Photoextrusion of SO₂ from Arylmethyl Sulfones: Exploration of the Mechanism by Chemical Trapping, Chiral, and CIDNP Probes[1]

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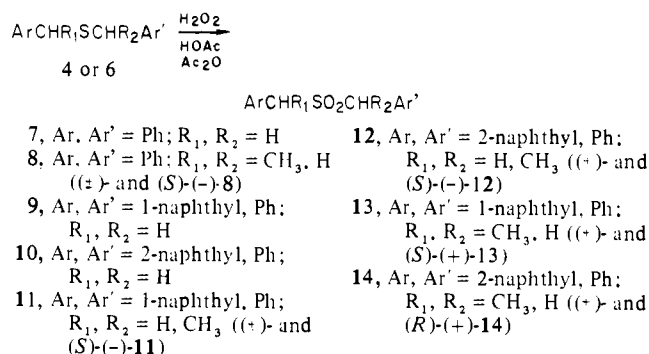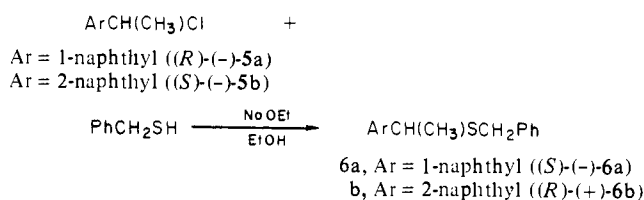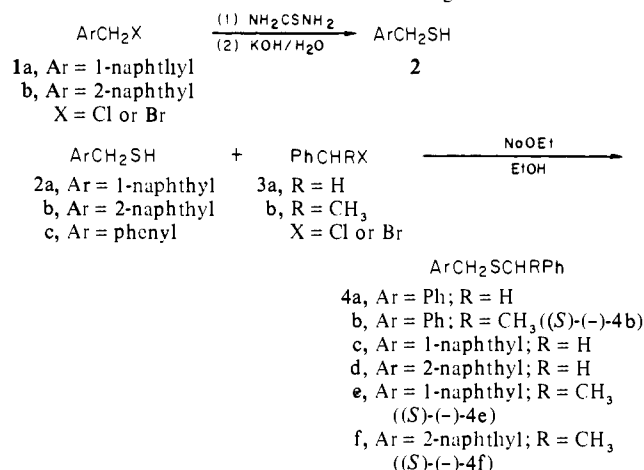
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Abstract: The photochemistry of eight benzylic sulfones, all of which efficiently extrude sulfur dioxide, was studied by a variety of methods. Optically active sulfones (S)-(–)-**8**, (S)-(–)-**11**, (S)-(–)-**12**, (S)-(+)-**13**, and (R)-(+)-**14** were employed to measure the extent of the "hidden" return of the initial photogenerated intermediates by the stereoequilibration of the chiral center. By comparison of the regioisomeric methyl sulfones **11** vs. **13** and **12** vs. **14**, preferential C–S bond fragmentation on the naphthyl side was established for the singlet excited sulfones. Added nucleophilic and proton trapping agents had no effect on the course of the reaction, ruling out ionic intermediates. The three hydrocarbon products of photodesulfonation from the unsymmetrical sulfones **8–14** provided a measure of the cage effects, which were highly structure and multiplicity dependent. Rate constants for reaction, and fluorescence, as well as the energy transfer rates from benzophenone were determined. The reaction rate constant for singlet reactivity from the 1-naphthyl sulfones was about three times greater than that for the 2-naphthyl derivatives. CIDNP studies showed a strong product signal for the 1-naphthyl sulfones from desulfonation of a triplet caged radical pair. Naphthaldehyde formation, a very minor, triplet process, was also detected by the CIDNP study of sulfones **9–12**.

Extrusion of sulfur dioxide from alkyl and aryl sulfones has proven to be a useful synthetic method for the construction of a wide variety of organic structures such as cyclophanes,[5] steroids,[6] and benzocyclobutenes.[7] Both thermally and photochemically initiated SO₂ extrusion reactions have been employed, each method having particular advantages and limitations. For example, the thermal expulsion of SO₂ generally requires high-temperature (>400 °C) vacuum methods but appears not to be limited by structural requirements,[8] whereas the milder photochemical process requires the presence of a chromophore situated β to the sulfonyl group for efficient extrusion with ordinary light sources.[9]

Despite the extensive interest in the thermal and excited state chemistry of sulfones, very little has appeared concerning the mechanistic aspects of these reactions, especially the photochemical extrusion of SO₂. Our interest in photoextrusion reactions in general[9a,10] and in photodesulfonylation in particular[9b,c] has stimulated the in-depth study of the mechanistic parameters including multiplicity and stereochemical factors as well as the

(1) (a) Paper 27 in the series. For paper 26, see: Matuszewski, B.; Burgstahler, A. W.; Givens, R. S. *J. Am. Chem. Soc.* **1982**, *169*, 6838–9. (b) A preliminary report has appeared: Givens, R. S.; Matuszewski, B. *Tetrahedron Lett.* **1978**, 865. (c) Reported in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 14, 1982. Abstract number: ORG 67.

(2) Taken in part from the Ph.D dissertation of J. H.-S. Liu, University of Kansas, 1980.

(3) On leave from the Institute of Chemistry, A. Mickiewicz University, Poznañ, Poland.

(4) An Undergraduate Research Participant, University of Kansas, summer 1979.

(5) (a) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65. (b) Misumi, S.; Otsubo, T. *Ibid.* **1978**, *11*, 251. (c) Rebafke, W.; Staab, H. A. *Angew. Chem.* **1973**, *85*, 831. (d) Vögtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515.

(6) (a) Nicolaou, K. C.; Barnette, W. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1119. (b) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (c) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 2017. (d) Gokel, G. W.; Gerdes, H. M.; Miles, D. E.; Hufnal, J. M.; Zerby, G. A. *Tetrahedron Lett.* **1979**, 3375. (e) Gerdes, H. M.; Gokel, G. W. *Ibid.* **1979**, 3379.

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(8) For a comparison of the structural requirements for one example of a sulfone extrusion reaction, see: Longone, D. T.; Küsefoglu; Gladysz, J. A. *J. Org. Chem.* **1977**, *42*, 2787 and 9a.

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Scheme 1. General Route to Sulfones 7 through 14

$$ArCH_2X \xrightarrow[\text{(2) KOH/H}_2\text{O}]{\text{(1) NH}_2\text{CSNH}_2} ArCH_2SH$$

1a, Ar = 1-naphthyl
b, Ar = 2-naphthyl
X = Cl or Br

2

$$ArCH_2SH \ + \ PhCHRX \xrightarrow[\text{EtOH}]{\text{NaOEt}}$$

2a, Ar = 1-naphthyl   **3a**, R = H
b, Ar = 2-naphthyl   **b**, R = CH₃
c, Ar = phenyl   X = Cl or Br

$$ArCH_2SCHRPh$$

4a, Ar = Ph; R = H
b, Ar = Ph; R = CH₃ ((S)-(–)-**4b**)
c, Ar = 1-naphthyl; R = H
d, Ar = 2-naphthyl; R = H
e, Ar = 1-naphthyl; R = CH₃ ((S)-(–)-**4e**)
f, Ar = 2-naphthyl; R = CH₃ ((S)-(–)-**4f**)

$$ArCH(CH_3)Cl \ + $$

Ar = 1-naphthyl ((R)-(–)-**5a**)
Ar = 2-naphthyl ((S)-(–)-**5b**)

$$PhCH_2SH \xrightarrow[\text{EtOH}]{\text{NaOEt}} ArCH(CH_3)SCH_2Ph$$

6a, Ar = 1-naphthyl ((S)-(–)-**6a**)
b, Ar = 2-naphthyl ((R)-(+)-**6b**)

$$ArCHR_1SCH_2Ar' \xrightarrow[\text{Ac}_2\text{O}]{\begin{array}{c}\text{H}_2\text{O}_2\\ \text{HOAc}\end{array}} ArCHR_1SO_2CHR_2Ar'$$

4 or 6

7, Ar, Ar' = Ph; R₁, R₂ = H
8, Ar, Ar' = Ph; R₁, R₂ = CH₃, H ((±)- and (S)-(–)-8)
9, Ar, Ar' = 1-naphthyl, Ph; R₁, R₂ = H
10, Ar, Ar' = 2-naphthyl, Ph; R₁, R₂ = H
11, Ar, Ar' = 1-naphthyl, Ph; R₁, R₂ = H, CH₃ ((±)- and (S)-(–)-11)
12, Ar, Ar' = 2-naphthyl, Ph; R₁, R₂ = H, CH₃ ((±)- and (S)-(–)-12)
13, Ar, Ar' = 1-naphthyl, Ph; R₁, R₂ = CH₃, H ((+)- and (S)-(+)-13)
14, Ar, Ar' = 2-naphthyl, Ph; R₁, R₂ = CH₃, H ((+)- and (R)-(+)-14)

nature of the bond-breaking step in the photochemistry of arylmethyl sulfones.

Results

Synthesis and Exploratory Photolysis of Sulfones. The eight benzyl- and naphthylmethyl sulfones were synthesized by the

Table I. Optical Rotations of Reactant Sulfones and the Major Coupling Product

sulfone	$[\alpha]^T_{589}$,[a] deg	% ee[b]	major product	$[\alpha]^T_{589}$, deg
(S)-(-)-8	-29.1	24%	(R)-(-)-15	-2.9
(S)-(-)-11	-30.9	54%	(-)-16	-2.8
(S)-(-)-12	-107.5	54%	(-)-17	-5.7
(S)-(+)-13	+1.6	4.8%		
(R)-(+)-14	+67.0	44%	(+)-18	+8.6

[a] Rotations of the sulfones and the major photoproduct were determined in ethanol at 30 °C (**8, 15**) or chloroform at 20 °C. [b] Percent enantiomeric excess.
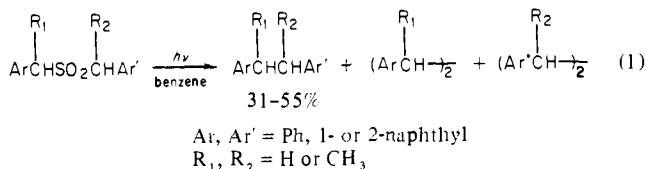
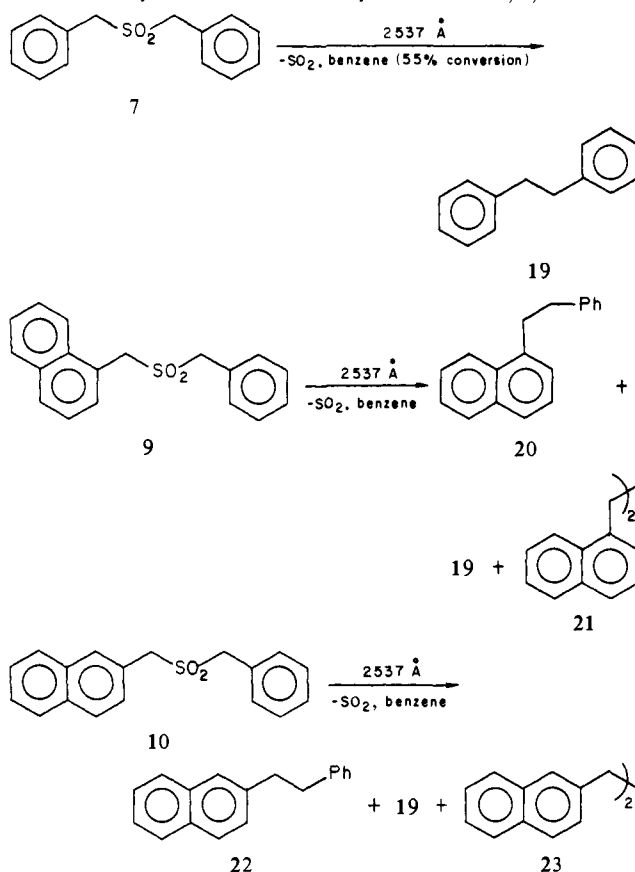**Chart I.** Photoextrusion Products from Naphthyl Sulfones **11-14** and Benzyl Sulfone **8**

Scheme II. Synthetic Photochemistry for Sulfones 7, 9, and 10

Table II. Quantum Efficiencies for Disappearance and Racemization of Sulfones **7-14**

sulfone	ϕ_D[a]	ϕ_{sens}[b]	ϕ_S[c]	ϕ_T[c]	(ϕ_{rac})-direct[d]	(ϕ_{rac})-sens[d]
7[e]	0.29	0.27	0.16	0.13		
8[e]	0.52	0.25	0.40	0.12	0.098	0.0
9	0.11	0.23	0.0	0.11		
10	0.014	0.003	0.012	0.002		
11	0.11	0.18	0.0	0.11	0.0088	0.0
12	0.028	0.0066	0.023	0.005	0.0019	0.0
13	0.099	0.39	0.0	0.099	0.096	f
14	0.033	0.031	0.014	0.017	0.014	0.0

[a] Direct (D) irradiations in benzene: 7 and 8 at 254 nm; 9-14 at 300 nm. [b] Sensitized (sens) irradiations: 7 and 8 with acetone as sensitizer and solvent at 300 nm; 9-14 in benzene with benzophenone as the sensitizer at 350 nm. [c] Singlet (S) and triplet (T) contribution to the direct irradiation disappearance efficiency. See eq 2 in the text. [d] Racemization (rac) quantum efficiencies for the direct or sensitized reactions were determined by measuring the percent of racemization of unreacted sulfone at <30% conversion and multiplying this value by the disappearance efficiency. All values were obtained by extrapolating the conversion-dependent efficiencies to 0% conversion. [e] Acetone (1.0 M) in benzene (as the solvent) was employed for the sensitization run. [f] Not determined.

general procedure given in Scheme I and are detailed in the Experimental Section. Optically active 1-phenylethyl sulfones[11] (S)-(-)-**8**, (S)-(-)-**11**, and (S)-(-)-**12** were also synthesized by the same sequence employing (R)-(+)-1-phenylethyl chloride ($[\alpha]^{20}_{589}$ +56.1° (c 0.79, EtOH), 54% optical purity) obtained from the (S)-(-)-1-phenylethyl alcohol[12] (of the same optical purity). The optically active 1-(1- or 2-naphthyl)ethyl benzyl sulfones, (S)-(+)-**13** and (R)-(+)-**14**, were derived from the resolved 1-(1-naphthyl)ethyl alcohols by the same procedure used for the resolution and synthesis of the phenylethyl chloride.[12] Optical purities and rotations are given in Table I.

