^{1}H NMR[23c] (CCl_3D) δ 1.5, 1.55, 1.60, 1.78 (10 H), 2.15 (1 H); IR[24c] (CCl_4) 925 (m), 1263 (m), 1480 (s), 1560 (s), 2875 (s), 2955 (vs) 3450 (vs, br); mass spectrum (70 eV), *m/e* 180 (M - H_2O), 178 (M - H_2O - H_2), 99 ($C_6H_{11}O$), 98 ($C_6H_{10}O$), 81 (C_6H_9), 55 (C_4H_7, C_3H_3O).

Materials. Ti, Cr, Co, Ni, Nd, and U were obtained from Research Chemicals or MC/B and were better than 99.5% pure. $TiCl_4$ was purchased from the Alfa division of Ventron Corp. and was used without purification. Cyclohexanone (analytical reagent grade), hexane (Spectrograde), and toluene (Spectrograde) were obtained from Mallinckrodt Chemical Works, were dried over molecular sieves, and were degassed by successive freeze–thaw cycles under reduced pressure (<10^{-3} mmHg).

Tetrahydrofuran (THF, Mallinckrodt, analytical reagent grade) was dried over Na/benzophenone or $LiAlH_4$ and distilled under N_2 prior to use.

General Procedure for Metal Atom Vapor Plus Cyclohexanone Cocondensation. At 40 °C approximately 15 mL of cyclohexanone (145 mmol) was condensed with from 0.1 to 0.7 g (2–15 mmol) of metal at −196 °C over 45–60 min. The pressure inside the reaction vessel was kept below 2×10^{-4} mmHg. For most metals used, a reaction could be seen to take place at −196 °C, with matrices turning orange to gold. After deposition was complete, the liquid N_2 bath was removed, and the matrix was allowed to warm to room temperature. Volatile products were pumped off and collected in a liquid N_2 trap. VPC analysis showed that only cyclohexanone was present. The reaction vessel was filled with N_2, and dry Et_2O was added. The reaction mixture was hydrolyzed slowly, dropwise, with H_2O. **Caution:** Highly divided metal powders are often pyrophoric and may react vigorously on hydrolysis with gas evolution. Hydrogen evolution was not observed for any of the metals studied. After 15 mL of H_2O had been added, the mixture was acidified with 1 M HCl. Organic products were extracted with Et_2O or pentane (3 × 50 mL). The combined extracts were dried over Na_2SO_4 and reduced to a 2–3-mL volume. Solutions were diluted to exactly 5 mL, and yields were determined by VPC ($^1/_4$ in. × 20 in. column, 10% UCW 982) using benzophenone as an external standard. The products were collected by preparative VPC ($^3/_8$ in. × 8 ft column, 20% OV 101) and identified spectroscopically by standard IR, ^{1}H NMR, and gas chromatographic–mass spectrometric techniques. Spectra were compared with the literature data.

General Procedure for Titanium Atom Vapor/Solvent Plus Cyclohexanone Cocondensation. Approximately 50 mL of dry, degassed hexane (380 mmol) as the solvent was condensed with approximately 0.10 g of titanium metal (2.1 mmol) at −196 °C, and approximately 5 mL of cyclohexanone (48 mmol) was condensed on top of the reaction matrix. The liquid N_2 bath was removed, and the temperature was raised to room temperature. The reaction vessel was filled with N_2, and a magnetic stir bar was added. The vessel was partially evacuated (approximately 350 mmHg), and the mixture was heated to reflux with stirring. The water-cooled electrodes served as the condenser. Refluxing continued for 2 h. After cooling to room temperature, the mixture was hydrolyzed, and the products were isolated and identified as before.

Cyclohexanone Reduction by Potassium-Reduced Titanium Tetrachloride Metal Powders.[6] A 1.99-g (50.9 mmol) sample of freshly cut K metal was added to approximately 60 mL of dry THF in a Schlenk flask under a N_2 atmosphere. The Schlenk flask was fitted with a reflux condenser, and the THF was heated with rapid stirring. Under THF reflux, the K melted, producing many small spherical globules. To this K sand was added 1.40 mL (12.7 mmol) of $TiCl_4$ dropwise by syringe. Addition of $TiCl_4$ to K–THF was followed by a vigorous reaction producing a great deal of heat and an insoluble violet solid. The mixture was refluxed for an additional 3 h, resulting in an insoluble black solid. A 2.65-mL sample of cyclohexanone (25.4 mmol) in 10 mL of THF was added dropwise over 5 min to the Ti metal powder. The reaction mixture was refluxed overnight (18 h). Unlike metal atom reactions, hydrolysis was vigorous. The products were obtained and identified as described.

Registry No. Bicyclohexylidene, 4233-18-5; 2-(1-cyclohexene-1-yl)cyclohexanone, 1502-22-3; 2-cyclohexylcyclohexanone, 90-42-6; [1,1-bicyclohexyl]-1,1'-diol, 2888-11-1; cyclohexanone, 108-94-1; Ti, 7440-32-6; Cr, 7440-47-3; Nd, 7440-00-8; U, 7440-61-1; Co, 7440-48-4; Ni, 7440-02-0; $TiCl_4$, 7550-45-0.

