elevated temperatures the hydroxynitrocyclohexadienyl radicals have sufficient time to equilibrate (PhNO₂ + OH \rightleftharpoons HO- $Ph-NO_2$) before being oxidized to the nitrophenols. The results in Table II show that decreasing the concentration of benzene increases the ratio of nitrophenols/phenol as expected for a reaction in which benzene and nitrobenzene compete for the hydroxylating species.

Since the elimination of OH radical from the hydroxycyclohexadienyl radical is a high activation energy process, this reaction cannot be observed at 25 °C²² or in the presence of oxidizing agents. Oxygen²³ and cupric ion²⁴ oxidize hydroxycyclohexadienyl radicals to phenol. Some results in the presence of oxygen and Cu^{2+} are shown in Table II (experiments 10-16). Oxidation competes with the dissociation to benzene and OH radicals, and thus decreases the yield of nitrophenols. At low oxygen concentration (experiment 10) nitrophenol is still formed, but if the solution is saturated with oxygen (experiments 11-14) phenol is the only product. If we compare experiments 2 and 10, we can see that the total product yield is about the same, but in experiment 10 we obtain more phenol and less nitrophenol compared to that found in experiment 2. Cu^{2+} shows a similar effect (compare experiments 3, 15, and 16).

If benzene is replaced by toluene no nitrophenols are formed. The only products are benzaldehyde and benzyl alcohol.²⁵ This observation also agrees with our proposed mechanism. Toluene radical cation instead of adding water will preferentially eliminate a proton to give benzyl radicals, which in turn are oxidized to benzaldehyde and benzyl alcohol.^{5,6,26} We therefore produce no OH radicals and no nitrophenols.

If in experiment 2 (Table I) benzene was replaced by 5×10^{-3} mol of anisole, we again do not observe any formation of nitro-

(26) K. Schested, J. Holoman, and E. J. Hart, J. Phys. Chem., 81, 1363 (1977); C. Walling and R. A. Johnson, J. Am. Chem. Soc., 97, 363 (1975).

phenols. Under these conditions 100% of SO₄- reacts initially with anisole.¹⁵ It is well known that anisole radical cation does not add water,^{7,8} and therefore according to our scheme does not produce OH radicals.

Other indirect evidence for the reversibility of OH radical addition to aromatics can be found in the literature. Balakrishnan and Reddy²⁷ have studied the radiation-induced hydroxylation of naphthalene and found with increasing temperature (27-94 °C) a remarkable decrease in β -hydroxylation. Although the authors did not discuss the mechanistic aspects of this change in isomer ratio, their results can be explained by a reversible addition and formation of the more stable α intermediate as required by theory.28

Experimental Section

All experiments were carried out with 2.5×10^{-3} mol of Na₂S₂O₈ in 500 mL of triple distilled water. The solutions were deoxygenated by bubbling Argon through the solution for about 30 min with occasional shaking. The benzene and/or nitrobenzene was injected through a rubber septum and the solution was vigorously shaken and heated in a water bath at 80 °C. The reaction was stopped by cooling in ice. The mixture was then extracted once with 200 mL of ether and three times with 100 mL of ether. The combined ether extracts were dried over Na₂SO₄ and concentrated to 10 mL and then analyzed by gas chromatography as described previously.^{4,5} The nitrophenols were analyzed after methylation with diazomethane.² Most experiments were repeated several times and the results were found to be reporducible within $\pm 10\%$ in the worst case. Most experiments were reproducible with $\pm 5\%$. In one experiment (no. 4, Table I) the disappearance of $S_2O_8^{2-}$ was determined iodometrically,²⁹ and it was found that 28% had reacted. In this experiment we have therefore obtained an almost quantitative product yield.

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Thermolysis of α -Azido Sulfides, Sulfoxides, and Sulfones: Dependence of Mechanism on Oxidation State of Sulfur

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Abstract: Thermolyses of α -azidobenzyl phenyl sulfide (1), sulfoxide (3), and sulfone (2) proceed at markedly different rates. Sulfone 2 requires the highest temperature (>150 °C), whereas sulfide 1 loses nitrogen at 120 °C with neighboring group participation by the sulfur atom to produce N-benzylidenebenzenesulfenamide 4 in 75% yield. Sulfoxide 3 readily decomposes at 70 °C through a radical-pair intermediate, which gives rise to a CIDNP effect in the reaction products. Kinetic data are presented supporting the suggested reaction mechanisms.