Preliminary photochemical studies of the sulfones (eq 1) showed

that the photoproducts were chiefly the hydrocarbon products

resulting from extrusion of sulfur dioxide. For dibenzyl sulfone, 1,2-diphenylethane (dibenzyl) was obtained in 82% yield (based on 55% conversion of the sulfone, Scheme II). Three hydrocarbon products were obtained from each of the remaining unsymmetrical sulfones, resulting from the coupling of the two arylmethyl radicals generated by homolysis of the two carbon–sulfur bonds. Yields of the extrusion product were substantially lower in these cases. The chiral arylethyl sulfones **8** and **11–14** also underwent SO₂ extrusion as the principal photoreaction (eq 1 and Chart I).

Mechanistic Studies: Optically Active Sulfones. The photoextrusion of SO₂ from optically active sulfones **8** and **11–14** was followed by the change in optical rotation with conversion; the

(11) Overberger, C. G.; Hoyt, J. M. *J. Am. Chem. Soc.* **1951**, 73, 3305.
(12) (a) Burwell, R. L.; Shields, A. D.; Hart, H. *J. Am. Chem. Soc.* **1954**, 76, 908. (b) Streitwieser, A.; Reif, L. *Ibid.* **1964**, 86, 1988. (c) Downer, E.; Kenyon, J. *J. Chem. Soc.* **1939**, 1156. (d) Housa, A. S. H.; Kenyon, J. *Ibid.* **1930**, 2260. (e) Eliel, E. L. *J. Am. Chem. Soc.* **1949**, 71, 3970. (f) Kantor, S. W.; Hauser, C. R. *Ibid.* **1953**, 75, 1744. (g) Dauben, H. Y.; McCoy, L. L. *Ibid.* **1959**, 81, 5404.

Table III. Rate Constants for Quenching of Acetophenone and Benzophenone Phosphorescence by Sulfones 7, 9, and 10 in CCl₄ at 20 °C

donor	acceptor	$k_q\tau$, M^{-1} [a]	k_q, M^{-1} s^{-1} [b]
acetophenone[c]	7	<26	$<1 \times 10^6$
($E_T = 74$	9	1.6 (±0.2) × 10⁵	8 (±2) × 10⁹
kcal/mol)[16]	10	1.5 (±0.3) × 10⁵	7 (±3) × 10⁹
benzophenone[d]	7	<26	$<4 \times 10^5$
($E_T = 68$	9	4.9 (±1.5) × 10⁵	8 (±5) × 10⁹
kcal/mol)[16]	10	3.0 (±0.7) × 10⁵	5 (±2) × 10⁹

[a] The slope, $k_q\tau$, was obtained from the Stern–Volmer relationship from duplicate runs for 5–7 different quencher concentrations. [b] The value used for τ was experimentally determined from the average values of the quenching rates obtained with naphthalene and *trans*-1,3-pentadiene. For acetophenone, the value was 2.1 ± 0.4 × 10⁻⁵ s⁻¹ while for benzophenone a value of 6.2 ± 0.2 × 10⁻⁵ s⁻¹ was determined. [c] Argon deaerated solutions (0.002 M) were irradiated at 330 nm. [d] Argon deaerated solutions (0.01 M) were irradiated at 385 nm.

chiral products were separated and their rotations were determined (Table I). Quantum efficiency for racemization was also measured and is given in Table II. When the sulfones were irradiated in the presence of the triplet sensitizers acetone or acetophenone, no racemization of the starting sulfone was noted and the product hydrocarbons formed were completely racemic.

Sensitization and Rates of Energy Transfer. Room temperature phosphorescence[13] quenching of benzophenone ($E_T = 69$ kcal/mol)[14] and acetophenone ($E_T = 74$ kcal/mol)[14] was examined for the acceptors dibenzyl sulfone (7) and the two naphthyl benzyl sulfones (9 and 10). A Stern–Volmer relationship was obeyed for all three yielding the energy transfer rates given in Table III. The transfer rates to the 1- and 2-naphthylmethyl sulfones from either sensitizer were essentially diffusion controlled, whereas energy transfer to dibenzyl sulfone did not occur.

Quantum Efficiencies. The disappearance quantum efficiencies were determined for direct irradiation and for sensitization with acetone or benzophenone and are reported in Table II. The appearance efficiencies for the major products from sulfones 11 and 12 are reported in Table IV. Unlike the ester photodecarboxylations[9a,10] which could not be sensitized,[15] the photoextrusion of SO₂ could be effected by the triplet energy sensitizers acetophenone and benzophenone or by acetone. Acetophenone and benzophenone gave very similar product ratios and quantum efficiencies; therefore, only the benzophenone results are given in Table II. The direct irradiation quantum efficiencies were partitioned between the singlet and triplet state contributions for the photoextrusion reaction according to eq 2, where $\phi_{singlet}$

$$\phi_{singlet} = \phi_{direct} - \phi_{isc}\phi_{sens} \qquad \phi_{triplet} = \phi_{direct} - \phi_{singlet} \qquad (2)$$

is the singlet state efficiency, ϕ_{sens} is the triplet state efficiency determined by sensitization, ϕ_{direct} is the overall efficiency upon direct irradiation, $\phi_{triplet}$ is the triplet contribution to the direct irradiation of efficiency, and ϕ_{isc} is the intersystem crossing efficiency obtained by pulsed laser photolysis for 9–14 as reported in the accompanying paper.[14,16]

Emission Studies. Fluorescence and phosphorescence spectra were obtained for a selected group of the sulfones. The fluorescence spectra were obtained in cyclohexane and are characteristic of methylnaphthalene fluorescence. The relative fluorescence quantum efficiencies and singlet lifetimes for the naphthyl sulfones were also determined and are presented in Table
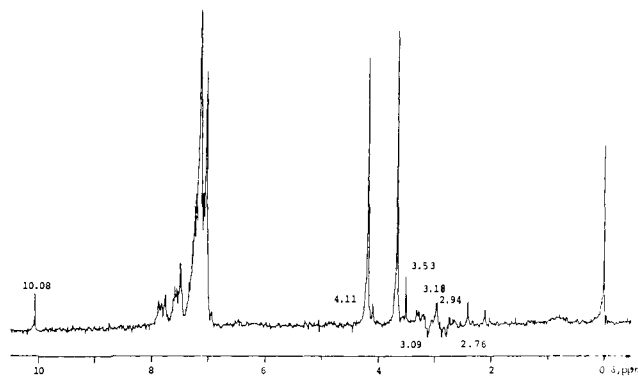
(13) (a) Saltiel, J.; Curtis, H. C.; Metts, L.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410. (b) Clark, W. D. R.; Litt, A. D.; Steel, C. *Ibid.* **1969**, *91*, 5413.

(14) (a) Gould, I. R.; Tung, C.-h; Turro, N. J.; Givens, R. S.; Matuszewski, B. *J. Am. Chem. Soc.*, the following paper in this issue. (b) The values for ϕ_{isc} obtained in acetonitrile are: 9, 0.72; 10, 0.66; 11, 0.59; 12, 0.73; 13, 0.57; 14, 0.62.

(15) (a) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. *J. Am. Chem. Soc.* **1977**, *99*, 1896. (b) Givens, R. S.; Matuszewski, B. *Ibid.* **1975**, *97*, 5617.

(16) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

Figure 1. 80-MHz spectrum obtained during direct irradiation of 1-naphthylmethyl benzyl sulfone (9) in benzene-d_6 at a flip angle of 60° and pulse width of 3.2 µs. Enhanced absorption signals at 10.08, 4.107, and 3.527 ppm and multiplet signals between 3.179 and 2.764 ppm disappeared after irradiation. (See Results and Discussion, Table VII.)
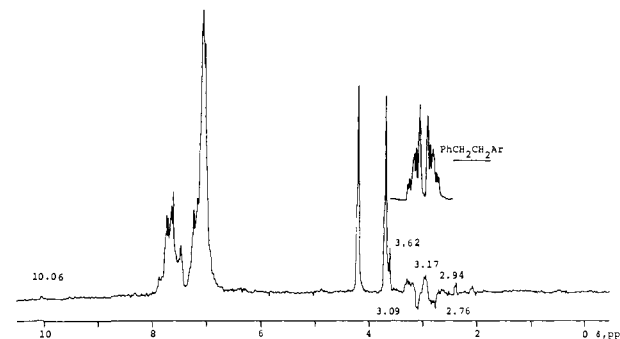

Figure 2. 80-MHz spectrum obtained during irradiation of 9 in benzene-d_6 sensitized by benzophenone. Enhanced absorption signals at 10.056 and 3.618 ppm and the multiplet signals between 3.173 and 2.764 ppm disappeared after terminating the irradiation. (See Results and Discussion Sections, Table VII.) Insert shows the methylene region for 20.
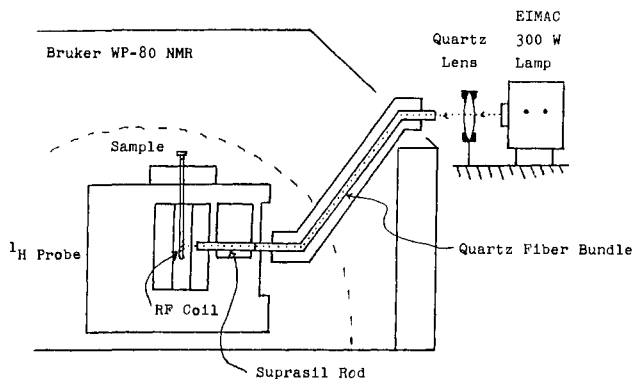

Figure 3. A schematic diagram illustrating the arrangement of lamp, lens, fiber bundle, and light-pipe used to photolyze the sample in the NMR Spectrometer for CIDNP studies. RF coil = radio-frequency coil.

V. Low temperature emission studies in EPA or CHCl₃ solvent revealed a characteristic phosphorescence emission for the aryl sulfones (Table VI), providing both the emission maxima and the triplet energies.

CIDNP Studies. Each of the sulfones was also examined for CIDNP effects upon photolysis in benzene-d_6 solutions. Whereas sulfones 7, 8, and 14 showed no CIDNP signals for either reactant or product(s), the other five sulfones gave interpretable signals

(17) Berlman, J. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed.; Academic Press: New York, 1971.

(18) (a) Kaptein, R. *Chem. Commun.* **1971**, 732. (b) Kaptein, R. "Chemically Induced Magnetic Polarization"; Lepley, A. R., Closs, G. L., Eds.; Wiley-Interscience: New York, 1973; Chapter 4. (c) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.

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Table IV. Quantum Efficiencies for Disappearance and Product Appearance for Sulfones 11 and 12

sulfone	sensitizer	$\phi_{dis}{}^{a}$	$\phi_{24}{}^{b}$	$\phi_{25}{}^{b}$	$\phi_{16/17}{}^{c}$	$\phi_{21/23}{}^{d}$	$\Sigma\phi_{app}{}^{e}$
(±)-11	none	0.11	0.014	0.013	0.057	0.018	0.10
	benzophenone	0.18	0.045^{f}		0.075	0.050	0.17
	acetophenone	0.28	0.029	0.032	0.090	0.044	0.20
(±)-12	none	0.028	0.0014	0.0016	0.0086	0.0053	0.0179
	benzophenone	0.007	0.0008^{f}		0.0022	0.0012	0.0042
	acetophenone	0.008	0.0007	0.0007	0.0017	0.0020	0.0051

^{a} Disappearance (dis) efficiency, in benzene at 300 nm. ^{b} Appearance efficiencies for d,l- or $meso$-2,3-diphenylbutane (24 or 25, respectively). ^{c} Appearance efficiency for 1-(1- or 1-(2-naphthyl)-2-phenylpropane (16 or 17). ^{d} Appearance efficiency for 1,2-di(1- or 2-naphthyl)ethane (21 or 23). ^{e} The sum of all appearance efficiencies. ^{f} The d,l and meso were not separated.