Studies of Sulfinyl Radicals. 1. Thermal Decompositions of Benzhydryl *p*-Tolyl Sulfoxide and Benzhydryl Methyl Sulfoxide

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The kinetics and mechanism of the thermal decompositions of benzhydryl *p*-tolyl sulfoxide (BTSO) and benzhydryl methyl sulfoxide (BMSO) were studied. Product analysis, ESR, and CIDNP results showed that both sulfoxides gave *p*-toluenesulfinyl and methanesulfinyl radicals, respectively, by the scission of carbon–sulfur bonds at 100–130 °C. The presence of a small amount of a base such as pyridine has been found to suppress the formation of other products than the coupling products (the corresponding thiosulfonates and tetraphenylethane), which may be formed by ionic reactions of BTSO and BMSO. The mechanism of BTSO decomposition is complex, since it is in equilibrium with benzhydryl *p*-toluenesulfenate (BTSN) at 100–130 °C. On the other hand, BMSO, showing simple decomposition behavior, indicated that the decomposition rates decreased on the addition of hydroxylic solvents.

Sulfinyl radicals,[1] unlike thiyl and sulfonyl radicals, are unreactive toward olefins such as 1,1-diphenylethylene,[2] styrene,[3] cyclohexene,[4] and 2-butene,[5] and benzoquinone,[4] which usually react with organic free radicals. So far, the only reaction which sulfinyl radicals are known to undergo is the coupling reaction which gives thiosulfonates probably through sulfenyl sulfinates (eq 1).[6] Disulfoxides [RS-

$$2RSO\cdot \rightarrow [RS(O)OSR] \rightarrow RSO_2SR \qquad (1)$$

(1) For reviews, see: (a) Kice, J. L. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 2. (b) Block, E. In "Reactions of Organosulfur Compounds"; Academic Press: New York and London, 1978; pp 208.
(2) Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898.
(3) Koch, P.; Cuiffarin, E.; Fava, A. *J. Am. Chem. Soc.* **1970**, *92*, 5971.
(4) da Silva Corrêa, C. M. M.; Waters, W. A. *J. Chem. Soc. C* **1968**, 1874.
(5) Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B.; Willcott, M. R., III; Inners, R. R.; Cornelis, A. *J. Am. Chem. Soc.* **1978**, *100*, 3874.

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Table I. Products in the Thermal Decompositions[a] of BTSO and BMSO in Benzene

	product yield, mol %			
	BTSO (R = *p*-Tol)		BMSO (R = CH_3)	
product	0.13 M	0.21 M[b]	0.54 M	0.35 M[c]
$(Ph_2CH)_2$	14	43	28	47
$RSSO_2R$	18	46	24	44
RSO_2CHPh_2	16		8	
$(Ph_2CH)_2O$	24		13	
$(RS)_2$	26		11	
$RSCHPh_2$	5		7	

[a] 120 °C, 26 h. [b] [Pyridine] = 0.62 M. [c] [Pyridine] = 0.25 M.

(O)S(O)R], expected to form from S–S coupling of sulfinyl radicals, have never been isolated, and attempts to prepare them led to the more stable isomeric thiosulfonates.[7]

Although ESR studies on aromatic and aliphatic sulfinyl radicals have been extensively done[8] and the rate constant for the coupling of *tert*-butanesulfinyl radicals has been reported to be 6×10^7 M^{-1} s^{-1} at −100 °C from ESR measurement,[9] there are few investigations concerning formations and reactions of these interesting radicals.

Miller, Rayner, Thomas, and Mislow[10] have found that optical active benzyl *p*-tolyl sulfoxide racemizes through a sulfinyl–benzyl radical pair formed by homolysis of the benzylic carbon–sulfur bond. The evidences for the above mechanism are that the rate of racemization at the chiral benzylic carbon of benzyl-α-*d* *p*-tolyl sulfoxide is the same as the rate of racemization at sulfur, and the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values obtained are reasonable for a bond scission (24.6 eu and 43.0 kcal/mol). The fact that the activation volume for this racemization is large and positive (26 ± 2 mL/mol) also supports this mechanism.[11] Unlike benzyl *p*-tolyl sulfoxide, racemization of benzyl methyl sulfoxide exhibited an induction period, and the rate of racemization was not first-order. During the course of the racemization of benzyl *p*-tolyl sulfoxide at 135–155 °C four decomposition products, bibenzyl (minor product), *p*-tolyl *p*-toluenethiosulfonate, benzyl *p*-tolyl sulfide, and benzaldehyde (major products), were obtained.[10] On the other hand, benzyl methyl sulfoxide was heated to 210–230 °C for 10–15 min and gave benzaldehyde and methanethiol in a high yield.[12]

Thermal decompositions of sulfoxides having no β-hydrogen[13] thus generate sulfinyl radicals and seem to be a convenient method for the studies of sulfinyl radicals, but as described above some complexities exist in these reactions. In this study thermal decompositions of benzhydryl *p*-tolyl sulfoxide and methyl sulfoxide have been investigated, and it was found that an addition of a small amount of pyridine made the decomposition behavior simple, namely, only the coupling products (thiolsulfonate and tetraphenylethane) were formed.