The thermolysis of azides with loss of nitrogen is one of the most characteristic and useful reactions of organic azides.¹ These reactions often involve nitrene intermediates¹ though there are a number of notable exceptions where apparent neighboring-group participation by adjacent nucleophilic groups obviates the normal nitrene intermediate. These reactions are characterized by their occurrence at significantly lower temperatures and, where the data have been determined, by having significantly negative entropies of activation.²

For some time, we have been interested in the chemistry of organic sulfur compounds which possess halogen atoms on the carbon bearing the sulfur functionality.³ Since azides are

⁽²²⁾ M. K. Eberhardt, unpublished preliminary results. (23) L. M. Dorfman, I. A. Taub, and R. F. Buhler, J. Chem. Phys., 36, 3051 (1962).

⁽²⁴⁾ K. Bhatia and R. H. Schuler, J. Phys. Chem., 78, 2335 (1974). (25) Using the same concentration and conditions as in Table I (experiment 2), except instead of benzene we used 4.7×10^{-3} mol of toluene, we obtained 14.0×10^{-5} mol of benzaldehyde, 11.8×10^{-5} mol benzyl alcohol, and a trace of bibenzyl.

⁽²⁷⁾ I. Balakrishnan and M. P. Reddy, J. Phys. Chem., 72, 4609 (1968). (28) D. H. Hey and G. H. Williams, Discuss. Faraday Soc., 14, 216 (1953).

⁽²⁹⁾ P. D. Bartlett and J. D. Cotman, Jr., J. Am. Chem. Soc., 71, 1419, (1949).

⁽¹⁾ Abramovitch, R. R.; Kyba, E. O. In "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971; Chapter 5.

⁽²⁾ Hall, J. H.; Dolan, F. W. J. Org. Chem. 1978, 43, 4608, and references therein.

pseudohalides, the study of α -azido organo sulfur compounds seemed a natural extension of our prior work. However, the chemistry we have found associated with the azides shows little resemblance to that we encountered with the halides, although, as is the case with α -halo sulfides, sulfoxides, and sulfones, the chemistry of these α -azido sulfur compounds varies considerably with the state of oxidation of the neighboring sulfur group.

Results and Discussion

The preparations of the α -azidobenzyl phenyl sulfide (1) and



sulfone (2) have been described previously.⁴ The corresponding sulfoxides, 3a and 3b, were prepared from the sulfide 1 by oxidation with 1 equiv of *m*-chloroperoxybenzoic acid (MCPBA). The sulfoxides are acid-sensitive compounds and, therefore, care should be taken in their handling.

When sulfone 2 was heated in refluxing chlorobenzene (132 °C), the mixture appeared stable for several minutes, whereupon a copious amount of nitrogen gas was released. This induction period varied widely, and characterization of the products (eq 1)

$$\begin{array}{c} N_{3} \\ | \\ PhSO_{2}CHPh & \frac{132 \cdot c}{H^{+}} PhCN + PhCHO + PhSO_{2}SPh + \\ 2 \\ PhSO_{3}H + PhSO_{3}H \cdot PhNH_{2} + PhSSPh (1) \end{array}$$

suggested that the reaction was being catalyzed by the acidic products. Indeed, when a solution of 2 at 120 °C was treated with a catalytic amount of p-toluenesulfonic acid, nitrogen gas was rapidly evolved. Sulfone 2 showed no sign of decomposition over a period of several hours at 150 °C in nitrobenzene in the presence of 2% (v/v) of 2,4-dimethylpyridine. Attempts to investigate the kinetics of the thermolysis of 2 at higher temperatures under a variety of conditions were unsuccessful because of our inability to maintain strictly neutral conditions⁵ during the course reaction. However, it is not unreasonable to suggest that under neutral conditions, α -azido sulfones will lose nitrogen in a manner like that of normal alkyl azides. However, in our work, azide 2 clearly is undergoing acid-catalyzed loss of nitrogen (eq 1).

Normal alkyl azides undergo thermolysis at temperatures in excess of 180 °C.1 However, azido sulfide 1 loses nitrogen readily at 120 °C,⁶ which suggests the reaction might involve neighboring group participation by the α -sulfur atom. The major product of this reaction is N-benzylidenebenzenesulfenamide (4), and its formation is consistent with intramolecular attack by sulfur on the neighboring azido group (eq 2). In addition to 4, which was



isolated in \sim 75% yield, smaller amounts of benzonitrile (\sim 10%), benzaldehyde (\sim 5%) and diphenyl disulfide were isolated. Sulfenamide 4 was stable under the reaction conditions, and the