Table V. Singlet State Lifetimes, Quantum Efficiencies, and Rate Constants for Fluorescence for Naphthyl Sulfones 9-14

sulfone	λ_{max}, nm^{a}	$\phi_f{}^{b}$	τ_S, ns^{c}	$k_f \times 10^{-6}$ s^{-1} ^{d}
9	330	0.11	17	6.8
10	335	0.064	16	4.1
11	332	0.12	15	8.0
12	335	0.077	16	4.8
13	337	0.091	12	7.8
14	335	0.081	15	5.2

^{a} Fluorescence spectra were obtained at room temperature in cyclohexane. ^{b} Absolute fluorescence efficiencies were calculated from a comparison with naphthalene (standard) which has a fluorescence efficiency (ϕ_f) of 0.23 in cyclohexane.[17] ^{c} Obtained from oxygen quenching[17] of the fluorescence in cyclohexane (see Experimental Section). ^{d} Calculated from the expression $k_f = \phi_f/\tau_S$.

Table VI. Phosphorescence Emission Maxima and Triplet Energies for Sulfones 7-10, 13, and 14

sulfone	phosphorescence maxima, nm^{a}	E_T, kcal/mol^{b}
7	468	>70.6
8	410, 433, 460	>69.8
9	480	59.6
10	475	60.2
13	495, 530, 570, 620	57.8
14	484, 518, 557, 602	59.1

^{a} For sulfones 7, 9, and 10, chloroform was the solvent; for sulfones 8, 13, and 14 EPA was employed. All spectra were taken in quartz tubes at 77 K. ^{b} Onset for the phosphorescence was used to determine the triplet energies. For dibenzyl sulfones 7 and 8, the absence of a 0,0 bond precluded an accurate determination of E_T.

either for the major hydrocarbon product or for minor side products. Signals for the reactant sulfones were observed for 11 and 12 only.

Figures 1 and 2 illustrate the CIDNP effects observed when a benzene-d_6 solution of benzyl 1-naphthylmethyl sulfone (9) was irradiated with the unfiltered light from a 300-watt EIMAC lamp focused into a 1-cm quartz fiber directed into a modified Bruker WP80 proton probe with a quartz condensing lens (see Experimental Section and Figure 3 for details). The NMR spectrum of the irradiated sample showed two new peaks: a singlet centered at 10.08 ppm and a complex A/E (absorption/emission) multiplet between 3.39 and 2.74 ppm. The first signal was assigned to 1-naphthaldehyde (29) by comparison of its chemical shift with the aldehyde CHO shift of an authentic sample of 29. The second signal was assigned to the major photoproduct, 1-(1-naphthyl)-2-phenylethane (20), by comparison of the chemical shift and the pattern of the A_2B_2 multiplet with those of an authentic sample of 20 with the observed CIDNP signal. Addition of high energy triplet sensitizers (E_T > 68 kcal/mol) to the benzene-d_6 solution enhanced the observed polarizations (Figure 2). Analysis of the multiplet effect by Kaptein's equation (eq 3) permits the assignment of the origin of the major product as follows:

$$\Gamma_m = \mu\epsilon a_i a_j J_{ij}\sigma_{ij} \qquad (3)$$

where Γ_m is the observed multiplet effect (here A/E or minus), μ is the multiplicity (here a triplet or plus), ϵ is the cage effect (here recombination in the cage or plus), a_i and a_j are the hfsc's for benzyl and 1-naphthylmethyl radicals (here minus), J_{ij} is the ^{1}H NMR coupling constant (here vicinal or plus), and σ_{ij} is the radical orientation factor (here on different fragments or minus). The product of these six contributors is also negative in accord with the assignment of the A/E spectral pattern.

Interestingly, aldehyde formation was also observed for sulfone 10. For both 9 and 10 the origin of the aldehyde is not known though an intramolecular rearrangement process can be envisaged. For the 1- and 2-naphthylmethyl 1-phenylethyl sulfones (11 and 12), several NMR signals were observed for the sulfone substrate. Table VII provides an analysis of the signals observed for these sulfones as well as photoproducts. The greater difference in the g-values for the ethyl sulfones probably contributes to the CIDNP effects which may enhance the ability to detect the products from these particular sulfones.

Trapping Studies. That evolution of sulfur dioxide occurred during photolysis was established for dibenzyl sulfone (7) by passing a nitrogen gas train through an acetonitrile solution of 7 and then through a 0.1 M aqueous solution of tetrachloromercurate. The trapped mercurate solution was analyzed by the method of West and Gaeke,[19] which gave a positive colorimetric indication for the presence of SO_2.

For naphthyl sulfones 13 and 14, attempts were made to intercept electrophilic or otherwise reactive intermediates such as benzyl carbonium ions or deprotonated sulfones. In the presence of methanol-O-d, neither methanol nor deuterium were consumed by the sulfone during either a direct or acetophenone-sensitized irradiation of 13 or 14. Similar experiments with 1-phenylethyl benzyl sulfone (8) in the presence of D_2O, CH_3OD, or CH_3OH gave no incorporation.

Discussion

The photochemistry of arylmethyl sulfones is summarized in Scheme III. The benzyl and β-naphthylmethyl sulfone desulfonylation reactions are chiefly from the singlet manifold whereas the α-naphthylmethyl sulfone reacts exclusively from its triplet state. All the reactions examined proceed by a stepwise homolysis of the two carbon–sulfur bonds releasing molecular sulfur dioxide with concomitant generation of two arylmethyl radicals. No ionic intermediates were trapped or detected.[14a]

The nature and fate of the arylmethyl radicals as well as the intermediate sulfonyl radicals are dependent on the structure of the sulfone. In the case of the benzyl sulfones (7 and 8), the product mixtures indicate a negligible cage effect resulting in a statistical combination of the cage-free radicals (step 12). Stereochemical studies with (S)-$(-)$-8, however, do show that there is a significant recombination of the initially formed radical pairs (step 8) but that it occurs exclusively within the singlet manifold. We estimate that at least 20% of these radical pairs return to sulfone.[20] The major product from (S)-$(-)$-8, $(-)$-1,2-diphenylpropane ($(-)$-15), is formed with a small retention of optical activity suggesting that some in-cage combination of the desul-

(19) West, P. W.; Gaeke, G. C. *Anal. Chem.* **1956**, 28, 1816.
(20) This is a lower limit. We cannot estimate the extent of recombination that occurs with net retention of configuration.

Table VII. Observed ClDNP Effects and Parameter Assignments for Sulfones and Photoproducts

irradiated sulfone	compd	observed effects, δ^a	μ	ϵ	a_i	a_j	J_{ij}	σ_{ij}	Δg	Γ_{ne} or $\Gamma_{nie}{}^c$	obsd
9	20	A/E, 3.39–2.74 (m), –CH₂CH₂–	+	+	–	–	+	–	(na)	–	A/E
9	1-naphthaldehyde (29)	A, 10.08 (s), –CHO	–	+	+	(na———)			–	+	A
10	2-naphthaldehyde (30)	A, 9.81 (s), –CHO	d	d	–	(na———)			–	+	A
11	1-naphthaldehyde (29)	A, 10.06 (s), –CHO	–	+	+	(na———)			–	+	A
11	11	A, 4.14 (s), –CH₂–	+	+	+	(na———)			+	+	A
		E, 1.50 (d), –CH₃	+	+	+	(na———)			–	–	E
		A, 3.77 (q), –CH–	+	+	–	(na———)			–	+	A
11	1-(1-naphthyl)-2-phenylpropane (16)	A, 3.40–2.79 (m), –CH₂–	+	+	+	(na———)			+	+	A
		E, 1.23–0.89 (d), –CH₃–	+	+	+	(na———)			–	–	E
		A, 3.40–2.79 (m), –CH–	+	+	+	(na———)			–	+	A
12	2-naphthaldehyde (30)	A, 9.80 (s), –CHO	–	+	+	(na———)			–	+	A
13	13	A, 3.61 (s), PhCH₂–	+	+	+	(na———)			+	+	A
		E, 1.60 (d), –CH₃	+	+	+	(na———)			–	–	E
		A, 4.72 (q), –CH–	+	+	–	(na———)			–	+	A
		E, 7.00 (s), -o-PhH	+	+	–	(na———)			+	–	E
13	1-phenyl-2-(1-naphthyl)-propane (28)	A/E, 3.20–2.85 (m), –CH₂–	+	+	–	–	+	–	(na)	–	A/E
		A/E, 1.21 (d), –CH₃	+	+	+	–	+	+	(na)	–	A/E
		A/E, 2.85–2.40 (m), –CH–	+	+	–	+	+	+	(na)	–	A/E

^{a} A = enhanced absorption; E = emission; A/E is a multiplet effect where the low field portion of the multiplet is an enhanced absorption. ^{b} Parameters for the Kaptein equations.[18] For the multiplet effect see eq 3 in the text. For the net effect, the Kaptein equation is: $\Gamma_{ne} = \mu \epsilon a_i \Delta g$. The added terms, Δg and J_{ij} for the multiplet effects are the sign of the g factor difference between the two reacting radicals and the NMR coupling constants for H_i and H_j. ^{c} Γ_{ne} or Γ_{me} are the signs of the product of the contributing parameters. For $\Gamma_{ne} = +$, enhanced absorption would be expected; –, emission. For $\Gamma_{me} = –$, a multiplet effect of low-field enhanced absorption, high-field emission is expected. ^{d} These two parameters for 2-naphthaldehyde (30) have not been determined. Either the aldehyde results from an out-of-cage triplet (both –) or an in-cage singlet (both +). The former is in accord with the interpretations for the results with isomeric 1-naphthaldehyde (29).

Scheme III. Photochemical Mechanism for Desulfonylation of Arylmethyl sulfones 7–14^a

$$ArCR_2SO_2CR_2'Ar' \xrightarrow{h\nu} [ArCR_2SO_2CR_2'Ar']^1 \qquad (1)$$
$$A^0 \qquad\qquad\qquad [A]^1$$

$$[A]^1 \xrightarrow{k_f} A^0 + h\nu' \qquad (2)$$

$$([A]^1 \xrightarrow{k_d} A^0) \qquad (3)$$

$$[A]^1 \xrightarrow{k_{isc}} [A]^3 \qquad (4)$$

$$[A]^3 \xrightarrow[77\,K]{k_p} A^0 + h\nu'' \qquad (5)$$

$$[A]^3 \xrightarrow{k_d} A^0 \qquad (6)$$

$$[A]^* \xrightarrow{k_r} *\overline{ArCR_2 \cdot \, \cdot SO_2CR_2'Ar'} + *\overline{ArCR_2SO_2 \cdot \, \cdot CR_2'Ar'} \qquad (7)$$
$$* = 1 \text{ or } 3 \qquad\qquad *\overline{B} \qquad\qquad *\overline{C}$$

$$^1\overline{B} \text{ or } ^1\overline{C} \xrightarrow{k_c} A^0 \qquad (8)$$

$$*\overline{B} \text{ or } *\overline{C} \xrightarrow{k_{-SO_2}} *\overline{ArCR_2 \cdot \, \cdot CR_2'Ar'} \qquad (9)$$
$$*\overline{D}$$

$$*\overline{D} \xrightarrow{k_{comb}} ArCR_2-CR_2'Ar' \qquad (10)$$

$$*\overline{B} \text{ or } *\overline{C} \xrightarrow{k_{esc}} ArCR_2 \cdot + Ar'CR_2' \cdot + SO_2 \qquad (11)$$

$$ArCR_2 \cdot + Ar'CR_2' \cdot \xrightarrow{k'_{comb}} (ArCR_2 \tfrac{1}{2} + ArCR_2CR_2'Ar' +$$
$$(Ar'CR_2' \tfrac{1}{2} \qquad (12)$$

^{a} The rate constants for the individual processes are indicated by the subscripts: f = fluorescence; d = decay; isc = intersystem crossing; r = reaction; c = combination; -SO₂ = desulfonylation; esc = escape from the cage; comb = radical–radical combination. R₂ (R₂') represents H, H or H, CH₃.

fonylated radical pair is occurring with incomplete racemization. The extent and nature of this process were not pursued, however.

The triplet radical pair reached either through intersystem crossing or by acetone sensitization shows little propensity to return to sulfone, nor is any optically active product obtained from 8.

Table VIII. Regiophotochemical Bond-Breaking Preferences from the Singlet State

	a	b		a	b
ϕ_{rac}	0.096	0.0088	ϕ_{rac}	0.014	0.0019
	92%	8%		88%	12%

Table IX. Rate Constants and Efficiencies for the Singlet Photochemistry of the Naphthyl Sulfones

sulfone	$\phi^S{}_r{}^a$	$\phi^{S+T}{}^b$	%S^c	$k^S{}_r \times 10^6{}^b$	$\phi^S{}_{TOT}{}^e$
9	0.105	0.22	48%	6.2	0.93
10	0.028	0.030	93%	1.8	0.75
11	0.105	0.22	48%	7.0	0.81
12	0.039	0.045	89%	2.4	0.85
13	0.105	0.20	52%	8.8	0.77
14	0.030	0.048	65%	2.0	0.73

^{a} The sum of the singlet contribution to the efficiency for photoextrusion of SO₂ and the sulfone racemization efficiency which occurs only from the singlet. (See Scheme II and Discussion.) ^{b} The sum of the efficiencies for photochemical reactions. ^{c} The percentage of singlet reaction ($\phi^S{}_r$) (racemization and extrusion) vs. total photochemical reaction ($\phi^{S+T}{}_r$). ^{d} Rate constant for reaction from the singlet: $k^S{}_r = \phi^S{}_r \tau_S{}^{-1}$ (τ_S from Table V). ^{e} $\phi^S{}_{TOT} = \phi^S{}_r + \phi^S{}_f + \phi^S{}_{isc}$ (see Table V and ref 14 and 22).

