase) ν 2933, 2866, 1596, 1491, 1237, 1096, 1017, 821 cm^{-1}; E$^+$ m/z 269.9 (M^+), 145.0, 124.9, 89.0, 69.0, 55.0; bp 340 °C dec. Anal. Calcd for $C_{15}H_{23}SCl$; C, 66.52; H, 8.55; S, 11.83. Found: C, 66.73; H, 8.95; S, 11.87.

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***n*-Octyl *m*-chlorobenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (t, 3H, J = 7 Hz), 1.15−1.65 (m, 12H), 2.35 (t, 2H, J = 8.0 Hz), 3.65 (s, 2H), 7.10−7.40 (m, 5H); IR (vapor phase) ν 2933, 2865, 1595, 1473, 1234, 1083, 876, 781, 692 cm^{-1}; E$^+$ m/z 270.0 (M$^+$), 157.9, 145.0, 124.9, 89.0, 69.0, 55.1; bp 346 °C dec. Anal. Calcd for $C_{15}H_{23}SCl$; C, 66.52; H, 8.55. Found: C, 66.59; H, 8.55.

***n*-Octyl *p*-fluorobenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (t, 3H, J = 7 Hz), 1.10−1.70 (m, 12H), 2.40 (t, 2H, J = 8.0 Hz), 3.65 (s, 2H), 6.90−7.40 (m, 4H); IR (vapor phase) ν 2933, 2866, 1605, 1511, 1235, 1158, 1093, 831, 735; E$^+$ m/z 254.0, 145.0, 109.0, 69.0, 54.7, 41.0; bp 300−301 °C/749 mmHg. Anal. Calcd for $C_{15}H_{23}SF$: C, 70.82; H, 9.10; S, 12.61. Found: C, 71.03; H, 9.43; S, 12.84.

***n*-Octyl *m*-methylbenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (t, 3H, J = 7 Hz), 1.15−1.70 (m, 12H), 2.35 (s, 3H), 2.40 (t, 2H, J = 8.0 Hz), 3.65 (s, 2H), 6.95−7.30 (m, 5H); IR (vapor phase) ν 3029, 2933, 2866, 1607, 1458, 1226, 1089, 779, 713; E$^+$ m/z 250.1 (M$^+$), 145.1, 105.1, 68.9, 55.1; bp 307−309 °C/749 mmHg. Anal. Calcd for $C_{16}H_{26}S$: C, 76.74; H, 10.46. Found: C, 76.56; H, 10.62.

***n*-Octyl *p*-methylbenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.0 Hz), 1.10−1.07 (m, 12H) 2.35 (s, 3H), 2.40 (t, 2H, J = 8.0 Hz), 3.65 (s, 2H), 7.20 (dd, 4H, J = 20.0 Hz); IR (vapor phase) ν 3025, 2933, 2866, 1513, 1234, 1022, 811 cm^{-1}; E$^+$ m/z 150.2 (M$^+$), 145.1, 105.1, 69.0, 54.2; bp 300 °C dec. Anal. Calcd for $C_{16}H_{26}S$: C, 76.74; H, 10.46. Found: C, 76.95; H, 10.76.

***n*-Octyl *p*-methoxybenzyl sulfide**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 3H, J = 7.0 Hz), 1.15−1.65 (m, 12H) 2.45 (t, 2H, J = 8.0 Hz), 3.70 (s, 2H), 3.80 (s, 3H), 7.05 (dd, 4H, J = 86.6 Hz); IR (vapor phase) ν 2934, 2865, 1609, 1511, 1250, 1173, 1041, 830; E$^+$ m/z 266.0 (M$^+$), 153.0, 121.1, 91.3, 78.0; bp 330 °C dec. Anal. Calcd for $C_{16}H_{26}OS$: C, 72.13; H, 9.83; S, 12.04. Found: C, 71.98; H, 9.77; S, 11.65.