Table I. Kinetic Data and Arrhenius Parameters for Thermal Decomposition of a-Azidobenzyl Phenyl Sulfide (1)

solvent	temp, °C	$k_1 \times 10^4$, s ^{-1a}	data at 120 °C ^b
diphenyl ether	120.2	5.24 ± 0.04	$k_1 = 5.18 \times 10^{-4}$
	131.1	13.4 ± 0.05	$\Delta H^{\ddagger} = 25.9 \pm 0.2$
	140.5	28.0 ± 0.03	$\Delta S^{\ddagger} = -8.2 \pm 0.5$
cyclohexanol	120.1	6.83 ± 0.33	$k_1 = 6.67 \times 10^{-4}$
	128.8	13.5 ± 0.08	$\Delta H^{\pm} = 25.5 \pm 1.4$
	136.4	26.1 ± 0.13	$\Delta S^{\ddagger} = -8.8 \pm 3.4$
decalin	120.1	4.43 ± 0.03	$k_1 = 4.40 \times 10^{-4}$
	129.0	9.51 ± 0.18	$\Delta H^{\ddagger} = 25.9 \pm 0.02$
	138.2	19.9 ± 0.01	$\Delta S^{\ddagger} = -8.6 \pm 0.4$
nitrobenzene	120.1	5.21 ± 0.1	$k_1 = 5.13 \times 10^{-4}$
	130.1	12.3 ± 0.03	$\Delta H^{\ddagger} = 26.9 \pm 0.6$
	138.2	24.8 ± 0.06	$\Delta S^{\ddagger} = -5.7 \pm 1.4$

^a Standard deviation. ^b Units for $k_{1,1} \Delta H^{\ddagger}$, and ΔS^{\ddagger} are s⁻¹, kcal/mol, and eu, respectively.

Table II. Kinetic Data and Activation Parameters for Thermal Decomposition of a-Azidobenzyl Phenyl Sulfoxide (3) in Chlorobenzene

temp, °C	$k_1 \times 10^4$, s ^{-1a}	data at 25 °C
55.0 60.0 65.1 75.0	$\begin{array}{c} 1.45 \pm 0.10 \\ 3.15 \pm 0.42 \\ 6.36 \pm 0.32 \\ 23.5 \pm 1.56 \end{array}$	$k_1 = 1.30 \times 10^{-6} \text{ s}^{-1}$ $\Delta H^{\ddagger} = 30.3 \pm 1.2 \text{ kcal/mol}$ $\Delta S^{\ddagger} = 16.2 \pm 3.2 \text{ eu}$

^a Standard deviation.

product ratios varied little in the solvents studied.

Although formation of sulfenamide 4 at the relatively low temperature (120 °C) of thermolysis is consistent with neighboring-group assistance by sulfur, we sought more convincing evidence through a kinetic study. Table I lists the kinetic data for the thermolysis of azido sulfide 1 in solvents of varying polarity and hydrogen bonding character. The two outstanding features of these data are the insensitivity of rate constants to the change in solvent and the observed negative entropies of activation (\sim -5-9 eu in the four solvent systems). Taken together, these data strongly support the idea of a nonionic and nonnitrene type process⁷ occurring in this reaction. Although there are a few reports of participation by sulfur atoms in the thermolysis of suitably substituted o-aryl azides,⁹ attempts to observe such reactions with sulfides and sulfoxides have met only with failure.¹⁰ The intramolecular participation we observe takes place via the threemembered-ring intermediate 5, whereas with ortho-substituted aryl azides, the intermediate would be a five- or six-membered ring. Whether our success is due to more favored three-membered-ring formation (cf. five-membered-ring formation) or a higher susceptibility of alkyl azides (cf. aryl azides) to intramolecular attack by a neighboring sulfide sulfur atom is unclear.

The results obtained with sulfide 1 and sulfone 2 led us to expect that sulfoxide 3 would behave in a manner intermediate to that observed for 1 and 2. However, we discovered that azido sulfoxide 3 was considerably less stable thermally than sulfide 1, and, although the products of thermolysis (eq 3) were analogous to those observed from sulfide 1, the low yield of the sulfinamide 6^{11} , suggested that reaction 3 might not be a simple analogy to

(7) Nitrenes are efficiently trapped by sulfides and sulfoxides,⁸ and, therefore, product 4 would be an expected major product if there were a nitrene intermediate.

(9) Ashby, J.; Suschitzky, H. Tetrahedron Lett. 1971, 1315. Also see ref 1 and Dyall, L. K. Aust. J. Chem. 1975, 28, 2147. (10) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gal-

lagher, P. T. Angew. Chem., Int. Ed. Engl. 1979, 18, 900.

⁽³⁾ Jarvis, B. B.; Marien, B. A. J. Org. Chem. 1977, 42, 2676. (4) Jarvis, B. B.; Nicholas, P. E. J. Org. Chem. 1980, 45, 2265. (5) α -Azido sulfones react with bases⁴ as well as acids.¹

⁽⁶⁾ α -Azido sulfides undergo Beckmann-type rearrangements in the presence of Lewis acids: Trost, B. M.; Vaultier, M.; Santiago, M. L. J. Am. Chem. Soc. 1980, 102, 7929.