(6) For the discussion of this mechanism, see ref 1a.
(7) For example, see: Chau, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711.
(8) (a) Nishikida, K.; Williams, F. *J. Am. Chem. Soc.* **1974**, *96*, 4781. (b) Chatgilialoglu, C.; Gilbert, B. C.; Kirk, M.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1084 and references therein.
(9) Haward, J. A.; Furimsky, E. *Can. J. Chem.* **1974**, *52*, 555.
(10) Miller, E. G.; Rayner, O. R.; Thomas, H. T.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4861.
(11) Brower, K. R.; Wu, T. *J. Am. Chem. Soc.* **1970**, *92*, 5303.
(12) Entwistle, I. D.; Johnstone, R. A. W.; Millard, B. *J. Chem. Soc. C* **1967**, 302.
(13) Alkyl sulfoxides containing β-hydrogens generally undergo pyrolysis by cis elimination to olefins and sulfenic acids.

Table II. Rate Constants for the Decompositions of BTSO in Benzene

temp, °C	[BTSO], M	[Py],[a] M	10^4k, s^{-1}	10^4k_{av}, s^{-1}
97.5	0.33	0.29	0.40_7	
102.1	0.30	0.20	0.72_7	
103.5	0.32	0.19	0.97_0	
108.1	0.30	0.23	1.5_0	
	0.33	0.22	1.1_3	1.3
112.2	0.33	0.27	1.7_4	
	0.36	0.21	1.8_4	1.8
115.4	0.30	0.25	3.3_0	
	0.32	0.18	2.3_3	2.8

[a] Pyridine.

Table III. Rate Constants for the Decompositions of BMSO in Benzene

temp, °C	[BMSO], M	[Py],[a] M	10^4k, s^{-1}	10^4k_{av}, s^{-1}
105	0.29	0.15	0.77_9	
	0.32	0.19	0.81_8	0.80
110	0.29	0.14	1.5_2	
	0.34	0.24	1.6_6	1.6
115	0.34	0.18	2.7_9	
	0.39	0.38	3.1_6	3.0
120	0.27	0.20	4.9_9	
	0.35	0.25	5.0_7	5.0

[a] Pyridine.

Table IV. Effect of Pyridine Concentrations on Rate Constants for the Decompositions of BMSO in Benzene at 120 °C

[BMSO], M	[Py],[a] M	10^4k, s^{-1}
0.27	0.20	5.0
0.35	0.25	5.1
0.38	1.2	4.8
0.33	2.0	4.3
0.29	4.8	4.1

[a] Pyridine.

Results

Thermal Decompositions of Benzhydryl *p*-Tolyl Sulfoxide (BTSO) and Benzhydryl Methyl Sulfoxide (BMSO) in the Presence of Pyridine. When BTSO in benzene-d_6 was thermally decomposed at 120 °C for 26 h, tetraphenylethane, *p*-tolyl *p*-toluenethiosulfonate, benzhydryl *p*-tolyl sulfone, bis(diphenylmethyl) ether, *p*-tolyl disulfide, and benzhydryl *p*-tolyl sulfide were mainly formed as shown in Table I. However, Table I shows that when the decomposition was carried out in the presence of a small amount of pyridine, only tetraphenylethane and *p*-tolyl *p*-toluenethiosulfonate were obtained.[14] The similar effect of pyridine addition was observed in BMSO decompositions (Table I). Since the reaction mixture was found to be acidic after reaction in the absence of pyridine, the acids, which would be neutralized by added pyridine, might induce the decompositions of the sulfoxides to form the other products in Table I. In fact, triphenylamine and *tert*-butylamine have similar effects, and BTSO decomposition in the presence of benzenesulfonic acid gave only very small amounts of the two coupling products and many other compounds. Miller et al.[10] have reported that the rate of racemization of benzyl methyl sulfoxide was not

(14) Preliminary experiments of thermal decompositions of benzyl *p*-tolyl sulfoxide in the presence of pyridine showed that some of the products (including the two coupling products) obtained were different from that in the absence of pyridine, and the rate was slower than that in the absence of pyridine.

Table V. Activation Parameters[34] for the Decompositions of BTSO and BMSO in Benzene[a]

	BTSO	BMSO
E_a, kcal/mol	28.9 ± 1.9	36.2 ± 1.4
$\Delta H^{\ddagger}$, kcal/mol	28.1 ± 1.9	35.5 ± 1.4
log A	12.7 ± 1.2	16.9 ± 0.8
$\Delta S^{\ddagger}$, eu	−3.1 ± 5.0	16.1 ± 3.7

[a] A small amount of pyridine (ca. 0.3 M) was added.

Table VI. Products in the Thermal Decompositions[a] of BTSO and BTSN in Benzene

	yield, mol %	
product	BTSO (0.53 M)	BTSN (0.5 M)
$(Ph_2CH)_2$	11	11
p-TolSSO$_2$Tol-p	22	22
p-TolSO$_2$CHPh$_2$	17	14
$(Ph_2CH)_2O$	28	28
$(p$-TolS$)_2$	24	25
p-TolSCHPh$_2$	3	

[a] 120 °C, 26 h.

of any simple order and showed an induction period. We have found that the decompositions of BTSO and BMSO showed that the rate increased rapidly as the reaction proceeded, but addition of pyridine altered it to clean first-order behavior.

Tables II and III list first-order rate constants for BTSO and BMSO at various temperatures, respectively. Although pyridine was used as an acid trapping agent, Table IV showed that the solvent effect of pyridine can be negligible in the small concentration range used in Tables II and III. The activation parameters calculated from the rate data in the tables are listed in Table V.