It thus appears that the triplet component can be treated as the radical sequence 7 (* = 3) → 9 → 11 → 12.

Additional detail is gained from the naphthylmethyl benzyl sulfones 10–14. These unsymmetrical sulfones permit an analysis of the initial bond cleavage step since two different aryl-substituted radicals are possible. By examining each optically active pair of methyl-substituted sulfones (i.e., 11 vs. 12 and 13 vs. 14), it is possible to assess the relative efficiency (Table II) for the regioselectivity competing of the C–S bond cleavage. As shown in Table VIII, a significant fraction of the singlet excited sulfones fragment from the naphthyl side with only a small contribution coming from the higher energy benzyl side.[21]

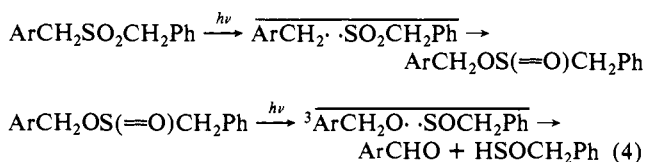1784 *J. Am. Chem. Soc., Vol. 106, No. 6, 1984*

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If it is assumed that the same fraction of **a** vs. **b** bond fragmentation also occurs for nonchiral benzyl naphthyl sulfones, the total contribution of all chemical processes from the singlet state of each sulfone can be deduced. This is given in Table IX as well as an assessment of the singlet contribution of the total photochemical reactivity of each sulfone. Furthermore, knowing the total fragmentation efficiency from the singlet and the fluorescence lifetime,[22] we are now able to determine the total rate constant for the bond-breaking step, k_r (step 7, * = 1, Scheme III). From the three sets of sulfones, the ratio of the rate constants ranges between 3 and 4 in favor of the 1-naphthyl sulfone. While comparisons with the photoextrusion of CO_2 from the same series of esters is somewhat tenuous, nevertheless it is interesting to note that the corresponding sulfone reactivities are in the reverse order of the ester reactivity.[23] In spite of the enhanced reactivity of the singlet sulfone series, the desulfonation process does not occur. Apparently all of the singlet radical pairs return to sulfone. Conversely, only half of the singlet radical pairs from 2-naphthyl sulfones undergo recombination, the remainder lose SO_2 and proceed to product.

Finally, by including the intersystem crossing efficiencies (step 4) determined independently by the Columbia group,[14] we can account for nearly all of the excited singlet state processes, e.g., steps 2, 4, and 7 (* = 1). In view of the cumulative experimental uncertainty[22] in the quantum efficiencies for the three measurements, it is reasonable to assume that decay from the singlet (step 3) is not important.

We were unable to assess the triplet reactivity in the same depth as accomplished with the singlet manifold. Although efficiencies for reaction could be determined, the lifetimes of the triplet were not available so that the relative rate constants could not be determined. Furthermore, the lack of racemization from the triplet chiral sulfones prevented a similar analysis of the regio-photochemical bond-breaking process. However, CIDNP signals were observed for two of the three 1-naphthyl sulfones, indicating that at least a small fraction do recombine in the cage (Table VII).

On the other hand, it is clear that the triplet does lead to two products with efficiencies that do not account for the total triplet population. From Table II it is seen that the extrusion reaction accounts for only ca. 25% of the sulfone triplet for the benzyl (**7** and **8**) and 20–40% for the 1-naphthyl (**9, 11,** and **13**) and less than 4% for the 2-naphthyl (**10, 12,** and **14**) sulfones. Clearly, decay (step 6) is the most important process.

The second product noted by CIDNP which originated from the triplet is naphthaldehyde. This is a very minor product, for it was not detected by GLC, HPLC, or in the larger scale synthetic runs. Its origin may be from a recombination of the radical pair at oxygen followed by a second photochemical disproportionation process (eq 4).

$$ArCH_2SO_2CH_2Ph \xrightarrow{h\nu} \overline{ArCH_2\cdot \;\; \cdot SO_2CH_2Ph} \rightarrow$$
$$ArCH_2OS(=O)CH_2Ph$$

$$ArCH_2OS(=O)CH_2Ph \xrightarrow{h\nu} {}^3\overline{ArCH_2O\cdot \;\; \cdot SOCH_2Ph} \rightarrow$$
$$ArCHO + HSOCH_2Ph \quad (4)$$

Our studies have thus far shown that aryl methyl sulfones undergo a general SO_2 photoextrusion process which is best represented as a sequential homolysis of the individual carbon-sulfur bonds. The radical pairs generated in this series of steps were examined with stereochemical and CIDNP probes for competition between recombination and further reaction. From the quantitative analysis of the results it was possible to show that

recombination occurs with the singlet radical pair almost exclusively. Furthermore, the desulfonylation reaction is most efficient from singlet radical pairs for the benzyl and 2-naphthylmethyl sulfones, while the triplet radical pair is the major route followed by the 1-naphthylmethyl sulfone derivatives. Further analysis of the triplet processes are presented in the accompanying paper.[14a]

Experimental Section

Melting points are uncorrected. Gas chromatographic separations were accomplished on a 0.125 in. × 5 ft SE-30 (3%, Chromosorb W) column. Mass spectra were obtained at 70 eV on a Varian MAT CH-5 or a Ribermag quadrupole instrument. Elemental analyses were performed in the Department of Medicinal Chemistry, University of Kansas. Optical rotations were measured with a Perkin-Elmer 141 Polarimeter in the Department of Medicinal Chemistry, University of Kansas. Irradiations were carried out using a Rayonet photochemical reactor, equipped with a "merry-go-round" sample holder, using RPR 3500-Å, RPR 3000-Å, or RPR 2537-Å lamps.

A. Synthesis. Dibenzyl Sulfone (7). This was synthesized by the method of Pomerantz and Connor.[24]

Resolution of 1-Phenylethyl Alcohol. The procedure of Downer and Kenyon[12c] with the modifications[12d-8] was employed and afforded 6.14 g of (S)-(−)-1-phenylethyl alcohol, $[\alpha]^{20}_D$ −41.6° (c 0.75, MeOH) with 91% optical purity (lit. $[\alpha]^{23}_D$ −45.5° (c 5, MeOH)) and 8.07 g of (R)-(+)-1-phenylethyl alcohol with $[\alpha]^{20}_D$ +23.3° (c 2.59, MeOH) [lit.[12] $[\alpha]^{19}_D$ +42.9° (neat)] with 54% optical purity.

(±)- and (R)-(+)-1-Phenylethyl Chloride (3b). The procedure of Hart et al.[12a] and Streitwieser et al.[12b] with some modifications was employed for synthesis of racemic and (R)-(+)-1-phenylethyl chloride ((±)- and (R)-(+)-3b). Thus, starting with 5.037 g (41.2 mmol) of (S)-(−)-1-phenylethyl alcohol ($[\alpha]^{20}_D$ −41.6° (c 0.75, MeOH)), using 3.05 g of dry HCl, 17 mL of pyridine, and 8.48 g of POCl$_3$ (55.05 mmol), and keeping the temperature of the solution below −30 °C during the additions gave 4.88 g (84%) of (R)-(+)-1-phenylethyl chloride ((R)-(+)-3b) $[\alpha]^{20}_D$ +56.1° (c 0.79, EtOH) with optical purity 54% (lit.[12] $[\alpha]_D$ +103.9°): NMR (CCl$_4$, Me$_4$Si) δ 7.25–6.98 (m, 4 H), 4.86 (q, 1 H), 1.76 (d, 3 H).

(S)-(−)-1-Phenylethyl Benzyl Sulfide ((S)-(−)-4b). To a refluxing solution of potassium benzyl mercaptide (prepared from 1.9 g (15 mmol) of benzyl mercaptan and 1.0 g of 85% KOH pellets in 100 mL of EtOH) was added dropwise a solution of (R)-(+)-1-phenylethyl chloride ((R)-(+)-3b) in 20 mL of ethanol. After refluxing for 2 h, the solution was cooled and 200 mL of water was added. The solution was extracted with chloroform and the combined extracts were washed with hot 25% KOH, water, and brine. After the solvent was dried and removed, 3.1 g (95%) of (S)-(−)-1-phenylethyl benzyl sulfide ((S)-1-(−)-4b) was obtained: $[\alpha]^{30}_D$ −83.1° (EtOH); NMR (CDCl$_3$) δ 1.52 (d, 3 H), 3.47 (s, 2 H), 3.8 (q, 1 H), 7.2 (s, 5 H), 7.3 ppm (s, 5 H); IR (neat) 3100, 3080, 3050, 2990, 2940, 2890, 1605, 1495, 1455, 1195, 1030, 770, 703 cm⁻¹.

(S)-(−)-1-Phenylethyl Benzyl Sulfone ((S)-(−)-8). A solution of 2.8 g (12.3 mmol) of (S)-(−)-4b in 50 mL of a 1:1 mixture of glacial acetic acid and acetic anhydride was cooled in an ice bath. To this solution, 6 mL (53 mmol) of 30% hydrogen peroxide was added dropwise. The mixture was stirred at room temperature for 60 h, and about 60 g of ice was added to the solution. The white precipitate was filtered and washed with water. Recrystallization from ethanol gave 1.97 g (62%) of (S)-(−)-1-phenylethyl benzyl sulfone ((S)-(−)-8): mp 97–99 °C; $[\alpha]^{30}_D$ −29.1° (CHCl$_3$); optical purity (ee), 68.8%; NMR (CDCl$_3$) δ 1.7 (d, 3 H), 3.9 (s, 2 H), 4.05 (q, 1 H), 7.15–7.4 (2s, 10 H); IR (KBr) 3080, 3060, 3025, 3000, 2980, 2915, 1485, 1435, 1405, 1300, 1285, 1130, 1120, 765, 690 cm⁻¹; UV (MeOH) λ$_{max}$ (ε) 268 nm (351), 263 (497), 262 (4717), 256 (629), 252 (463); mass spectrum (81 °C), m/e (relative intensity) 260 (M⁺), 196 (2), 107 (10), 105 (100), 104 (18), 103 (6), 90 (11), 79 (8), 77 (8), 65 (4).

Anal. Calcd for C$_{15}$H$_{16}$O$_2$S: C, 69.23; H, 6.15. Found: C, 69.06; H, 6.20.

1-Naphthylmethyl Benzyl Sulfone (9). 1-Naphthylmethyl benzyl sulfide (4c 6.3 g, 23.9 mmol), prepared from 6.1 g (34 mmol) of 1-(chloromethyl)naphthalene and 4.1 g (33 mmol) of benzyl mercaptan by refluxing in a solution of 2.2 g of KOH/EtOH (71%, mp 57 °C), was oxidized to the sulfone by treatment with 50 mL of a 1:1 mixture of glacial acetic acid and acetic anhydride and 13 mL of 30% H$_2$O$_2$ at −5 °C. After the solution stirred 48 h, the addition of 50 g of cracked ice gave off-white crystals, which were washed several times with H$_2$O and 50% aqueous ethanol. Recrystallization from 50% ethanol-50% benzene gave 5.0 g (71%) of 1-naphthylmethyl benzyl sulfone (9), mp 159–162 °C. Further recrystallization from ethanol–pentane–benzene (3:4:3) gave

(21) A less likely possibility would be sequential bond breaking of both C–S bonds with racemization followed by entrapment of the caged SO$_2$ molecule by the two radicals.

(22) This assumes no solvent effect on the rates of intersystem crossing and fluorescence, which were measured in acetonitrile and cyclohexane, respectively.

(23) Givens, R. S.; Matuszewski, B.; Neywick, C. V. *J. Am. Chem. Soc.* **1974,** *96,* 5547.

(24) Pomerantz, A.; Connor, R. *J. Am. Chem. Soc.* **1939,** *61,* 3386.

3 with mp 163–164 °C. The spectral data were as follows: NMR (Me$_2$SO-d_6, Me$_4$Si) δ 8.28–7.28 (m, 12 H), 5.00 (s, 2 H), 4.65 (s, 2 H); IR (KBr) 3060, 3036, 2988, 2940, 1590, 1504, 1489, 1450, 1306, 1280, 1252, 1225, 1211, 1200, 1160, 1146, 1118, 1070, 1028, 1011, 922, 895, 880, 857, 821, 800, 772, 738, 717, 695, 644, 600 cm^{-1}; UV (CH$_3$CN) λ$_{max}$ (log ε) 317 (2.40), 313 (2.78), 295 (3.80), 284 (3.97), 274.5 (3.88), 265 (3.68); mass spectrum, m/e (%) 91 (10%), 141 (100%), 296 (4.7%, M$^+$), 297 (1.0%, (M$^+$ + 1)).

Anal. Calcd for C$_{18}$H$_{16}$SO$_2$: C, 72.94; H, 5.44. Found: C, 72.85; H, 5.38.