^{(8) (}a) Ando, W. Acc. Chem. Res. 1977, 10, 179; (b) Anderson, D. J.; Horwell, D. C.; Stanton, E.; Gilchrist, T. L.; Rees, C. W. J. Chem. Soc., Perkin Trans. 1 1972, 1317.

⁽¹¹⁾ Sulfinamide 6 is stable under the reaction conditions, though 6 will give benzonitrile if heated for an extended period at 80 °C.¹² Also, a small amount of added water to the benzene or carbon tetrachloride solutions in the thermolysis of 3 had no apparent effect either on the rate of reaction or product distribution.

⁽¹²⁾ Davis, F. A.; Friedman, A. J.; Kluger, E. W. J. Am. Chem. Soc. 1974, 96, 5001.

the reaction of azido sulfide 1 (eq 2).



 $PhSSPh + PhSO_2SPh$ (3)

In addition to the low temperature of thermolysis, another curious feature is that the two diastereomers of 3 (3a and 3b)¹³ decompose at the same rate and yield the same ratios of products. Furthermore, 3a and 3b do not interconvert under the conditions of the reaction. These data are inconsistent with intramolecular assistance by the sulfinyl group in the thermolysis of azido sulfoxide 3. We experienced difficulties in measuring the rates of thermolysis of 3 by the technique (manometric measurement of the nitrogen evolved) used in the case of azido sulfide 1. However, we have been able to obtain reproducible kinetic data by using NMR spectroscopy, and Table II reports our data. The most striking difference in the data associated with reactions 2 and 3 is the entropy of activation factor. For the thermolysis of azido sulfide 1, $\Delta \hat{S}^{\hat{4}}$ is significantly negative, whereas for the thermolysis of azido sulfoxide 3, ΔS^* is positive. Furthermore, we have compared the effect of changing the azides from benzyl to adamantyl and find the rate of thermolysis of benzyl azide 1 (at 120 °C) is very close to the rate of thermolysis of adamantyl azido sulfide 7, whereas with the corresponding azido sulfoxides, 3 and 8, their rates of thermolysis are considerably different, with the benzyl azide 3 being 10² times faster at 110 °C than the rate of thermolysis of adamantyl azide 8.



Figure 1 illustrates the results of a CIDNP¹⁴ experiment conducted with sulfoxide 3a at 73 °C. The strong enhancement observed for the benzylic proton (δ 8.6) in sulfinamide 6 is unequivocal evidence for radical intermediates. The peak at δ 8.4 showing emission rapidly disappears during the course of the reaction, and at the same time the resonance for benzaldehyde¹⁵ begins to appear at δ 9.8. At the end of the reaction, integration of the peaks at δ 8.6 and 9.8 indicated a ratio of 3:2 for sulfinamide 6/benzaldehyde. Although it is tempting to connect the disappearance of the emission resonance at δ 8.4 with the ensuing formation of benzaldehyde, we have no direct evidence that benzaldehyde is derived from this intermediate. We suspect that the intermediate which shows emission at δ 8.4 may be the sulfenate ester isomer 9 which may yield both benzaldehyde and benzonitrile.¹⁶ Alternately, benzaldehyde might arise from a recombination of radical pair 10/11 to give sulfenate azide 12.18

⁽¹⁶⁾ Compound 9 is analogous in structure to O-sulfinyloxime i which others¹⁷ have shown reacts rapidly at 35 °C via a radical pathway to yield benzonitrile and benzaldehyde



^{(17) (}a) Hudson, R. F.; Record, K. A. F. J. Chem. Soc., Chem. Commun. 1976, 831; (b) Brown, C.; Hudson, R. F.; Record, K. A. F. J. Chem. Soc., Perkin Trans. 2 1978, 822.



Figure 1. NMR spectra of the decomposition of α -azidobenzyl phenyl sulfoxide (3a) at 73 °C. (A) Initial spectrum, (B) reaction time = 3.3 min, (C) reaction time = 6.5 min, (D) reaction time = 10.3 min, (E) reaction time = 28 min, (F) final spectrum.



This ester is likely to undergo sulfur-oxygen bond cleavage¹⁹ to give benzaldehyde. The overall mechanism is outlined in Scheme I.

When the thermolysis of azido sulfide 1 at 120 °C was monitored in the same fashion by NMR spectroscopy, there was no evidence of any CIDNP effect. These data clearly emphasize the difference in the ease with which sulfides and sulfoxides undergo C-S bond homolysis.²³ Previous workers have noted the relative

⁽¹³⁾ The diastereomers 3a and 3b were separated by fractional crystallization, but no attempt was made to assign the stereochemistry.

^{(14) (}a) Ward, H. R. Acc. Chem. Res. 1972, 5, 18; (b) Lawler, R. G. Ibid. 1972, 5, 25.