ESR Spectra Obtained during BTSO Decompositions. A broad singlet, having $g = 2.0090$ and showing no hyperfine splitting, was obtained in the BTSO decomposition in mesitylene at 80–120 °C. This may be attributed to the p-toluenesulfinyl radical since a similar g value (2.0089[15] and 2.0092[16]) and a broad singlet[15] at a high temperature (160 °C) were obtained for the p-toluenesulfinyl radical. No signal for the BMSO decomposition was obtained even at 140 °C, probably due to strong line-broadening[15] for alkanesulfinyl radicals at high temperatures.

Rearrangement of BTSO to Benzhydryl p-Toluenesulfenate (BTSN) during Decomposition. NMR spectra showed that BTSO was partly rearranged to BTSN. This type of the rearrangement was reported in the racemization of benzyl p-tolyl sulfoxide.[10] Table VI shows that a product distribution similar to that from BTSO decomposition was obtained when BTSN was decomposed in the absence of pyridine. It suggests that the equilibrium of eq 2 was established soon after the reaction

$$\text{BTSO} \underset{}{\overset{K}{\rightleftharpoons}} \text{BTSN} \qquad (2)$$

was started. The equilibrium constants have been found to be 0.18_4 and 0.18_0 from the NMR when BTSO and BTSN are heated at 120 °C for 2 min, respectively. This value indicates that BTSO is ~1 kcal/mol more stable than BTSN at 120 °C.

Chemically Induced Dynamic Nuclear Polarization (CIDNP). No CIDNP was observed when BTSO was decomposed at 120 °C in benzene-d_6 which contained pyridine-d_5. However, when a small amount of methanol-d_4 was added, emission signals at the methine proton of BTSO (4.94 ppm) and BTSN (5.77 ppm) formed by the rearrangement were observed as shown in Figure 1. These emissions continued until almost all the BTSO was decomposed. Similarly, emission signals of the methyl and methine protons of BMSO were observed during decomposition in the presence of methanol (Figure 2). CIDNP was also observed when phenol was used instead of methanol.

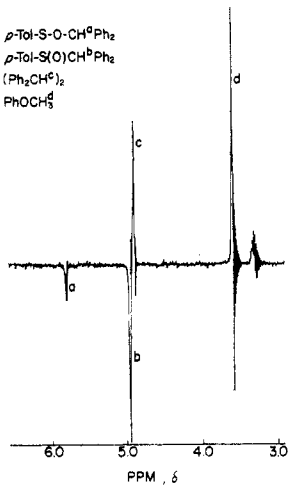


Figure 1. NMR spectrum of the decomposition of BTSO (0.153 mmol) after 15 min at 115 °C in methanol-d_4 (2.70 mmol)–pyridine-d_5 (0.115 mmol)–benzene-d_6 (3.75 mmol). Anisol (0.0361 mmol) was used as an internal standard.

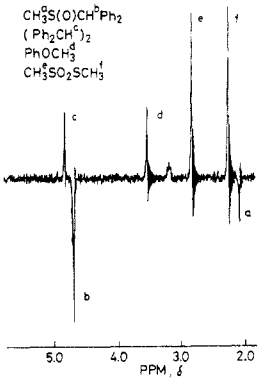


Figure 2. NMR spectrum of the decomposition of BMSO (0.152 mmol) after 55 min at 160 °C in methanol-d_4 (2.63 mmol)–pyridine-d_5 (0.178 mmol)–benzene-d_6 (3.76 mmol). Anisol (0.061 mmol) was used as an internal standard.

Table VII. Rate Constants for the Decompositions[a] of BMSO in the Presence of Methanol or Phenol

temp, °C	[BMSO], M	[Py],[b] M	additive (concn, M)	10^4k, s^{-1}
115	0.41	0.40	methanol (4.7)	1.4_6
	0.32	0.28	phenol (0.84)	0.78
120	0.33	0.26	methanol (3.9)	2.2_6
	0.33	0.38	phenol (0.93)	1.1_5
125	0.34	0.26	methanol (4.3)	3.7_4
	0.33	0.40	phenol (0.88)	2.2_5
130	0.35	0.37	methanol (4.6)	6.2_9
	0.33	0.42	phenol (0.85)	4.1_6

[a] Benzene solvent. [b] Pyridine.

Effects of Hydroxylic Solvents on the Rates of BMSO Decompositions. Table VII shows that the rate constants for BMSO decompositions decreased on the

(15) Gilvert, B. C.; Kirk, C. M.; Norman, R. O. C.; Laue, H. A. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 497.
(16) Gilbert, B. C.; Gill, B. *J. Chem. Soc., Chem. Commun.* **1978**, 78.