***n*-Octyl *p*-*tert*-butylbenzyl sulfide**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.0 Hz), 1.10−1.75 (m, 12H) 1.40 (s, 9H), 2.45 (t, 2H, J = 7.3 Hz), 3.71 (s, 2H), 7.10−7.50 (dd, 4H, J = 10.7 Hz); IR (vapor phase) ν 2934, 2866, 1463, 1368, 1267, 1100, 1020, 824 cm^{-1}; E$^+$ m/z 292.1 (M$^+$), 147.0, 132.0, 117.0, 105.0, 91.0, 57.1; bp 335 dec. Anal. Calcd for $C_{19}H_{32}S$: C, 78.01; H, 11.03; S, 10.96. Found: C, 78.00; H, 11.14; S, 10.99.

1,2-Di-*p*- or -*m*-Substituted Arylethanes. The bibenzyls were prepared using substituted benzyl bromides or chlorides by their Grignard substitution reactions according to the literature procedure.[15] 1,2-Bis(*p*-methoxyphenyl)ethane was identified by its GC/IR and GC/MS spectra.[16]

1,2-Bis(*m*-methylphenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.45 (s, 6H), 3.00 (s, 4H), 6.95−7.45 (m, 8H); IR (vapor phase) ν 3030, 2994, 2871, 1607, 1489, 1090, 882, 775, 699 cm^{-1}; E$^+$ m/z 209.0 (M$^+$), 105.0, 77.0, 51.0. (GC/AED). Anal. Calcd for $C_{16}H_{18}$: C, 91.38; H, 8.62. Found: C, 91.21; H, 8.78.

1,2-Bis(*p*-chlorophenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.85 (s, 4H), 6.95−7.35 (m, 8H); IR (vapor phase) ν 3034, 2939, 2869, 1499, 1097, 1016, 816, 638 cm^{-1}; E$^+$ m/z 251.8 (M$^+$, ^{37}Cl), 249.8 (M$^+$, ^{35}Cl), 125.0, 88.9, 63.0; mp 110−111 °C (lit.[17] mp 112 °C).

1,2-Bis(*p*-fluorophenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.90 (s, 4H), 6.85−7.30 (m, 8H); IR (vapor phase) ν 3044, 2939, 2869, 1877, 1605, 1512, 1236, 1159, 1089, 1017, 822, 732 cm^{-1}; E$^+$ m/z 218.0 (M$^+$), 109.0, 83.0, 57.0; mp 85−86 °C. (GC/AED). Anal. Calcd for $C_{14}H_{12}F_2$: C, 77.05; H, 5.54. Found: C, 77.05; H, 5.51.

1,2-Bis(*p*-*tert*-butylphenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35 (s, 18H), 2.92 (s, 4H), 7.10−7.40 (m, 8H); IR (vapor phase) ν 3027, 2987, 2877, 1514, 1369, 1267, 1195, 1108, 1019, 821 cm^{-1}; E$^+$ m/z 294.2 (M$^+$), 279.2, 147.1, 132.1, 116.8, 105.1, 91.0, 57.0, 40.9; mp 150−152 °C. (GC/AED). Anal. Calcd for $C_{22}H_{30}$: C, 89.74; H, 10.26. Found: C, 89.70; H, 10.31.

1,2-Bis(*m*-chlorophenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.90 (s, 4H), 6.90−7.45 (m, 8H); IR (vapor phase) ν 3070, 2946, 2870, 1929, 1857, 1753, 1596, 1478, 1340, 1088, 1001, 667, 777 cm^{-1}; E$^+$ m/z 252.2 (M$^+$, ^{37}Cl), 250.2 (M$^+$, ^{35}Cl), 178.3, 127.1; mp 97−99 °C (lit.[16] mp 98−99 °C).

1,2-Bis(*p*-methylphenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.35 (s, 6H), 2.90 (s, 4H), 7.10 (s, 8H); IR (vapor phase) ν 3024, 2934, 2873, 1888, 1783, 1515, 1449, 1341, 1211, 1108, 1022, 805 cm^{-1}; E$^+$ m/z 210.1 (M$^+$), 178.1, 165.1, 115.0, 105.1, 77.1; mp 83−84 °C (lit.[16] mp 83−84 °C).

1,2-Bis(*p*-cyanophenyl)ethane: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.0 (s, 4H), 7.15 (d, J = 9 Hz, 4H), 7.59 (d, J = 9 Hz, 4H); IR (vapor phase) ν 3041, 2847, 2235, 1815, 1610, 1509, 1449, 1021, 827 cm^{-1}; E$^+$ m/z 232.0 (M$^+$), 203.1, 116.0, 89.0, 63.0; mp 202−204 °C.