⁽¹⁵⁾ We also observed an emission line for the aldehydic proton in benzaldehyde under slightly different conditions, i.e., higher reaction temperature (76 °C) and in the presence of Me₂SO- d_6 , which was used for an internal lock on the FT NMR instrument.

⁽¹⁸⁾ Since radical 10 and 11 could recombine to give both 3 and 12, presumably, if recombination does occur, it must occur in the cage and with only minor rotation of the radicals involved. If recombination were to occur after significant rotation of 10 and/or 11, epimerization of 3 would have been observed.

⁽¹⁹⁾ Sulfenates are reasonably stable compounds below $100 \circ C^{20}$ but are very reactive toward electrophiles and nucleophiles.²¹ Sulfenates and sulfenic acids are surprisingly good nucleophiles,^{21,22} and a benzylic system such as in 12 might be expected to rapidly undergo hydrolysis in the presence of trace amounts of water to give benzaldehyde.

⁽²⁰⁾ Kharasch, M.; Potempa, S. J.; Wehrmeister, H. L. Chem. Rev. 1946, 39, 269.

^{(21) (}a) Kuhle, E. Synthesis 1971, 617; (b) Hogg, D. R. Compr. Org. Chem. 1979, 4, 261.

α -Azido Sulfides, Sulfoxides, and Sulfones

ease whith which benzyl²⁵ and benzhydryl²⁶ sulfoxides undergo homolyses at 150 and 130 °C, respectively. In our case, one would expect the α -azido group in 11 to offer some stabilization (thus lowering the temperature for homolysis) of the incipient benzyl radical.²⁷ Furthermore, the azide group in 11 appears to function as an internal trap yielding 13, thus significantly increasing the overall forward rate of reaction.

There have been very few reports in literature concerning α -azido radicals,^{27,28} although there are scattered reports of the chemistry of radicals more distant from the azide group.^{1,29} Roberts and Winter²⁷ apparently generated α -azido radicals, but even at low temperatures the only radicals observable (ESR spectroscopy) were iminyl radicals. In view of the high heat of formation of molecular nitrogen, it is not surprising that radical 11 readily loses nitrogen to form radical 13. Attempts to brominate benzyl azide under free radical conditions with Nbromosuccinimide gives benzonitrile in high yield,³⁰ which also is consistent with the suggested instability of radical 11. However, we note that radical 11 is no doubt a π -radical, whereas radical 13, in its most stable form,³¹ is a σ -radical. Application of the Woodward-Hoffmann rules suggests that $11 \rightarrow 13$ is a symmetry-forbidden process. We currently are examining more closely this question as well as the chemistry of α -azido radicals.

In conclusion, although the chemistry of α -azido sulfur compounds certainly differs markedly from the chemistry of α -halo sulfur compounds, nonetheless the chemistry of both systems turns out to depend very strongly upon the oxidation state of sulfur.

Experimental Section

General. Melting points were determined on a Fisher-Johns hot-stage melting-point apparatus and are uncorrected. Infrared spectra were determined in carbon tetrachloride or potassium bromide on a Perkin-Elmer 281 recording spectrophotometer. The polystyrene absorption at 1601.8 cm⁻¹ was used for calibration of the infrared spectra. Nuclear magnetic resonance spectra were determined in deuteriochloroform on a Varian EM-360 or XL-100 spectrometer with tetramethylsilane as an internal standard. Gas chromatographic analysis was performed on a Hewlett Packard 7610A instrument equipped with flame-ionization detector and operated as follows: He flow, 40 mL/min; injection temperature 200 °C; FID temperature 285 °C; oven temperature, 70 °C for 6 min then 70-180 °C at 8 °C/min and hold. The column used was a 6 ft × 2 mm glass column (3% OV-225 on 100/120 Supelcoport). Flash chromatography was performed by using 40-60 μ m silica gel 60 (E. M. Merck) as described by Still.³² Microanalyses were carried out by Dr. Franz Kasler of the University of Maryland.

Preparation of α -Azidobenzyl Phenyl Sulfoxide (3). Two grams of α -azidobenzyl phenyl sulfide (8.3 mmol)⁴ was dissolved in 15 mL of reagent grade dichloromethane and 1.5 g of sodium bicarbonate was added to the solution. The solution was cooled to 0-5 °C and 1.68 g of 85% MCPBA (8.3 mmol) in 20 mL of dichloromethane was added over

(26) Mizuno, H.; Matsuda, M.; Iino, M. J. Org. Chem. 1981, 46, 520. These authors through a combination of kinetic, ESR, and CIDNP data confirmed the ease with which benzhydryl p-tolyl sulfoxide and benzhydryl (27) Roberts, B. P.; Winter, J. N. J. Chem. Soc., Perkin Trans. 2 1979,

1353.