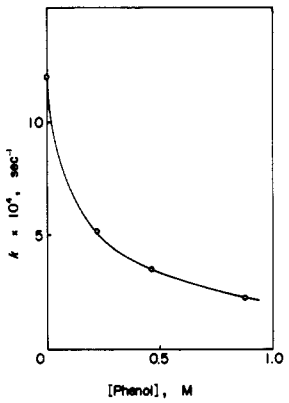
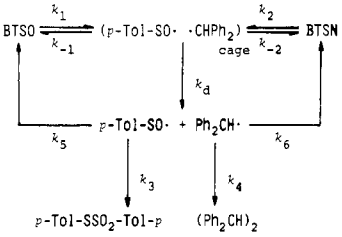
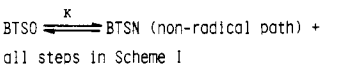


Figure 3. The effect of phenol concentration on the rate constants for the decomposition of BMSO (~0.15 mmol, ~0.3 M solution) at 125 °C in pyridine-d_5 (~0.1 mmol)–benzene-d_6 (~5 mmol).

Scheme I



Scheme II



addition of a small amount of methanol (3.9–4.7 M; methanol-d_4 vs. benzene-d_6, volume ratio 1:~5). Phenol, which has an effect similar to that of methanol for CIDNP phenomena, has a striking solvent effect even in a very small concentrations (Table VII, 0.8–0.9 M, volume ratio 1:~15), and in Figure 3, the rate decreased to nearly half by the addition of only 2% (by volume) of phenol.

Discussion

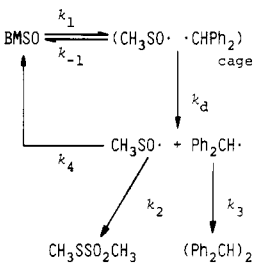
Mechanism of BTSO and BMSO Decompositions. In BTSO decompositions BTSN is present in equilibrium with BTSO (eq 2). Since the dynamic equilibrium is established at a very early stage of reaction, a product distribution similar to that in BTSO decomposition was obtained in BTSN decomposition (Table II). CIDNP, as will be described later, indicates that this rearrangement occurs through a radical pair, at least partly.

From Scheme I, in which the equilibrium between BTSO and BTSN is established through the radical pair ($K = k_1k_{-2}/k_{-1}k_2$), the rate of BTSO disappearance can be expressed as eq 3 from a steady-state assumption for the radicals.

$$-\mathrm{d[BTSO]}/\mathrm{d}t = k_1\left(\frac{k_d}{k_{-1}}\right)\left[\frac{2(k_3k_4)^{1/2}}{k_5 + k_6 + 2(k_3k_4)^{1/2}}\right][\mathrm{BTSO}] \quad (3)$$

However, it must be considered that there is another mechanism (Scheme II) in which a major part of the rearrangement (BTSO–BTSN interconversion) may proceed by an intramolecular nonradical pathway, and the equilibrium between BTSO and BTSN may be established by this reaction. Miller et al.[10] have suggested that this type of reaction may occur for benzyl *p*-tolyl sulfoxide rearrangement. In this case the rate equation (eq 5) can be derived as shown in eq 4. Both Schemes I and II lead to

Scheme III



$$-\mathrm{d[BTSO]}/\mathrm{d}t = (k_1 + k_2K) \times \left(\frac{k_d}{k_{-1} + k_{-2} + k_d}\right)\left[\frac{2(k_3k_4)^{1/2}}{k_5 + k_6 + 2(k_3k_4)^{1/2}}\right][\mathrm{BTSO}] \quad (4)$$

first-order kinetics, in accord with experiment. Miller et al.[10] have reported that the rate constant for the rearrangement of benzyl *p*-toluenesulfenate to the sulfoxide is 3.28×10^{-5} s^{-1} at 110 °C. Our experiment shows that the rate constant (8.8×10^{-5} at 50 °C) for BTSN is much greater than that for benzyl *p*-toluenesulfenate. The radical mechanism for the rearrangement (Scheme I) seems to be reasonable from this result, since the benzhydryl radical is more stable and more easily formed than the benzyl radical. However, an intramolecular mechanism (Scheme II) may assume[17] a partial positive charge on the benzyl or benzhydryl carbon in the transition state, and the same order of the stabilities between them may be expected; at present we have no preference for Scheme I or II.

On the other hand, the mechanism for dialkyl sulfoxide BMSO decomposition may be simple, since the participation of the sulfenate (BMSN) may not need to be considered in this case because of the reasons given below. No BMSN was detected, unlike BTSN, during BMSO decomposition, and the attempts to prepare BMSN from methanesulfenyl chloride with lithium benzhydryl alcoholate were unsuccessful, leading to complex mixtures probably due to a rapid decomposition of BMSN. So, BMSN may be very unstable, compared with BMSO, and even if the equilibrium between BMSO and BMSN exists,[18] only a negligible amount of BTSN is present.

Entwistle, Johnstone, and Millard[12] have proposed that the mechanism of pyrolysis of benzyl methyl sulfoxide and BMSO at 210–230 °C to give the corresponding carbonyl compounds and methanethiol occurs through a rearranged sulfenate (eq 5). BMSO in mesitylene gave tetra-

$$\mathrm{RR'CHS(O)CH_3} \rightarrow (\mathrm{RR'CHOSCH_3}) \rightarrow \mathrm{RR'C{=}O + CH_3SH} \quad (5)$$

phenylethane (48%), in addition to benzophenone (12%) and methanethiol. In our reactions, however, the pyrolysis of BMSO in the presence of pyridine at 105–130 °C gave only tetraphenylethane and methyl methanethiosulfonate (no detection of benzophenone and methanethiol). So, it

(17) Maricich, T. J.; Harrington, C. K. *J. Am. Chem. Soc.* **1972**, *94*, 5115.