2-Naphthylmethyl Benzyl Sulfone (10). A similar procedure to that employed for **9** was followed. From 7.6 g (34 mmol) of 2-(bromomethyl)naphthalene and 4.1 g (33 mmol) of benzyl mercaptan was obtained 7.0 g (77%) of 2-naphthylmethyl benzyl sulfide (**4d**), mp 51.5–52.5 °C. This was oxidized to the sulfone in 81% yield as for **9**. The 2-naphthylmethyl benzyl sulfone (**10**, mp 184.5–185.5 °C) had the following spectral data: NMR (Me$_2$SO-d_6, Me$_4$Si) δ 8.03–7.42 (m, 12 H), 4.67 (s, 2 H), 4.55 (s, 2 H); IR (KBr) 3052, 3039, 2979, 2932, 1596, 1505, 1492, 1452, 1417, 1365, 1329, 1302, 1285, 1255, 1215, 1171, 1142, 1127, 1072, 1046, 1030, 1018, 972, 956, 920, 900, 866, 833, 782, 775, 755, 723, 698, 650, 600 cm^{-1}; UV (CH$_3$CN) λ$_{max}$ (log ε) 318 (2.32), 311 (2.43), 304.5 (2.56), 287 (3.54), 277 (3.73), 268.5 (3.737), 260 nm (3.59); mass spectrum, m/e (%) 91 (8 %) 115 (32), 141 (100.0), 162 (40), 163 (50), 296 (4.9%, M$^+$) 297 (1.1%, (M$^+$ + 1)).

Anal. Calcd for C$_{18}$H$_{16}$SO$_2$: C, 72.94; H, 5.44. Found: C, 73.15; H, 5.31.

1- and 2-(Mercaptomethyl)naphthalene (2a and 2b). These mercaptans were obtained in two steps. Treatment of 1-chloromethyl- (**1a**, 14.876 g, 80 mmol) or 2-bromomethylnaphthalene (**1b**, 16.470 g, 74.5 mmol) with thiourea (1:1 mol equiv) in 60 mL of absolute ethanol gave, after workup and recrystallizations from ethanol, the 1- or 2-naphthylmethylisothiouronium chloride or bromide salts (white crystals, 81% and 88% yield, 222–226 °C dec and 180–182 °C dec, respectively).

After these salts were heated at reflux in KOH/H$_2$O (13.2 molar excess of KOH), acidification with 9 M H$_2$SO$_4$, extraction with ether, and workup gave 10.12 g (90%) and 9.51 g (89%) of 1- and 2-naphthylmethyl mercaptans (**2a** and **2b**), respectively.

1-(Mercaptomethyl)naphthalene (**2a**, clear, slightly yellow liquid) was purified by vacuum "bulb-to-bulb" distillation giving material with the following spectral data: NMR (CCl$_4$, Me$_4$Si) δ 7.10–7.92 (m, 7 H), 3.98 (d, 2 H), 1.58 (t, 1 H); IR (neat) 3096, 3077, 3058, 2584, 1689, 1595, 1511, 1451, 1435, 1399, 1355, 1271, 1250, 1029, 1220, 1170, 1143, 1080, 970, 950, 865, 800, 780, 739, 720, 684, 631 cm^{-1}; mass spectrum (140 °C), m/e (%) 127 (14.8), 139 (13.5), 141 (100.0), 174 (31.0, M$^+$), 175 (6.6, (M$^+$ + 1)), 176 (4.7, (M$^+$ + 2)).

Anal. Calcd for C$_{11}$H$_{10}$S: C, 75.82; H, 5.78. Found: C, 76.10; H, 5.75.

2-(Mercaptomethyl)naphthalene (**2b**, white crystals, after two recrystallization from EtOH, mp 48–49 °C), had the following spectral data: NMR (CCl$_4$, Me$_4$Si) δ 7.13–7.64 (m, 7 H), 3.70 (d, 2 H), 1.52 (t, 1 H); IR (KBr) 3040, 3012, 2950, 2924, 1626, 1592, 1499, 1416, 1379, 1357, 1267, 1236, 1205, 1167, 1140, 1120, 1014, 980, 958, 945, 887, 852, 812, 780, 742, 724, 682, 610 cm^{-1}; mass spectrum (46 °C), m/e (%) 115 (14.5), 139 (8.1), 141 (100.0), 142 (12.0), 174 (35.4, M$^+$), 175 (4.9, M$^+$ + 1)), 176 (2.0, (M$^+$ + 2)).

Anal. Calcd for C$_{11}$H$_{10}$S: C, 75.82; H, 5.78. Found: C, 76.01; H, 5.77.

(±)- and (S)-(-)-1-Naphthylmethyl 1-Phenylethyl Sulfides ((±)- and (S)-(-)-4e). In a typical run, to a cooled solution of sodium ethoxide, which was prepared from 132 mg of sodium (5.7 mmol) in 3.5 mL of absolute EtOH, was added 1.0 g (5.7 mmol) of 1-(mercaptomethyl)-naphthalene (**2a**) followed by 807 mg (5.7 mmol) of (±)- or (R)-(+)-1-phenylethyl chloride ((±)- or (R)-(+)-**3b**) in 20 mL of absolute EtOH over a period of 30 min with constant stirring and under N$_2$. After addition was completed, the solution was allowed to warm to room temperature and then was heated at reflux for 3 h. Overnight stirring at room temperature, extraction with ether, workup, and vacuum "bulb-to-bulb" distillation of the crude material gave the desired sulfide.

(±)-1-Naphthylmethyl 1-phenylethyl sulfide ((±)-**4e**, 96%): NMR (CCl$_4$, Me$_4$Si), δ 7.77–6.95 (m, 12 H), 3.72 + 3.64 (s + q, 2 H + 1 H), 1.45 (d, 3 H); IR (neat) 3062, 3048, 3030, 2968, 2927, 2868, 1684, 1590, 1505, 1485, 1448, 1392, 1370, 1348, 1215, 1165, 1078, 1054, 1026, 1015, 965, 945, 908, 800, 790, 775, 763, 735, 698 cm^{-1}; mass spectrum (122 °C, m/e (%) 105 (81.7), 115 (14.1), 141 (100.0), 142 (42.7), 173 (12.6), 278 (34.4, M$^+$), 279 (7.0, (M$^+$ + 1)), 280 (2.2, (M$^+$ + 2)).

Anal. Calcd for C$_{19}$H$_{18}$S: C, 81.97; H, 6.52. Found: C, 81.90; H, 6.52. This material after a few days of standing at room temperature solidified, giving slightly yellow crystals, mp 39.5–41.0 °C.

(S)-(-)-1-Naphthylmethyl 1-phenylethyl sulfide ((S)-(-)-**4e**) ([α]^{20}$_D$ -137.3 (c 1.76, EtOH), 92%, was obtained from (R)-(+)-1-phenylethyl

chloride ((R)-(+)-**3b**, [α]^{20}$_D$ +56.1 (c 0.79, EtOH)).

(±)- and (S)-(-)-2-Naphthylmethyl 1-Phenylethyl Sulfides ((±)- and (S)-(-)-4f). A procedure similar to that described for **4e** was employed here. Thus, starting with 5.5 g (32 mmol) of 2-(mercaptomethyl)-naphthalene (**2b**) and an equivalent amount of (±)-1-phenylethyl chloride gave 8.15 g (93%) of (±)-2-naphthylmethyl 1-phenylethyl sulfide ((±)-**4f**) as a clear, slightly green, oily liquid: NMR (CCl$_4$, Me$_4$Si) δ 7.84–6.68 (m, 12 H), 3.55 + 3.42 (q + s, 1 H + 2 H), 1.39 (d, 3 H); IR (neat) 3097, 3070, 3040, 2980, 2940, 2880, 1698, 1634, 1602, 1510, 1493, 1454, 1420, 1372, 1362, 1275, 1240, 1224, 1060, 1030, 1022, 962, 915, 898, 864, 823, 765, 758, 704 cm^{-1}; mass spectrum (110 °C), m/e (%) 105 (100.0), 141 (95.2), 173 (28.4), 278 (25.8, M$^+$), 279 (13.9, (M$^+$ + 1)).

Anal. Calcd for C$_{19}$H$_{18}$S: C, 81.97; H, 6.52. *Found*: C, 81.80; H, 6.51.

Similarly, from 3.0 g (17 mmol) of 2-(mercaptomethyl)naphthalene and an equivalent amount of (R)-(+)-1-phenylethyl chloride ((R)-(+)-**3b**), [α]^{20}$_D$ +56.1° (c 0.79, EtOH), was obtained 4.33 g (90%) of optically active (S)-(-)-2-naphthylmethyl 1-phenylethyl sulfide ((S)-(-)-**4f**) with [α]^{20}$_D$ -191.0° (c 1.48, EtOH).

(±)- and (S)-(-)-1-Naphthylmethyl 1-Phenylethyl Sulfone ((±)-11 and (S)-(-)-11). Starting with 4.108 g (14.8 mmol) of (±)-**4e** and using a procedure similar to that used for the synthesis of **9** gave 3.72 g (81%) of (±)-1-naphthylmethyl 1-phenylethyl sulfone ((±)-**11**): mp 144.5–145.5 °C (after four recrystallizations from EtOH); NMR (CDCl$_3$, Me$_4$Si) δ 7.90–7.05 (m, 12 H), 4.34 + 4.17 (s + q, 3 H), 1.72 (d, 3 H); IR (KBr) 3050, 3028, 2985, 2942, 1590, 1502, 1490, 1448, 1420, 1390, 1378, 1350, 1295, 1287, 1266, 1230, 1214, 1180, 1164, 1131, 1114, 1090, 1072, 1042, 1023, 1009, 975, 950, 915, 890, 860, 802, 780, 775, 734, 712, 698, 683, 636 cm^{-1}; mass spectrum (125 °C), m/e (%) 105 (66.1), 141 (100.0), 142 (31.8), 205 (5.9), 246 (10.5), 310 (4.4, M$^+$), 311 (1.1, (M$^+$ + 1)).

Anal. Calcd for C$_{19}$H$_{18}$SO$_2$: C, 73.52; H, 5.84. Found: C, 73.14; H, 5.81.

Similarly, from 4.0 g (14 mmol) of (S)-(-)-**4e** ([α]^{20}$_D$ -137.3° (c 1.76, EtOH) was obtained 3.5 g (80%) of (S)-(-)-1-naphthylmethyl 1-phenylethyl sulfone ((S)-(-)-**11**): mp 141.5–143.5 °C; [α]^{20}$_D$ -31.6° (c 0.98, CHCl$_3$).

(±)- and (S)-(-)-2-Naphthylmethyl 1-Phenylethyl Sulfone ((±)-12 and (S)-(-)-12). A procedure similar to that described for **9** was employed here. Thus, from 4.102 g (14.7 mmol) of (±)-**4f** was obtained 4.18 g (91%) of (±)-2-naphthylmethyl 1-phenylethyl sulfone ((±)-**12**): mp 118–119 °C; NMR (CDCl$_3$, Me$_4$Si) δ 7.68–7.17 (m, 12 H), 4.05 + 3.98 (s + q, 3 H), 1.69 (d, 3 H); IR (KBr) 3060, 3048, 3028, 2994, 2984, 2948, 1594, 1503, 1490, 1449, 1408, 1378, 1361, 1338, 1300, 1295, 1275, 1255, 1230, 1204, 1192, 1178, 1132, 1121, 1091, 1051, 1044, 1025, 1015, 1000, 980, 955, 948, 911, 891, 861, 830, 819, 786, 772, 768, 751, 712, 691, 680, 642, 615, 600 cm^{-1}; mass spectrum (160 °C) m/e (%) 77 (11.4), 103 (10.0), 105 (78.5), 115 (15.4), 141 (100.0), 142 (33.8), 205 (7.9), 246 (9.8), 310 (4.6, M$^+$), 311 (1.1, (M$^+$ + 1)).

Anal. Calcd for C$_{19}$H$_{18}$SO$_2$: C, 73.52; H, 5.84. Found: C, 73.48; H, 5.76.

The same procedure was followed by using 4.0 g (14 mmol) of (S)-(-)-**4f**, and 3.31 g (74%) of (S)-(-)-2-naphthylmethyl 1-phenylethyl sulfone ((-)-**12**) was obtained: mp 116–124 °C; [α]^{20}$_D$ -114.0° (c 1.21, CHCl$_3$).

Resolution of 1-(1-Naphthyl)ethyl Alcohol. The procedure of Downer and Kenyon[12c] with the modification indicated for resolution of 1-phenylethyl alcohol[12d-g] (above) was employed. From the (+)-hydrogen phthalate salt ([α]^{20}$_D$ +58.3° (EtOH)) was obtained on hydrolysis the (S)-(-)-1-(1-naphthyl)ethyl alcohol, [α]^{30}$_D$ -60.9° (EtOH).

(R)-(-)-1-(1-Naphthyl)ethyl Chloride ((R)-(-)-5a). The procedures of Streitwieser et al.[12b] and Hart et al.[12a] were employed to give 1.2 g of (R)-(-)-1-(1-naphthyl)ethyl chloride ((R)-(-)-**5a**): [α]^{30}$_D$ -40.4° (EtOH); NMR (CDCl$_3$) δ 1.85 (d, 3 H), 3.7 (q, 1 H), 7.1–8.15 (m, 7 H).