***p*- or *m*-Substituted Arylnonanes.** The arylnonanes were prepared by the Grignard reaction of the magnesium salt of 1-bromooctane and a substituted benzyl bromide or chloride. The products were purified by liquid chromatography on silica gel (4:1 hexane:dichloromethane) in 10−30% yield.

1-Fluoro-4-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.10−1.70 (m, 14H), 2.55 (t, J = 8 Hz, 2H), 6.85−7.20 (m, 4H); IR (vapor phase) ν 3044, 2939, 1605, 1512, 1236, 1159, 1089, 1017, 822, 733 cm^{-1}; E$^+$ m/z 222.2 (M$^+$), 122.1, 109.1, 71.0, 57.0, 43.0 (GC/AED). Anal. Calcd for $C_{15}H_{23}F$: C, 81.04; H, 10.42. Found: C, 80.88; H, 10.58.

1-Chloro-4-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.10−1.75 (m, 14H), 2.60 (t, J = 8 Hz, 2H), 7.00−7.40 (m, 4H); IR (vapor phase) ν 3033, 2935, 2866, 1493, 1352, 1096, 1016, 816 cm^{-1}; E$^+$ m/z 240.2 (M$^+$, ^{37}Cl), 238.2 (M$^+$, ^{35}Cl), 167.1, 125.1, 91.2, 71.0, 57.0, 43.1. (GC/AED). Anal. Calcd for $C_{14}H_{23}Cl$: C, 75.44; H, 9.70; Cl, 14.86. Found: C, 75.56; H, 9.87; Cl, 14.53.

1-Methyl-4-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.10−1.70 (m, 14H), 2.32 (s, 3H), 2.60 (t, J = 8 Hz, 2H), 7.10 (s, 4H); IR (vapor phase) ν 3023, 2934, 2866, 1515, 1460, 1351, 1118, 1022, 802 cm^{-1}; E$^+$ m/z 218.2 (M$^+$), 203.0, 175.3, 147.1, 132.0, 105.1, 77.0. (GC/AED). Anal. Calcd for $C_{16}H_{26}$: C, 88.01; H, 11.99. Found: C, 87.97; H, 12.03.

1-Chloro-3-nonyl benzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (t, J = 7 Hz, 3H), 1.10−1.70 (m, 14H), 2.55 (t, J = 8 Hz, 2H), 6.90−7.25 (m, 4H); IR (vapor phase) ν 2935, 2866, 1598, 1471, 1351, 1206, 1086, 878, 776, 600 cm^{-1}; E$^+$ m/z 240.2 (M$^+$ ^{37}Cl), 238.2 (M$^+$, ^{35}Cl), 203.2, 167.1, 126.1, 91.1, 57.1, 43.1. (GC/AED). Anal. Calcd for $C_{15}H_{23}Cl$: C, 75.44; H, 9.69; Cl, 14.86. Found: C, 75.32; H, 9.67; Cl, 15.01.

1-*tert*-Butyl-4-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 6.9 Hz, 3H), 1.15−1.70 (m, 23H), 2.55 (t, J = 8 Hz, 2H), 7.05−7.40 (m, 4H); IR (vapor phase) ν 3026, 2934, 2867, 1465, 1368, 1267, 1100, 1019, 825 cm^{-1}; E$^+$ m/z 260.2 (M$^+$), 245.4, 231.1, 173.1, 147.1, 132.0, 117.1, 91.0, 41.0. (GC/AED). Anal. Calcd for $C_{19}H_{32}$: C, 87.63; H, 12.37. Found: C, 87.51; H, 12.49.

1-Methyl-3-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.10−1.70 (m, 14H), 2.35 (s, 3H), 2.55 (t, J = 8 Hz, 2H), 6.90−7.30 (m, 4H); IR (vapor phase) ν 3023, 2936, 2869, 1461, 1352, 1263, 725, 652 cm^{-1}; E$^+$ m/z 218.4 (M$^+$), 175.2, 147.2, 119.0, 106.2, 91.0, 77.1. (GC/AED). Anal. Calcd for $C_{16}H_{26}$: C, 88.01; H, 11.99. Found: C, 88.07; H, 11.92.