(18) The stabilities of benzhydryl arenesulfenate ($Ph_2CHOSAr$) and benzhydryl alkanesulfenate (Ph_2CHOSR) seem to be Ar = *p*-nitrophenyl > Ar = phenyl (Abdulvaleeva, F. A.; Khodak, A. A.; Zefirof, N. S. *Zh. Org. Khim.* **1972**, *8*, 433) and R = CCl_3 > R = CH_3 (no isolation). Benzhydryl trichloromethanesulfenate did not rearrange to the corresponding sulfoxide but decomposed to chlorodiphenylmethane and benzyl chloride, respectively (Braverman, S.; Stabinsky, J. *Isr. J. Chem.* **1967**, *5*, 125), while, benzyl trichloromethanesulfenate was found[22] to rearrange into the sulfoxide probably through an ion pair.

seems that the assumption of a sulfenate intermediate is unnecessary under our experimental conditions.

From Scheme III, the rate of BMSO disappearance is given by eq 6, where f is the efficiency of radical production from a solvent cage times that of the product formation of escaped radicals.

$$-\mathrm{d[BMSO]} = k_1\left(\frac{k_d}{k_{-1}+k_d}\right)\left[\frac{2(k_2k_3)^{1/2}}{k_4+2(k_2k_3)^{1/2}}\right][\mathrm{BMSO}] = fk_1[\mathrm{BMSO}] \quad (6)$$

Effects of Hydroxylic Solvents on the Rates of BMSO Decompositions and CIDNP Phenomena. The decrease in the rates by the addition of methanol or phenol (Table VII and Figure 3) can be explained by a strong solvation (hydrogen bonding) to the reactant (BMSO) and to a lesser extent to sulfinyl radical[19] in the transition state. Association constants (eq 7) of phenol and n-butyl and

$$\mathrm{ROH} + \mathrm{Me_2SO} \overset{K}{\rightleftharpoons} \mathrm{ROH{\cdots}O{=}S(CH_3)_2} \quad (7)$$

n-heptyl alcohols with dimethyl sulfoxide were reported to be ~200 M^{-1} for phenol and 9 M^{-1} for the latter two alcohols.[20] This explains the marked decrease of the rates (stronger solvation to BMSO than methanol) in the case of phenol addition.

CIDNP results also support the above explanation. CIDNP observed in BTSO and BMSO decompositions in the presence of methanol or phenol can be interpreted as the spectra of the caged products from the CIDNP rule[21] and $g(CH_3SO\cdot$ or p-TolSO$\cdot) > g(Ph_2CH\cdot)$ (eq 8 and 9).

$$p\text{-TolS(O)C}\underline{\mathrm{H}}\mathrm{Ph_2} \rightleftarrows (p\text{-TolSO}\cdot\ \cdot\mathrm{CHPh_2}) \rightleftarrows p\text{-TolSOC}\underline{\mathrm{H}}\mathrm{Ph_2} \quad (8)$$
E cage E

$$\mathrm{C}\underline{\mathrm{H}}_3\mathrm{S(O)C}\underline{\mathrm{H}}\mathrm{Ph_2} \rightleftarrows (\mathrm{CH_3SO}\cdot\ \cdot\mathrm{CHPh_2}) \quad (9)$$
E E cage

These results indicate that at least a part of the rearrangement occurs through a radical pair. There are several mechanisms proposed in sulfoxide–sulfenate rearrangement, including radical pair, ion pair,[22] and concerted mechanisms,[17] and as described before, it is uncertain that BTSO–BTSN rearrangement occurs only by radical mechanism or not.

The reason why CIDNP was observed in the presence of methanol or phenol can be explained as follows.[23] Solvation of these solvents to BMSO or BTSO may make "in cage" return more favorable, i.e., may increase k_{-1}/k_d. In the absence of methanol or phenol, polarizations of the sulfoxides formed in a cage may be canceled out by the reverse polarizations of the sulfoxides formed outside a cage in a comparable amount. This explanation may not be applicable to CIDNP of the sulfenate in eq 8, since less polar BTSN does not seem to be strongly solvated. Rapid formation from polarized BTSO may be one possible explanation.

Bond Dissociation Energy for Carbon–Sulfur Bond in Sulfoxides. Activation parameters for BMSO decompositions reflect the step with k_1, as shown in eq 6, unlike the case of BTSO decompositions in which the presence of BTSN rearranged from BTSO makes an interpretation of the activation parameters unclear (eq 4 or 5).

With the assumption that the activation energy for the radical recombination step (k_{-1} in Scheme III) is zero, it follows that eq 10 holds, where $D(CH_3S(O)\text{–}CHPh_2)$, E_1,

$$D(\mathrm{CH_3S(O)\text{–}CHPh_2}) = E_1 - E_{-1} \simeq E_1 \quad (10)$$

and E_{-1} are bond dissociation energy (BDE) for sulfinyl sulfur–benzhydryl carbon scission and the activation energies for scission (k_1) and recombination (k_{-1}), respectively.