(S)-(-)-1-(1-Naphthyl)ethyl Benzyl Sulfide (6a). A cooled sodium ethoxide solution which was prepared from 145 mg (6.3 mmol) of sodium in 10 mL of ethanol was added in 782 mg (6.3 mmol) of benzyl mercaptan. To the solution was then added 1.2 g (6.3 mmol) of (R)-(-)-1-(1-naphthyl)ethyl chloride ((R)-(-)-(**5a**) in 50 mL of ethanol over a period of 15 min with constant stirring and under nitrogen. After refluxing for 2 h the solution was allowed to stand at room temperature overnight. The solution was extracted with ether, and the ether extracts were washed and dried. The solvent was removed to give 0.91 g (52%) of (S)-(-)-1-(1-naphthyl)ethyl benzyl sulfide (**6a**): [α]^{30}$_D$ -14.4° (EtOH); NMR (CDCl$_3$) δ 1.6 (d, 3 H), 3.4 (s, 2 H), 4.5 (q, 1 H), 7.1–7.85 (m, 12 H); IR (neat) 3070, 3040, 2980, 2940, 1600, 1515, 1500, 1455, 1400, 805, 785, 705 cm^{-1}; mass spectrum (45°), m/e 278 (M$^+$).

(S)-(+)-1-(1-Naphthyl)ethyl Benzyl Sulfone ((S)-(+)-13). A procedure similar to that used for **9** was employed here. Thus, from 0.91 g (3.3 mmol) of (S)-(−)-**6a** was obtained 0.72 g (71%) of (S)-(+)-1-(1-naphthyl)ethyl benzyl sulfone ((S)-(+)-**13**): mp 114–116 °C; [α]^{30}$_D$ +1.71° (CHCl₃); (ee) 4.8%; NMR (CDCl₃) δ 1.77 (d, 3 H), 3.93 (s, 3 H), 4.95 (q, 1 H), 6.85–7.85 (m, 12 H); IR (CHCl₃) 3075, 3020, 1590, 1510, 1490, 1450, 1395, 1310, 1200, 1130, 1120 cm⁻¹; UV (EtOH) λ$_{max}$ (ε) 315 nm (172), 310 (477), 296 (7631), 282 (10850), 274 (10254), 264 (7154), 218 (42607); mass spectrum (72 °C), m/e (relative intensity) 310 (M⁺), 246 (4), 156 (12), 155 (100), 154 (8), 153 (16), 115 (44), 59 (32).

Anal. Calcd for C₁₉H₁₈O₂S: C, 73.52; H, 5.84. Found: C, 73.90; H, 5.89.

Resolution of 1-(2-Naphthyl)ethyl Alcohol. The procedure of Downer and Kenyon[12c] with modifications outlined for 1-phenylethyl alcohol (above) was employed. From the (−)-hydrogen phthalate salt, mp 97–99 °C, [α]^{30}$_D$ −42.1° (CHCl₃), was obtained the (R)-(+)-1-(2-naphthyl)-ethyl alcohol, mp 62–64 °C, [α]^{30}$_D$ +35.2° (EtOH).

(S)-(−)-1-(2-Naphthyl)ethyl Chloride ((S)-(−)-5b). The procedures of Streitwieser et al.[12a] and Hart et al.[12b] were employed to give 2.73 g (95%) of the (S)-(−)-1-(2-naphthyl)ethyl chloride ((S)-(−)-**5b**): [α]^{30}$_D$ −18.9° (EtOH); NMR (CCl₄) δ 1.83 (d, 3 H), 5.07 (q, 1 H), 7.2–7.75 (m, 7 H).

(R)-(+)-1-(2-Naphthyl)ethyl Benzyl Sulfide ((R)-(+)-6b). A cooled sodium ethoxide solution, which was prepared from 327 mg (14.2 mmol) of sodium in 10 mL of ethanol, was added to 1.76 g (14.2 mmol) of benzyl mercaptan. To the solution was then added 2.7 g (14 mmol) of (S)-(−)-**5b** in 20 mL of ethanol over a period of 15 min under nitrogen. The solution was refluxed 2 h and then cooled to room temperature, ethanol was removed, and about 30 mL of water was added to the solution. The solution was extracted with ether, and the combined ether extracts were washed and dried. Removal of the solvent gave 3.0 g (75%) of (R)-(+)-1-(2-naphthyl)ethyl benzyl sulfide ((R)-(+)-**6b**): [α]^{30}$_D$ +92.6° (EtOH); NMR (CCl₄) δ 1.45 (d, 3 H), 3.25 (d, 2 H), 3.73 (q, 1 H), 7.0 (s, 5 H), 7.1–7.7 (m, 7 H); IR (neat) 3060, 3020, 2960, 2920, 1600, 1505, 1490, 1450, 855, 815, 750, 700 cm⁻¹; mass spectrum (41 °C), m/e 278 (M⁺).

(R)-(+)-1-(2-Naphthyl)ethyl Benzyl Sulfone ((R)-(+)-14). A similar procedure to that employed for **9** was used here. Thus, starting with 2.97 g (10.7 mmol) of (R)-(+)-**6b** gave 1.78 g (54%) of (R)-(+)-1-(2-naphthyl)ethyl benzyl sulfone ((R)-(+)-**14**): mp 107–110 °C; [α]^{30}$_D$ +68.4° (CHCl₃); optical purity (ee), 43.8%; NMR (CDCl₃) δ 1.85 (d, 3 H), 3.95 (s, 2 H), 4.20 (q, 1 H), 7.20 (s, 5 H), 7.25–7.80 (m, 7 H); IR (CHCl₃) 3050, 3000, 1585, 1495, 1482, 1440, 1300, 1105 cm⁻¹; UV (EtOH) λ$_{max}$ (ε) 318 nm (143), 310 (430), 285 (4450), 276 (6610), 266 (6640), 260 (5430), 222 (41320); mass spectrum (85 °C), m/e (relative intensity) 310 (M⁺), 246 (4), 156 (14), 155 (100), 154 (10), 153 (12), 152 (5), 124 (5), 123 (5), 122 (5), 90 (5), 77 (2).

Anal. Calcd for C₁₉H₁₈O₂S: C, 73.55; H, 5.81. Found: C, 73.31; H, 5.69.

B. Synthetic Photochemistry. Dibenzyl Sulfone (7). A solution of 537 mg (2.18 mmol) of dibenzyl sulfone in 60 mL of dry benzene was irradiated for 50 min with 15 RPR 2537-Å lamps in a merry-go-round photoreactor. After evaporation of the solvent, the 466 mg of residue was triturated with pentane. The white solid recovered (295 mg, 55%) was identified as the sulfone **7** by mp, GLC, and spectroscopic analysis. The pentane solution was evaporated and chromatographed on a 1.5 × 60 cm silica gel column eluted with hexane–ether from which 147 mg (82%) of dibenzyl was obtained.

Dibenzyl sulfone was also irradiated in dioxane to 75% conversion. Dibenzyl (isolated in 48% yield) was the major product. Many unidentified minor products were also formed.

1- and 2-Methylnaphthyl Benzyl Sulfone (9 and 10). In a typical run, a degassed, dry benzene solution (75 mL) of 420 mg (1.421 mmol) of sulfone **10** was irradiated with 14 RPR 2537-Å lamps for 13 h. GLC analysis indicated a 30% conversion of **10** to products. After the solvent was removed, 408 mg of the brown residue was triturated with pentane giving 206 mg (0.696 mmol, 49%) of white sulfone. The pentane extract was chromatographed on silica gel (1.5 × 60 cm) to give 87 mg (0.4 mmol, 55% based on recovered **10**) of 1-(2-naphthyl)-2-phenylethane (**22**). Dibenzyl (**19**) and 1,2-di-(2-naphthyl)ethane (**23**) were also identified in the product mixture (GLC).

A similar irradiation was carried out for sulfone **9** from which 1,2-di-(1-naphthyl)ethane (**21**) and 1-(1-naphthyl)-2-phenylethane (**20**) were isolated in addition to **19**.

Photolysis of (±)-1-Naphthylmethyl 1-Phenylethyl Sulfone (11). A solution of 1.054 g (3.40 mmol) of **11** in 120 mL of reagent grade benzene was divided among eight Pyrex tubes, degassed with nitrogen for 20 min, and irradiated with 16 RPR 3000-Å lamps for 10 h. The combined photolysis samples were washed with 100 mL of 15% NaOH,

the basic layer was acidified with 20% HCl and extracted with ether, the ether layer was dried over Na₂SO₄, and after ether removal 10 mg of brown residue was obtained which was a mixture of many minor photolysis products. The benzene layer was washed with water and brine and dried over Na₂SO₄, and after benzene removal 1.012 g of dark-yellowish residue was obtained. This was washed with n-pentane and ether leaving an insoluble solid (395 mg, 37.5%) sulfone identified by its NMR spectrum (62.5% conversion based on recovered sulfone). The combined n-pentane and ether-soluble portion (541 mg) was chromatographed on an alumina column (Woelm-neutral, activity grade 1, 75 × 2 cm), and the eluent was monitored by a UV detector (fraction volume 25 mL): 35.7 (8%) mg of a mixture of dl-2,3-diphenylbutane (**24**) and meso-2,3-diphenylbutane (**25**) was obtained in fractions 37–72 (hexane or 0.5% benzene/hexane as eluents) in different ratios of **24:25** varying from 1.0:4.3 (fractions 37–48) to 15.6:1.0 (fractions 69–72); 185.4 mg of 1-(1-naphthyl)-2-phenylpropane (**16**) (36% yield based on sulfone consumed) was isolated in fractions 159–285 (3–6% benzene/hexane), the purity of which varied from 67% to >99% of **16**. Finally, 72.1 mg (12%) of 1,2-di-(1-naphthyl)ethane (**21**) was obtained in fractions 362–412 (15–20% benzene/hexane). GLC analyses of the remaining fractions indicated complicated mixtures of many minor, unidentified products, one of which was shown to be 1-methylnaphthalene (fractions 73–88, 0.5% benzene/hexane) by coinjection with an authentic sample. Hydrocarbons **24**, **25**, and **21** were identified by comparison of their spectra and physical properties with those reported.[25] The spectral data of **16**: NMR (CDCl₃) δ 8.13–7.06 (m + s, 12 H), 3.25–3.09 (d + q, 3 H) 1.24 (d, 3 H); IR (neat) 3060, 3030, 2963, 2933, 2875, 1595, 1508, 1491, 1450, 1394, 1372, 1018, 798, 790, 782, 760, 711, 700 cm⁻¹; mass spectrum (30 °C), m/e (relative intensity) 77 (6.9), 105 (77.5), 115 (14.7), 141 (100.0), 246 (32.0, M⁺), 247 (6.0, (M⁺ + 1)).

Anal. Calcd for C₁₉H₁₈: C, 92.63; H, 7.36. Found: C, 92.48; H, 7.47.

On the basis of (±)-**11** sulfone consumed, the total yield of cross coupling products **16**, **21**, **24**, and **25** isolated in this preparative run was ~60%, in a ratio of (**24** + **25**):**16**:**21** equal to 1:4.4:1.4.

Photolysis of (±)-2-Naphthylmethyl 1-Phenylethyl Sulfone ((±)-12). A solution of 1.040 g (3.35 mmol) of (±)-**12** in 120 mL of benzene was divided among eight Pyrex tubes, degassed with nitrogen for 20 min, and irradiated with 16 RPR 3000-Å lamps for 63 h. The combined photolysis samples were washed with 100 mL of 15% NaOH, and the basic layer was acidified and extracted to give 3.9 mg of brown residue. Evaporation of the benzene layer gave 981 mg of brown residue which was triturated with n-pentane and ether, leaving an insoluble solid (523 mg) identified as the starting sulfone (±)-**12** (~50% conversion based on recovered sulfone). The combined n-pentane and ether soluble layers (458 mg) were chromatographed on a alumina column as above: 53.9 (15%) mg of a mixture of **24** and **25** were obtained in fractions 49–122 (hexane or 1% benzene/hexane) in ratios of **24:25** varying from practically pure **25** in fractions 49–55 to 47:1 in fractions 95–106; 155.8 mg of 1-(2-naphthyl)-2-phenylpropane (**17**) (38% yield based on sulfone decomposed) was isolated in fractions 123–341 (2 to 12% benzene/hexane), the purity of which varied from 60% to >96% of **17**. Finally, 53.2 mg of 1,2-di-(2-naphthyl)ethane (**23**) was obtained in fractions 382–442 (20–50% benzene/hexane). GLC analyses of the remaining fraction indicated a very complicated mixture of many minor products; among these was 2-methylnaphthalene identified by coinjection with an authentic sample.

Compounds **23**, **24**, and **25** were identified by comparison of their spectra and physical properties with those reported.[25] The spectral data of **17**: NMR (CDCl₃) δ 7.77–7.25 (m + s, 12 H), 2.98 (m, 3 H), 1.24 (d, 3 H); IR (neat) 3055, 3022, 2960, 2920, 1595, 1502, 1487, 1445, 1368, 1013, 849, 814, 783, 760, 742, 720, 694 cm⁻¹; mass spectrum (68 °C), m/e (relative intensity) 105 (86.4), 115 (16.3), 141 (100.0), 246 (44.7, M⁺), 247 (8.4, M⁺ + 1); peak matching. Calcd. for C₁₉H₁₈, M⁺ 246.14076; found, M⁺ 246.14032. After several days of standing in the refrigerator, the sample of **17** solidified giving the white crystals with mp 46–48 °C.