1-Cyano-4-nonylbenzene: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, J = 7 Hz, 3H), 1.10−1.75 (m, 14H), 2.65 (t, J = 8 Hz, 2H), 7.55 (d, J = 9 Hz, 2H), 7.85 (d, J = 9 Hz, 2H); IR (vapor phase) ν 3040, 2938, 2867, 2233, 1912, 1609, 1507, 1022, 824 cm^{-1}; E$^+$ m/z 229.1 (M$^+$), 158.0, 130.1, 117.1, 89.0, 71.1, 57.0. (GC/AED). Anal. Calcd for $C_{16}H_{23}N$: C, 83.79; H, 10.10. Found: C, 83.62; H, 10.19.

n-Octyl disulfide was prepared by the I_2 oxidation of 1-octanethiol (5 g, 0.035 mol):[18] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 7 Hz, 6H), 1.10−1.80 (m, 24H), 2.65 (t, J = 8 Hz, 4H); IR (vapor phase) ν 2994, 2865, 1461, 1294 cm^{-1}; E$^+$ m/z 290.3 (M$^+$), 178.0, 145.2, 115.1, 71.1, 57.1; bp 295−296 °C/750 mm Hg.

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Determination of the Relative Rate of Fragmentation of Substituted Benzyl *n*-Octyl Sulfides. Solutions of *n*-octyl-substituted benzyl sulfides (0.025−0.05 M) in acetone (10 mL) were subjected to a hydrogen plasma (H_2 flow rate; 6 mL/min, 3.5 Torr, 5−15 min), and the product mixtures were analyzed by gas chromatography. The relative rates were calculated by determining the amounts of *n*-octane, nonylarenes, *n*-octanethiol, and *n*-octyl disulfide formed.

The relative rates of fragmentation between primary alkyl and substituted-benzyl groups (k_{G^1}/k_{1°) were calculated using eq 9, and the relative rates of fragmentation between substituted- and unsubstituted-benzyl sulfides were calculated using eq 11.

It was assumed that the rate of fragmentation to form the primary radical (k_{1°) was not affected by the substituent G in the benzylic fragment.

Determination of the Relative Rates of Disappearance of *n*-Octyl Substituted-Benzyl Sulfides. Acetone solutions (10 mL) of a 1:1 mixture of (0.01−0.05 M) *n*-octyl benzyl sulfide, *n*-octyl substituted-benzyl sulfide, and 1-chloroheptane (internal standard) were subjected to hydrogen plasma (hydrogen flow rate = 6 mL/min, 3.5 Torr, 5−15 min) at −78 °C. The initial and final product mixtures were analyzed by gas chromatography using a 105 m × 0.25 mm × 0.5 μm R_{tx-1} glass capillary column fitted to a Varian 6000 chromatograph equipped with a hydrogen flame detector interfaced to a Varian vista CDS 401 chromatography data system. The rates of disappearance of *n*-octyl substituted-benzyl sulfides (G) relative to the unsubstituted analog (H) were calculated (eq 12) using the area ratios of those compounds (A_G, A_H) with respect to the internal standard (A_S).

$$\frac{k_{G^1}}{k_{1^\circ}} = \frac{\left[R\text{—}SH + 2\ R\text{—}S\text{-}S\text{—}R \right]}{\left[R\text{—}CH_3 + \text{G-C}_6\text{H}_4\text{—}CH_2\text{—}R \right]} \quad (9)$$

$$\frac{k_H}{k_{1^\circ}} = \frac{\left[R\text{—}SH + 2\ R\text{—}S\text{-}S\text{—}R \right]}{\left[R\text{—}CH_3 + \text{C}_6\text{H}_5\text{—}CH_2\text{—}R \right]} \quad (10)$$

$R = C_7H_{15}$

$$\frac{k_{G^1}}{k_H} = \frac{\text{eq. 2}}{\text{eq. 3}} = \frac{k_{G^1}/k_{1^\circ}}{k_H/k_{1^\circ}} \quad (11)$$

$$\frac{k_G}{k_H} = \frac{\ln[(A_G/A_S)/(A_G/A_S)^\circ]}{\ln[(A_H/A_S)/(A_H/A_S)^\circ]} \quad (12)$$

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