If we assume that $D(CH_3S(O)\text{–}CH_3) - D(CH_3S(O)\text{–}CHPh_2) = 24$ kcal/mol, which is taken from twice[24] the difference between the $D(CH_3S(O_2)\text{–}CH_3)$ value of 68 kcal/mol and the $D(CH_3S(O_2)\text{–}CH_2Ph)$ value of 56 kcal/mol,[25] and we use $D(CH_3S(O)\text{–}CH_3) = 55 \pm 2$ kcal/mol (the value estimated by Benson[25]), then we can estimate that $D(CH_3S(O)\text{–}CHPh_2) = 31 \pm 2$ kcal/mol, in rough agreement with our experimental value of 36 kcal/mol. Our value obtained in benzene may not be much different from the BDE in the gas phase (other BDE values above are those in the gas phase), because benzene is not a polar solvent. Kice has suggested that large differences in BDE for sulfur compounds having different oxidation states [$D(CH_3S\text{–}CH_3) > D(CH_3S(O_2)\text{–}CH_3) > D(CH_3S(O)\text{–}CH_3)$ and $D(S\text{–}S) > D(S\text{–}S(SO_2)) > D(S\text{–}S(O))$] can be attributed to the stabilities of the radicals formed, namely, RS$\cdot$ < RS(O$_2$)$\cdot$ < RS(O)$\cdot$.[1a] However, Benson[25] has explained this "bond-weakening effect" of the sulfoxide group on adjacent bonds by the instability of the parent molecule ($D(R_2S(O){=}O) - D(R_2S{=}O) \simeq 23$ kcal/mol). Although we cannot offer the data concerning it, the reluctant reactivity of sulfinyl radicals described at the beginning of the paper and the similar behavior of RSS$\cdot$[26] and RNS$\cdot$,[27] which are formed from decompositions of RSSSSR and RNSSNR, in which parent compounds are divalent sulfur compounds unlike sulfoxide, suggest that main reason for it may be the stabilities of sulfinyl radicals.

Experimental Section

General Remarks. Melting points are uncorrected. NMR spectra were obtained by using either a JEOL JNM-PS-100 (100 MHz) or a JEOL C-60HL (60 MHz) spectrometer. Electronic absorption spectra were recorded with a Cary 14 spectrophotometer. ESR spectra were obtained with a Varian E-4 spectrometer.

Materials. Benzhydryl p-tolyl sulfoxide (BTSO) and benzhydryl p-toluenesulfenate (BTSN) were prepared by the method of Miller et al.[10] BTSO, separated by a silica gel chromatography,[10] was recrystallized from benzene and then twice from ethanol: mp 142–144 °C (lit.[10] mp 137–138 °C); IR (KBr) 1040 cm^{-1} (S=O); NMR ($CDCl_3$) δ 2.33 (s, 3 H, CH_3), 4.78 (s, 1 H, CH), 7.1–7.4 (m, 14 H, aromatic).

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.57; H, 6.29; S, 10.41. Found: C, 78.39; H, 5.92; S, 10.47.

BTSN was recrystallized from ether at a low temperature: IR (KBr) 970 cm^{-1} (sulfenate), no absorption at 1040 cm^{-1}; NMR ($CDCl_3$) δ 2.30 (s, 3 H, CH_3), 5.56 (s, 1 H, CH), 7.1–7.5 (m, 14 H, aromatic).

Benzhydryl methyl sulfoxide (BMSO) was prepared[10] by $NaIO_4$ oxidation of benzhydryl methyl sulfide.[12] After a chromatographic

(19) This reaction is endothermic, so the transition state may be product-like, and formation of sulfinyl radical may be almost accomplished.
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(23) We thank a referee for helpful suggestions regarding this explanation.
(24) This assumption seems to be valid. For example, $D(CH_3\text{–}H)$ (104 kcal/mol) - $D(PhCH_2\text{–}H)$ (85 kcal/mol) = $D(PhCH_2\text{–}H)$ (85 kcal/mol) - $D(Ph_2CH\text{–}H)$ (66 kcal/mol) = 19 kcal/mol (Benson, S. W.; O'Neal, H. E. Report NSRDS-NBS21; U.S. Government Printing Office: Washington, DC, 1970).
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separation of silica gel, in which elutions with benzene and ethanol gave the unreacted sulfide and the sulfoxide, respectively, BMSO was recrystallized from a petroleum ether–ethanol mixture: mp 112 °C (lit.[12] mp 112–114 °C); IR (KBr) 1050 cm^{-1} (S=O); NMR ($CDCl_3$) δ 2.33 (s, 3 H, CH_3), 4.71 (s, 1 H, CH), 7.1–7.6 (m, 10 H, aromatic).

The other compounds used in this study, benzhydryl *p*-tolyl sulfide,[28] bis(diphenylmethyl) ether,[28] *p*-tolyl disulfide, methyl disulfide, benzhydryl *p*-toluenesulfinate,[29] benzhydryl methyl sulfone,[12] and methyl methanethiosulfonate,[30] were prepared according to the methods described in the literature.