On the basis of sulfone consumed, the total yield of cross coupling products **24**, **25**, **17**, and **23** isolated in this preparative run was ~61% with an isolated molar ratio of (**24** + **25**):**17**:**23** equal to 1:2.47:0.74.

Photolysis of (S)-(−)-1-Naphthylmethyl 1-Phenylethyl Sulfone ((S)-(−)-11) and (S)-(−)-2-Naphthylmethyl Phenylethyl Sulfone ((S)-(−)-12) in Benzene at 300 nm. a. Optical Rotation Measurements. Two samples, one containing 80.4 mg of (S)-(−)-**11** and another with 80.3 mg of (S)-(−)-**12**, each in 15 mL of benzene, were degassed with nitrogen and

(25) (a) Inukai, T. *J. Org. Chem.* **1966**, *31*, 1124. (b) "Physical Constants of Hydrocarbons"; Egloff, G., Ed.; Reinhold: New York, 1947; ACS Mongr. Ser., Vol 4, p 320. (c) Serijan, K. T.; Wise, P. H. *J. Am. Chem. Soc.* **1952**, *74*, 365.

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irradiated with 15 RPR 3000-Å lamps. The aliquots were removed from the photolysis solutions, the optical rotations were measured, and the aliquots were transfered back to the photolysis solution for further irradiation. After photolysis, the solvent was removed in vacuo and the residue triturated with *n*-pentane and hexane. The hexane/pentane insoluble fractions containing recovered sulfones were analyzed and specific rotations were measured in CHCl₃. It was found that specific rotations of these fractions were within experimental error, only slightly lower than that for starting (*S*)-(−)-11 sulfone and even higher than that of sulfone (*S*)-(−)-12. The samples were then recrystallized from ethanol to yield very pure sulfones (by GLC). However, the specific rotations of the purified sulfones were higher than those for the reactants, apparently due to partial resolution of the sulfone during recrystallization. It was found that purification of the sulfone after photolysis by column chromatography gave consistent results for specific rotation measurements and was used in the second series of experiments. The changes in specific rotation observed are therefore almost exclusively due to photodesulfonylation rather than photoracemization.

b. Product Isolation. Two samples, one containing 98.0 mg of (*S*)-(−)-11 with 11.3 mg of *n*-tetracosane as internal standard and the other containing 99.5 mg of (*S*)-(−)-12 with 10.4 mg of *n*-tetracosane, each in 15 mL of benzene, were degassed with nitrogen and irradiated with 16 RPR 3000-Å lamps.

In the case of 1-sulfone, (*S*)-(−)-11, irradiation was for 3 h to 24% conversion. The solvent was removed and 104.6 mg of residue was obtained which was chromatographed on a silica gel column (SilicAR CC-7, 1.5 × 40 cm, fraction volume 25 mL). Eluting with hexane gave in fractions 1–4 *n*-tetracosane; then hexane and 2% ether–hexane gave in fractions 9–16 a mixture of hydrocarbons 24, 25, 16, and 21, which contained 65% of 16; 50% ether–hexane gave the sulfone in fractions 42–52. The specific rotations for (*S*)-(−)-11 used for irradiation and for material obtained in fractions 9–16 and 42–52 were measured and are given in Table 1.

The 2-sulfone, (*S*)-(−)-12, was irradiated for 15 h to a conversion of 30%. Solvent was removed and the 102.5 mg of residue was chromatographed on a silica gel column (as above). Eluting with hexane gave in fractions 1–4 *n*-tetracosane; hexane and 2% ether–hexane gave in fractions 10–17 a mixture of hydrocarbons 24, 25, 17, and 23 containing 73.5% of 17; 20–30% ether–hexane gave in fractions 36–43 starting 2-sulfone. For (*S*)-(−)-12 used for irradiation and for material obtained in fractions 10–17 and 36–43, the specific rotations were measured and are given in Table 1.

Benzophenone-Sensitized Photolysis of (*S*)-(−)-1-Naphthylmethyl 1-Phenylethyl Sulfone ((*S*)-(−)-11) and (*S*)-(−)-2-Naphthylmethyl 1-Phenylethyl Sulfone ((*S*)-(−)-12) in Benzene at 350 nm. A solution of 278.8 mg of (*S*)-(−)-11, 664.3 mg of benzophenone, and 42.3 mg of internal standard (*n*-C₂₄H₅₀) in 60 mL of benzene was divided among four Pyrex tubes. Similarly, a solution of 251.8 mg of (*S*)-(−)-12, 650.1 mg of benzophenone, and 43.1 mg of *n*-C₂₄H₅₀ in 60 mL of benzene, divided among four Pyrex tubes, was prepared. All samples were degassed with nitrogen and irradiated with 15 RPR 3500-Å lamps.

For (*S*)-(−)-11, 49% conversion of sulfone was noted after 15 min of irradiation. The solvent was removed and the residue was chromatographed on a silica gel column. Eluting with hexane (25-mL fractions) gave in fractions 1–2 *n*-tetracosane and in fractions 3–4 a mixture of hydrocarbons 24, 25, 16, and 21 containing 56% and 22% of 16, respectively; 2–20% ether–hexane, fractions 17–33, gave benzophenone; 50% ether–hexane, fractions 34–43, gave starting 1-sulfone. For (*S*)-(−)-11 used for irradiation and for the materials obtained in fractions 3 and 34–43, specific rotations were measured and employed for determining the racemization quantum efficiency given in Table 11.

For 2-sulfone (*S*)-(−)-12, after 7 h of irradiation, 41% sulfone conversion was noted. The solvent was removed from the combined solutions, and the residue was chromatographed on a silica gel column. Eluting with hexane (25-mL fraction) gave in fraction 1 mostly *n*-tetracosane together with some hydrocarbon products and in fractions 2–4 a mixture of hydrocarbons 17, 23, 24, and 25, (containing 38% of 17 in fraction 3); 2–8% ether–hexane gave in fractions 5–26 benzophenone; 20% ether–hexane gave in fractions 27–38 starting 2-sulfone. For (*S*)-(−)-12 used for irradiation and for the materials obtained in fractions 3 and 27–38, specific rotations were measured. For recovered 2-sulfone it was noted that the specific rotation increased in going from fraction 27 to 38. It is apparent then that partial resolution occurs on a silica gel column. Therefore, the average values of optical rotation measured for all 2-sulfone-containing fractions 27–38 were employed in determining the racemization quantum efficiencies in Table 11.

Photolysis of (*R*)-(+)-1-(2-Naphthyl)ethyl Benzyl Sulfone ((*R*)-(+)-14) in Benzene at 300 nm. A solution of 244.7 mg of (+)-14 in 60 mL of benzene was divided among four Pyrex tubes. Internal standard (12.1 mg of tetracosane) was also added to one of these tubes. The

samples were degassed with nitrogen and irradiated with 16 RPR 3000-Å lamps. After 3 h, 58.5% conversion of sulfone was noted. From the combined photolysis samples, the solvent was removed and the residue was chromatographed on a silica gel column. Eluting with hexane (25-mL fractions) gave in fractions 2–10 a mixture of hydrocarbon 18, 19, 26, 27, and *n*-tetracosane containing 43% of 18; eluting with 20–50% ether–hexane gave in fractions 28–35 starting sulfone. A specific rotation was measured for fractions 2–10 and for the fractions containing recovered sulfone. The optical rotations measured in all fractions containing recovered (*R*)-(+)-14 were averaged and the average value is given in Table 1.

The mixture of hydrocarbons from fractions 2–10 was rechromatographed on a Woelm alumina (activity 1) 1.2 × 35 cm column to give in fractions 4–14 (0.5–1% ether–hexane) 34.7 mg of material containing mostly 18. The purity of recovered 18 in different fractions varied from 63% to 98%. The specific rotation was measured for all fractions containing compound 18 taking into account the different content of 18 in these fractions. It was noted, that specific rotations were the same, within experimental error, for all samples examined. The value given in Table 1 is for the isolated 18 with 98% purity.

Photolysis of (*S*)-(−)-1-Phenylethyl Benzyl Sulfone ((*S*)-(−)-8). (a) A solution of 873.6 mg (3.36 mmol) of (*S*)-(−)-8 ([α]³⁰_D −29.1) in 105 mL of benzene was divided among seven quartz tubes and degassed with purified nitrogen. The samples were irradiated using 15 RPR 2537-Å lamps for 1.67 h. Removal of the solvent afforded 833 mg of a pale yellow liquid which was washed with hexane. The hexane-insoluble solid was identified as the starting material by its NMR spectrum and melting point. The optical rotation of the recovered sulfone was [α]³⁰_D +0.17° (CHCl₃). The hexane-soluble portion (350 mg) was chromatographed on an alumina column (activity 1). Elution with 5% ether–hexane gave 20 mg (5%) of *meso*-2,3-diphenylbutane (25), 42 mg (10%) of *dl*-2,3-diphenylbutane (24), 211 mg (55%) of (−)-1,2-diphenylpropane (15, [α]³⁰_D −2.89° (CHCl₃)), and 105 mg (30%) of dibenzyl (19).

(b) Solutions of 100.8 mg, 119.4 mg, and 115.5 mg of the (*S*)-(−)-8 in 15 mL of benzene were placed in three quartz tubes and degassed with nitrogen for 15 min. The samples were irradiated with 4 RPR 2537-Å lamps for a period of 1, 2, and 3 min, respectively. The sulfone was recovered from the mixture by the technique described previously. The specific rotations of (*S*)-(−)-8 were obtained: *t* = 0 min, [α]³⁰_D −29.1° (CHCl₃); *t* = 1, −27.94°; *t* = 2, −26.65°; *t* = 3, −24.83°.

Photolysis of (±)-1-(1-Naphthyl)ethyl Benzyl Sulfone ((±)-13). A solution of 878 mg of the sulfone, (±)-13, in 100 mL of benzene was divided among six quartz tubes and degassed with nitrogen for 15 min. The sample was irradiated with 15 RPR 2537-Å lamps for 15.5 h. Removal of the solvent afforded a brown oil which was washed with ether. The ether-soluble portion was chromatographed on silica gel; elution with hexane gave dibenzyl (19) and 2-(1-naphthyl)-1-phenylpropane (28). The spectral data for 28: NMR (CDCl₃) δ 1.25 (d, 3 H), 2.45–3.21 (m, 7 H), 3.45–4.05 (m, 1 H), 7.0 (s, 5 H), 7.15–8.05 (m, 7 H); IR (neat) 3050, 2950, 2905, 2860, 1570, 1495, 1480, 1440, 1380, 1365, 780, 765 cm⁻¹; mass spectrum (143 °C), *m/e* (relative intensity) 246 (10, M⁺), 156 (14), 155 (100), 154 (5), 153 (19), 152 (5), 119 (43), 117 (48), 90 (19). The *meso*- and *d,l*-2,3-di-1-naphthylbutanes were not isolated.

Photolysis of (±)-1-(2-Naphthyl)ethyl Benzyl Sulfone ((±)-14). A solution of 822.6 mg of the sulfone (±)-14 in 120 mL of benzene was divided among 8 quartz tubes and degassed with nitrogen for 15 min. The sample was irradiated with 15 RPR 2537-Å lamps for 7 h. Removal of the solvent gave 734 mg of a brown oil which was then washed with ether. The ether-insoluble portion (600 mg) was chromatographed on silica gel; elution with hexane (25 mL fractions) gave four products: 2-ethylnaphthalene, 2-vinylnaphthalene, dibenzyl (19), and 2-(2-naphthyl)-1-phenylpropane (18). The NMR (CDCl₃) spectral data for 18: δ 1.23 (d, 3 H), 2.83 (d, 3 H), 2.55–3.55 (m, 1 H), 6.95 (s, 5 H), 7.0–7.65 (m, 7 H). The mass spectrum (44 °C) of 18: *m/e* (relative intensity) 246 (19, M⁺), 156 (17), 155 (100), 154 (8), 153 (12), 152 (4), 115 (6), 90 (2), 77 (2).

Photolysis of (*S*)-(+)-1-(1-Naphthyl)ethyl Benzyl Sulfone ((*S*)-(+)-13). A solution of 135.4 mg of (*S*)-(+)-13 ([α]³⁰_D +1.624° [benzene]) in 10 mL of benzene was placed in a Pyrex tube and degassed with nitrogen. The solution was irradiated with 16 RPR 3000-Å lamps. Aliquots were removed from the photolysis solution for optical rotation measurements, and the aliquots were transferred by a syringe back to the solution for further irradiation. The specific rotations of (*S*)-(+)-13: *t* = 0 min, [α]³⁰_D +1.624°; *t* = 60, +1.034°; *t* = 170, +0.517°.