(28) Wagner, P. J.; Scheve, B. J. J. Am. Chem. Soc. 1979, 101, 378. (29) Benati, L.; Montevecchi, P. C.; Spagnolo, P. Tetrahedron Lett. 1978, 815

(30) Jarvis, B. B.; Tuthill, D., unpublished results.
(31) Wood, D. E.; Lloyd, R. V.; Pratt, D. W. J. Am. Chem. Soc. 1970, 92, 4115

(32) Still, W. C.; Kahn, M.; Nitra, A. J. Org. Chem. 1978, 43, 2923.

a period of 2 min. Stirring was continued for 5 min, after which the reaction mixture was poured into 100 mL of cold (0-5 °C) water solution of 5 g each of sodium carbonate and sodium thiosulfate followed by dichloromethane extraction. The dichloromethane extract was treated with a few drops of triethylamine and dried (Na_2SO_4) . The amount of dichloromethane was reduced to approximately 10 mL by rotary evaporation. Addition of hexane yielded 730 mg (34%) of α -azidobenzyl phenyl sulfoxide diastereomer **3a**; mp 100–101 °C; IR (CCl₄) 2118 (N₃) and 1058 (SO) cm⁻¹; ¹H NMR (CDCl₃) & 5.77 (s, 1 H) and 6.9-7.6 (m, 10 H). Anal. Calcd for C₁₃H₁₁N₃OS: C, 60.68; H, 4.31. Found: C, 60.55; H, 4.42

The mother liquor from above was crystallized from benzene-pentane to give 1.0 g of a 40:60 mixture of diastereomers 3a and 3b. Several recrystallizations from aqueous ethanol yielded 3b: mp 96-102 °C (decomp); IR (CCl₄) 2116 (N₃) and 1055 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 5.13 (s, 1 H) and 6.8-7.6 (m, 10 H). Anal. Calcd for C₁₃H₁₁N₃OS: C, 60.68; H, 4.31. Found: C, 60.65; H, 4.30.

Preparation of the Diastereomers of *α*-Azido-1-adamantylmethyl Phenyl Sulfoxide (8a and 8b). In a like manner sulfide 7⁴ was oxidized to a mixture of 8a and 8b (54%, ratio of 8a/8b of 3:1), which was fractionally crystallized from dichloromethane-hexane to give 8a: mp 133-134 °C (decomp); IR (CCl₄) 2100 cm⁻¹ (N₃) and 1045 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 7.4-7.7 (m, 5 H), 3.51 (s, 1 H), 1.6-2.2 (m, 15 H). Anal. Calcd for $C_{17}H_{21}N_3OS$: C, 64.73; H, 6.71; N, 13.32. Found: C, 64.72f H, 7.00; N, 13.02

For 8b: mp 80-81 °C; IR (CCl₄) 2100 (N₃), 1030 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 7.3-7.7 (m, 5 H), 3.78 (s, 1 H) 1.6-2.2 (m, 15 H). Anal. Calcd for C₁₇H₂₁N₃OS: C, 64.73; H, 6.71; N, 13.32. Found: C, 64.65; H, 7.00; N, 13.36.

Thermolysis of α -Azidobenzyl Phenyl sulfide (1). In an experiment run in triplicate, accurately weighed amounts of 1 (\sim 40 mg) and *n*tetradecane (\sim 20 mg of internal standard) were sealed in a Carius tube containing 3 mL of chlorobenzene which had been freshly distilled from calcium hydride and purged with dry nitrogen. The tube was heated at 120 °C for 3 h. GC analysis of the resulting solution (average of three runs) showed: 74% 4, 4% benzaldehyde, and 11% benzonitrile. In addition, $\sim 5 \text{ mg/run}$ of diphenyl disulfide was obtained. When this reaction was run on a large scale (5 g of 1), a 50% yield of 4, mp 42.5-43.5 °C (lit.33 mp 44 °C) was isolated.

Thermolysis of α -Azidobenzyl Phenyl Sulfoxide (3). A solution of 1.0 g of 3a in 20 mL of carbon tetrachloride was held at reflux under nitrogen for 1.5 h. The resulting oil after solvent removal was subjected to preparative TLC (five 2-mm silica gel plates). Development with 25% petroleum ether (bp 30-60 °C) in dichloromethane gave five major bands which were extracted with ether to yield 297 mg (33.4%) of 6, mp 78-80 °C (lit.¹² mp 78-79 °C). The remaining extracts were combined and subjected to gas chromatographic analysis (n-hexadecane as internal standard), which indicated the presence of 50 mg of diphenyl disulfide, 60 mg (15%) of benzonitrile, 85 mg (20%) of benzaldehyde, and 90 mg of phenylthiobenzenesulfonate.