Thermal Decompositions of BTSO, BTSN, and BMSO. A solution of BTSO (3.71 g, 0.012 mol) in benzene (22.6 mL) in a reaction tube was degassed on a vacuum line by a freeze–thaw method, and the tube sealed was heated at 120 °C for 26 h. The reaction mixture was then analyzed by chromatography on silica gel. Elution with benzene gave tetraphenylethane, bis(diphenylmethyl) ether, *p*-tolyl disulfide, and *p*-tolyl *p*-toluenethiosulfonate, respectively. Tetraphenylethane: mp 208–209 °C (lit.[31] mp 210 °C); NMR ($CDCl_3$) δ 4.73 (s, 2 H, CH), 6.7–7.3 (m, 20 H, aromatic). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.03; H, 6.76. Bis(diphenylmethyl) ether: mp 108–109 °C (lit.[32] mp 109–110 °C); NMR ($CDCl_3$) δ 5.38 (s, 2 H, CH), 7.1–7.5 (m, 20 H, aromatic); this compound was identified by comparison of its NMR and IR spectra with those of the authentic sample prepared[32] and by a mixture melting point experiment. *p*-Tolyl disulfide: mp 46 °C; NMR ($CDCl_3$) δ 1.94 (s, 6 H, CH_3), 6.6–7.6 (m, 8 H, aromatic); this compound was identified by comparison with an authentic sample. *p*-Tolyl *p*-toluenethiosulfonate: mp 75–76 °C (lit.[4] mp 75–76 °C); NMR ($CDCl_3$) δ 2.34 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 7.0–7.6 (m, 8 H, aromatic). Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07; S, 23.03. Found: C, 60.22; H, 5.22; S, 22.89. Elution with 20% ethyl acetate in benzene gave benzhydryl *p*-tolyl sulfone: mp 190–191 °C (lit.[33] mp 192–193 °C); NMR ($CDCl_3$) δ 2.33 (s, 3 H, CH_3), 5.22 (s, 1 H, CH), 6.9–7.6 (m, 14 H, aromatic). Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.51; H, 5.63; S, 9.94. Found: C, 74.45; H, 5.04; S, 9.67.

The yields of the products were determined from the NMR peak areas of the methine or/and methyl protons of each product by using anisole (methyl protons) as an internal standard. In this case, the reactions were carried out in a sealed NMR tube immersed in a thermostat after the reaction mixture in benzene-d_6 (99.7%) was degassed, and the products obtained were analyzed by NMR without isolation of the products.

BTSN gave the same products as those for the case of BTSO decompositions, and the yields were determined by the NMR method.

Similarly, in the thermal decompositions of BMSO, tetraphenylethane, methyl methanethiosulfonate, methyl disulfide, benzhydryl methyl sulfone, bis(diphenylmethyl) ether, and benzhydryl methyl sulfide were identified by using the authentic samples. The yields were also obtained from the NMR method without isolation of the products.

The product yields in the presence of pyridine, methanol, or phenol were determined from the NMR by using pyridine-d_5 (99.4%), methanol-d_4 (99.5%), or phenol, in addition to BTSO (or BMSO) and benzene-d_6 (99.7%).

CIDNP was observed during the decomposition in the presence of methanol or phenol as described in Results, and no CIDNP signal was observed at room temperature.

Rate of the Decompositions. The rate for the disappearance of BMSO was followed by the measurements of the NMR peak areas of the methine proton of BMSO and the methyl protons of anisole as an internal standard. The reaction was carried out in a NMR tube at 105–130 °C, and NMR measurements were taken at room temperature after the mixture was cooled to stop the reaction at regular time intervals.

In the case of BTSO, since methine proton signals of BTSO and tetraphenylethane overlap with each other at room temperature but overlap little at higher temperatures, the rate was followed directly at the reaction temperatures (97.5–115.4 °C) by regulating the temperature of the NMR cavity, which was measured by a copper–constantan thermocouple immersed in an NMR tube. At 120 °C δ values (Me_4Si as standard) of all the compounds used here were shifted toward lower field by 0.1–0.3 ppm. The peak areas were averaged from at least three integrations.

In both cases, good first-order rate plots were obtained over about 80% reaction.

Equilibrium between BTSO and BTSN and Rearrangement Rate of BTSN to BTSO. Equilibrium constants were determined by NMR at 120 °C. Similar compositions of BTSO–BTSN mixtures were obtained after 2 min at 120 °C when BTSO or BTSN in benzene-d_6 was heated. The rearrangement rate of BTSN to BTSO was followed by degassed dioxane solution spectrophotometrically at 50 °C. At regular time intervals, reaction mixtures in a 1-cm cell were cooled to stop the reaction, and the quantity of BTSN that remained was determined from absorption at 317 nm [λ_{max} of BTSN (ε 2300)] where BTSO had little absorption [λ_{max} 262 nm, (ε 9000)]. The reaction obeyed good first-order kinetics in the early stages of the reaction.

Registry No. Benzhydryl *p*-tolyl sulfoxide, 5427-07-6; benzhydryl *p*-toluenesulfenate, 21127-57-1; benzhydryl methyl sulfoxide, 2863-45-8; tetraphenylethane, 632-50-8; bis(diphenylmethyl) ether, 574-42-5; *p*-tolyl disulfide, 103-19-5; *p*-tolyl *p*-toluenethiosulfonate, 2943-42-2; benzhydryl *p*-tolyl sulfone, 5433-78-3; benzhydryl *p*-tolyl sulfide, 32110-49-9; methyl methanethiosulfonate, 2949-92-0; benzhydryl methyl sulfone, 25195-40-8; methyl disulfide, 624-92-0; benzhydryl methyl sulfide, 15733-08-1.

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