Thermolysis of α -Azidobenzyl Phenyl Sulfone (2). Under dry nitrogen, a solution of 2.60 g (9.52 mmol) of 2 in 50 mL of dry chlorobenzene was heated at reflux for 1.5 h. The solvent was removed in vacuo, and the addition of 5 mL of carbon tetrachloride precipitated 735 mg of a brown solid, which was separated by filtration. Filtrate was saved for further analysis. The solid was washed with warm pentane to leave 255 mg of solid with appreciably lightened color. Recrystallization from methanol-isopropyl ether yielded 115 mg of an off-white solid, mp 220-228 °C. The IR (KBr) of this material was identical with that of an authentic sample of PhSO₃H·PhNH₂: 3300-2500 (broad), 1500, 1445, 1180, 1125, 1035, 1020, 995, 760, 750, 725, 690, 610 cm⁻¹.

The pentane wash was evaporated to leave a reddish brown oil which was readily soluble in water, providing a strongly acidic solution. Approximately 100 mg of oil was dissolved in 4 mL of 25% aqueous ethanol; the solution was neutralized to phenolphthalein end point with dilute sodium hydroxide solution and then treated with three drops of 0.1 N hydrochloric acid. To this was added 0.5 g of S-(p-chlorobenzyl)thiuronium chloride dissolved in 4 mL of 25% aqueous ethanol, which gave 130 mg of an off-white solid recrystallized from 50% aqueous ethanol yielding 95 mg of S-(p-chlorobenzyl)thiuronium benzenesulfonate, mp 190-191 °C, undepressed with an authentic sample.

The carbon tetrachloride filtrate was evaporated to leave a light-yellow oil. Column chromatography through 30 g of silica gel with pentane and then an ether-pentane mixture up to 10% of former, yielded 150 mg of diphenyl disulfide, 260 mg of benzonitrile, \sim 20 mg of benzaldehyde, and 647 mg of phenylthiobenzenesulfonate, identification being accomplished by spectral properties.

Thermolysis of α -Azido-1-adamantylmethyl Phenyl Sulfide (7). A solution of 246 mg of 7 in chlorobenzene under nitrogen was heated at 120 °C for 8 h. ¹H NMR spectrum of the chlorobenzene solution with

⁽²²⁾ Ciuffarin, E.; Gambarotta, S.; Isola, M.; Senatore, L. J. Chem. Soc., Perkin Trans. 2 1978, 554.

⁽²³⁾ Bond dissociation energy for the C-S bond in sulfoxides is estimated to be >20 kcal/mol lower than for the corresponding bond dissociation energy in sulfides.²⁴ For further examples of the ease of homolysis of sulfoxides, see: Anastassiou, A. G.; Wetzel, J. C.; Chao, B. Y.-H. J. Am. Chem. Soc. 1975, 97, 1124; Marichich, T. J.; Jourdenais, R. A.; Albright, T. A. Ibid. 1973, 95, 5830. Also see Kwart, H.; Benko, D. A. Ibid. 1979, 101, 1277. The benzenesulfinyl radical is a particularly stable species: Boothe, T. E.; Greene J. L., Jr.; Shevlin, P. B.; Willcott, M. R., III; Inners, R. R.; Cornelis, A. Ibid. 1978, 100, 3874.

⁽²⁴⁾ Block, E. "Reactions of Organosulfur Compounds"; Academic Press:

New York, 1978; p 302.
 (25) Miller, E. G.; Rayner, D. R.; Thomas, H. T.; Mislow, K. J. Am. Chem. Soc. 1968, 90, 4861.

added Me₄Si internal standard showed a singlet at δ 8.6 as well as the upfield adamantyl peaks. Subsequent solvent removal (at 132 °C) yielded 203 mg of an oil. An infrared spectrum showed a peak at 2900 cm⁻¹ as the only strong band; medium strength bands appeared at 1601, 1580, 1470, and 1440 cm⁻¹. ¹H NMR spectroscopy showed peaks at δ 7.60 (s), a multiplet centered at δ 7.20, and broad adamantyl peaks centered at δ 1.80 with integration ratio 1:6:15. These results suggest that 7 initially yields a sulfenimine.³⁴ Preparative TLC gave three bands. Extraction with ether and characterization indicated extensive decomposition of original compound to two products: diphenyl disulfide (80.5 mg) and adamantylcarboxaldehyde (110 mg, 82%), which proved identical with an authentic sample.

Thermolysis of α -Azido-1-adamantylmethyl Phenyl Sulfoxide (8). A solution of 150 mg of 8 (mixture of diastereomers) was treated in a similar manner (120 °C for 1 h) to give the sulfide analogue above. Gas chromatographic analysis using *n*-hexadecane as internal standard showed the presence of diphenyl disulfide (20 mg), adamantylcarbonitrile (21.8 mg, 28.5%), adamantylcarboxaldehyde (3.2 mg, 4.1%), and phenylthiobenzenesulfonate (45 mg).

Kinetic Experiments. The thermal decomposition of α -azidobenzyl phenyl sulfide was followed by the gas evolution method in four different

solvents.² Good first-order rate constants were obtained and are summarized in Table I.

The pyrolysis of α -azidobenzyl phenyl sulfoxide in chlorobenzene was monitored by ¹H NMR spectroscopy. The decrease in integration for δ 5.77 benzylic proton peak as a ratio to the silicon oil peak (added as internal standard) was observed. The resultant first-order rate constants showed good correlation r > 0.98. Table II summarizes these data.

The same procedure as for the latter case was followed for determination of first-order constants of α -azido-1-adamantylmethyl phenyl sulfide (7) and sulfoxide (8). In this case, the diminishment of methyl proton peaks were followed. Rate constant for 7 at 130 °C was $3.25 \pm$ 0.21×10^{-4} s⁻¹, while that of 8 at 110 °C was $2.04 \pm 0.13 \times 10^{-3}$ s⁻¹; both determinations were carried out in chlorobenzene.

CIDNP Experiments. ¹H NMR spectra were obtained on a Varian FT-80A instrument operating at 80 MHz in the Fourier transform mode. Ten milligrams of α -azidobenzyl phenyl sulfoxide (3) was dissolved in $\simeq 0.4$ mL of carbon tetrachloride and 0.2 mL of dioxane- d_8 (²H lock) in a 5-mm tube. Approximately 60-90 s was needed for thermal equilibration after which single transient FID pulses (40 μ s pulse, 80° flip angle, 1 kHz spectral width, 4.096 data points) were obtained and stored on a "floppy" disc. The spectra were then transformed after 30 min of collection. Similar procedures were repeated for 3 at 76 °C but with dimethyl- d_6 sulfoxide (²H lock) and for α -azidobenzyl phenyl sulfide (1) at 118 °C in tetrachloroethylene and dioxane- d_8 . Spectra for sulfoxide 3 are shown in Figure 1.

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Oxygenation with Molecular Oxygen. Thermal and Photochemical Epoxidation of Propylene in the Presence of Sulfur Dioxide in Acetonitrile at Ambient Temperature

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Abstract: Irradiation of a mixture of propylene and sulfur dioxide in acetonitrile at ice-cold temperature causes absorption of molecular oxygen and gives propylene oxide as the sole volatile product. Also, in the absence of light, the addition of nitrite or nitrate salts to a mixture of sulfur dioxide and propylene in acetonitrile under oxygen at room temperature leads to the smooth formation of propylene oxide as the only volatile product. Both reactions show quite similar solvent dependence and are retarded by the additives with ionizaiton potentials lower than ca. 9.5 eV. The main byproduct is poly(propylenesulfonate). The mechanisms of the epoxidation reactions are discussed.

The reactivity of molecular oxygen has been the subject of great interest from both practical and theoretical points of view.¹ The ability to use oxygen in a procedure which selectively oxidizes organic compounds under mild conditions would surely be desirable. Much research and debate are now concentrating on oxygenation via non-singlet-oxygen mechanisms, especially ones which involve electron-transfer processes to produce epoxides.² We here report a new reaction system in which molecular oxygen oxidizes olefins to epoxides both thermally and photochemically in the presence of sulfur dioxide under ambient conditions. Since propylene has the combination of solubility, reaction rate, and ease of product detection under our present conditions, it is most suited for the initial study on these interesting but rather complex reactions reported here.

Photochemical Reactions

The irradiation of a mixture of propylene and sulfur dioxide in oxygen-saturated acetonitrile with a 400 W medium-pressure mercury-arc lamp through Pyrex at an ice-cold temperature produces propylene oxide essentially as the only volatile product. The formation of propylene oxide was confirmed by GC/mass analysis of the reaction mixture and the infrared and NMR spectra of the isolated product. Two other products are obtained. One is a viscous and colorless liquid which is obtained when the solvent is removed from the reaction mixture (see below for the structure determination of the nonvolatile sulfur-containing product). The other is a white solid which settles out on the reaction vessel wall during irradiation sporadically from run to run. The solid was easily identified as poly(propylene sulfone)³ by the infrared

⁽³³⁾ Almog, J.; Barton, D. H. R.; Magnus, P. D. J. Chem. Soc., Perkin Trans. 1 1974, 853.

⁽³⁴⁾ Unsymmetrical sulfenimines are known to exist as geometric isomers which are interconvertible (see Carr, E. L.; Smith, Jr., G. E. P.; Alliger, G. J. Org. Chem. 1949, 14, 921). Apparently the less stable isomer in this case has its imidoyl ¹H NMR peak at δ 8.6, while the more stable isomer exhibits the peak at δ 7.6.

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⁽³⁾ Hunt, M.; Marvel, C. S. J. Am. Chem. Soc. 1935, 57, 1691.