Optical Rotations of (+)-2-(2-Naphthyl)-1-phenylpropane (18) from the Photolysis of (*R*)-(+)-1-(2-Naphthyl)ethyl Benzyl Sulfone ((*R*)-(+)-14). A solution of 133.4 mg of (*R*)-(+)-14 in 60 mL of benzene was divided among 4 Pyrex tubes and degassed with nitrogen. The solutions were irradiated with 16 RPR 3000-Å lamps for 60, 120, 240, and 480 min, respectively. The photolysis mixtures were chromatographed on a

silica gel column; elution with hexane of the four samples gave (R)-$(+)$-**18**: $t = 50$ min, not enough product separated for optical rotation measurement; $t = 120$, 2.1 mg, $[\alpha]^{30}{}_D$ $+15.24°$ (CHCl$_3$); $t = 240$, 5.8, $+12.41°$; $t = 480$, 11.3; $+4.78°$.

Benzophenone-Sensitized Photolysis of (R)-$(+)$-1-(2-Naphthyl)ethyl Benzyl Sulfone $((R)$-$(+)$-14). A solution of 78.1 mg (R)-$(+)$-**14**, 182.4 mg of benzophenone, and 9.5 mg of *n*-tetracosane in 15 mL of benzene was degassed with nitrogen and irradiated with 15 RPR 3500-Å lamps. Before and after 15, 30, 60, 90, 120, and 210 min of irradiation, the aliquots were removed from the photolysis solution and GLC analyses and optical rotation measurements were performed. The aliquots were transferred back to the solution for further irradiation. It was found that rate of racemization as measured by the decrease in optical rotation at different wavelengths was exactly the same as the rate of photolysis of the sulfone as measured by GLC. Therefore, in contrast to the direct irradiations, no racemization of starting (R)-$(+)$-**14** was observed during sensitized irradiation.

C. Control Experiments. Photolysis of 1-Phenylethyl Benzyl Sulfone (8) in the Presence of Nucleophilic Trapping Agents. (i) A solution of 141.4 mg of **8** and 43 mg of deuterium oxide in 15 mL of benzene was placed in a quartz tube and degassed with nitrogen. The sample was irradiated by using 6 RPR 2537-Å lamps for 20 min (20% conversion). The NMR spectrum of recovered sulfone was unchanged indicating no deuterium incorporation. (ii) A solution of 119.5 mg of CH$_3$OD and 240 mg of **8** in 15 mL of benzene was placed in a quartz tube and degassed with nitrogen. The sample was irradiated as above for 25 min (30% conversion). The NMR spectrum of the recovered sulfone was unchanged indicating no deuterium incorporation. No methanol adducts were detected. (iii) A solution of 129.4 mg of **8** in 15 mL of methanol was placed in a quartz tube and degassed with nitrogen. The sample was irradiated as above for 53 min (50% conversion). The photolysis mixture was analyzed by NMR and GLC (15% SE 30 column), and only two minor, unidentified products were observed along with the usual four major hydrocarbon photoproducts.

Photolysis of 1-(1-Naphthyl)ethyl Benzyl Sulfone (13) with Nucleophilic Trapping Agents. General Procedure. The photolyses were carried out in Pyrex tubes for 1 h. The samples were analyzed by NMR and GLC (10% SE 30 column). (i) A solution of 73.4 mg of **13** and 117.8 mg of CH$_3$OD in 15 mL of benzene was irradiated with 16 RPR 3000-Å lamps. (ii) A solution of 61.1 mg of **13**, 165.5 mg of CH$_3$OD, and 202.8 mg of acetophenone in 15 mL of benzene was irradiated with 15 RPR 3500-Å lamps. (iii) A solution of 59.7 mg of **13** in 15 mL of methanol was irradiated with 16 RPR 3000-Å lamps. (iv) A solution of 56.3 mg of **13** and 179.4 mg of acetophenone in 15 mL of methanol was irradiated with 15 RPR 3500-Å lamps.

The NMR spectra obtained from the above were identical with the spectra of the reactant sulfone and GLC showed no new product formation.

Photolysis of 1-(2-Naphthyl)ethyl Benzyl Sulfone (14) with Nucleophilic Trapping Agents. (i) A solution of 53.4 mg of **14** and 135.3 mg of CH$_3$OD in 15 mL of benzene was irradiated with 16 RPR 3000-Å lamps. (ii) A solution of 85.3 mg of **14**, 145 mg of CH$_3$OD, and 251 mg of acetophenone in 15 mL of benzene was irradiated with 15 RPR 3500-Å lamps. (iii) A solution of 45.1 mg of **14** and 343.5 mg of acetophenone in 15 mL of methanol was irradiated with 15 RPR 3500-Å lamps. (iv) A solution of 102.2 mg of **14** in 15 mL of methanol was irradiated with 16 RPR 3000-Å lamps.

The NMR spectra obtained from the above were identical with the spectra of the reactant sulfones and GLC showed no new product formation.

Photolysis of 2-(1-Naphthyl)-1-phenylpropane (28). A solution of 21.7 mg of **28** in 5 mL of benzene was placed in a Pyrex tube and degassed with nitrogen. The sample was irradiated with 16 RPR 3000-Å lamp, and aliquots were removed from the solution at 120, 180, 240, and 300 min of irradiation. The GLC analysis showed no significant change in the amount of the starting material or new photoproducts.

Photolysis of 2-(2-Naphthyl)-1-phenylpropane (18). A solution of 24.5 mg of **18** in 5 mL of benzene was placed in a Pyrex tube and degassed with nitrogen. The sample was irradiated with 16 RPR 3000-Å lamps and the aliquots were removed from the solution at 120, 180, 240, and 300 min of irradiation. The GLC analysis showed no significant change in the amount of the starting material and no new photoproducts.

Sulfur Dioxide Detection in the Photolysis of Dibenzyl Sulfone (7). In two quartz irradiation tubes fitted with gas diffusion tubes were placed 15 mL of a stock solution of 1.0394 gm (4.22 mmol) of **7** in 100 mL of acetonitrile. Nitrogen was continually passed through the photolysis sample and the effluent gas was subsequently passed through two consecutive tubes containing an aqueous solution of 0.1 M sodium tetrachloromercurate (HgCl$_2$ (0.1 M) and NaCl (0.2 M)) according to the method of West and Gaeke.[19] Irradiation of the sulfone sample with 16

RPR 2537-Å lamps was conducted for 20 min with constant nitrogen flow which was continued for an additional 30–60 min after the irradiation.

Dilution of the mercurate solution (1:100) and addition of 1 mL of a 0.004% HCl–rosaniline solution and 1 mL of 0.2% formaldehyde to 10 mL of sample was employed to develop the color test. Analysis was carried out after 1 h at 560 nm. The samples were shown to have trapped 13 and 22 μmol (or ca. 10%) of the SO$_2$ produced during the irradiation.

D. Quantum Efficiency Determination. General Procedure. A solution of the sulfone in 15 mL of solvent in a Pyrex tube was degassed with nitrogen and placed in the "merry-go-round" apparatus. Irradiations were carried out using 16 or less, either RPR 2537-Å, RPR 3000-Å or 3500-Å lamps. Light output was monitored by potassium ferrioxalate actinometry, according to the method of Hatchard and Parker.[26]

Quantum efficiencies were measured at different sulfone conversions and were extrapolated to 0% conversion. In the case of sensitized irradiations, the sulfone and sensitizer concentration were adjusted so that the sensitizer absorbed >95% of light at 350 nm and sulfone concentration was high enough to ensure efficient quenching of a sensitizer triplet state. Results are given in Table II.

1-Naphthylmethyl 1-Phenylethyl Sulfone $((\pm)$-11) in Benzene: (a) Direct irradiation, initial sulfone concentration 1.31×10^{-2} M, 6 RPR 3000-Å lamps, light output 2.40 ± 0.06 mE/h. (b) Benzophenone-sensitized irradiation initial sulfone concentration 1.32×10^{-2} M, benzophenone concentration 7.27×10^{-2} M, 6 RPR 3500-Å lamps, light output 1.74 ± 0.03 mE/h. (c) Acetophenone-sensitized irradiation, initial sulfone concentration 1.35×10^{-2} M, acetophenone concentration 0.50 M, 6 RPR 3500-Å lamps, light output 1.74 ± 0.03 mE/h (Table IV).

2-Naphthylmethyl 1-Phenylethyl Sulfone $((\pm)$-12) in Benzene: (a) Direct irradiation, initial sulfone concentration 1.33×10^{-2} M, 6 RPR 3000-Å lamps, light output 2.40 ± 0.06 mE/h. (b) Benzophenone-sensitized irradiation, initial sulfone concentration 1.35×10^{-2} M, benzophenone concentration 5.86×10^{-2} M, 15 RPR 3500-Å lamps, light output 3.37 ± 0.13 mE/h. (c) Acetophenone-sensitized irradiation, initial sulfone concentration 1.38×10^{-2} M, acetophenone concentration 0.45 M, 15 RPR 3500-Å lamps, light output 3.37 ± 0.13 mE/h (Table IV).

1-Phenylethyl Benzyl Sulfone (8) in Benzene. Initial sulfone concentration 3.32×10^{-2} M (in benzene), 4 RPR 2537-Å lamps, light output 1.125 mE/h (Table II).

1-Phenylethyl Benzyl Sulfone (8) in Acetone. Initial sulfone concentration 3.24×10^{-2} M (in acetone), 16 RPR 3000-Å lamps, light output 1.017 mE/h (Table II).

1-(1-Naphthyl)ethyl Benzyl Sulfone (13) in Benzene. Initial sulfone concentration 1.31×10^{-2} M (in benzene), 16 RPR 3000-Å lamps, light output 0.899 mE/h (Table II).

1-(2-Naphthyl)ethyl Benzyl Sulfone (14) in Benzene. Initial sulfone concentration 1.51×10^{-2} M (in benzene), 16 RPR 3000-Å lamps, light output 0.899 mE/h (Table II).

Benzophenone-Sensitized Irradiation of 1-(1-Naphthyl)ethyl Benzyl Sulfone 13. Initial sulfone concentration 1.25×10^{-2} M (in benzene), benzophenone concentration 7.29×10^{-2} M, 15 RPR 3500-Å lamps, light output 1.49 mE/h (Table II).

Benzophenone-Sensitized Irradiation of 1-(2-Naphthyl)ethyl Benzyl Sulfone 14. Initial sulfone concentration 1.21×10^{-2} M (in benzene), benzophenone concentration 7.95×10^{-2} M, 15 RPR 3500-Å lamps, light output 1.49 mE/h (Table II).

E. Emission Spectroscopy. Quenching of Acetophenone and Benzophenone Phosphorescence at Room Temperature. Argon deaerated carbon tetrachloride (spectrograde) solutions of acetophenone or benzophenone were analyzed at room temperature (20 °C) for phosphorescence emission. The deaeration was continued until the phosphorescence reached a constant intensity. For acetophenone, 0.002 M solutions were excited at 345 nm and the full emission was monitored employing the ratio mode of the spectrofluorimeter; for benzophenone, 0.01 M solutions were excited at 385 nm. The spectra obtained were in good agreement with those reported by Saltiel et al.[13a] and by Steel et al.[13b]

The Stern–Volmer quenching of the emission was determined for piperylene, naphthalene, or sulfones **7**, $(\pm)$-**9**, or $(\pm)$-**10** as quenchers. The average value obtained from duplicate experiments and their standard deviations are presented in Table III.

Fluorescence Measurements for Sulfones 9–14. Fluorescence emission spectra were determined in a 1-cm quartz cell with an Aminco-Bowman spectrofluorimeter using the IP 28 photomultiplier with an excitation wavelength of 310 nm. Both benzene and cyclohexane were used as solvents. Samples were deaerated with argon. Before recording the fluorescence emission, the UV spectra of the sulfones were always taken

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(26) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

by using the Cary 14 spectrophotometer. For fluorescence quantum efficiency measurements, the concentrations of naphthalene, as a standard, and of all sulfones were adjusted so that the absorptions of the systems were practically the same at λ_{ex} 310 nm. The measured fluorescence intensities (I_f) at the wavelength corresponding to the maximum of fluorescence were used to calculate the quantum efficiencies (I_f) relative to sulfone **9**. Small variations, in the absorbances values (A) at λ 310 nm were included in the calculation. The quantum yields (Table V) were then calculated according to the following expression:[27]

$$\frac{\Phi_f}{\Phi_f'} = \frac{I_f(1 - 10^{-A'})}{I_f'(1 - 10^{-A})}$$

Fluorescence Decay Time (τ_s). The fluorescence decay times were calculated from the Stern–Volmer relationship for oxygen quenching of the fluorescence emission in cyclohexane[17] according to the following expression:

$$L_o/L = 1 + \tau_s k_q[Q']$$

where L and L_o are the fluorescence intensities with and without air, τ_s is the mean decay time of the deaerated solution, k_q is the quenching rate constant for oxygen, and $[Q']$ is the concentration of dissolved oxygen. The value of $k_q[Q']$ was taken as 6×10^7 s^{-1}.[17] The fluorescence intensity measurements were first obtained with samples deaerated with argon and then repeated after saturation with air, to give the L_o and L values. The results, together with k_f values calculated from the expression $k_f = \phi_f \tau_s^{-1}$, are presented in Table V.

Fluorescence of the Sulfones 8, 13, and 14. The spectra were obtained in EPA (ether:isopentane:ethanol = 5:5:2). The emission maxima were observed at 317 nm for **8** $(\lambda_{ex}$ 254 nm), 348 for **13** $(\lambda_{ex}$ 310 nm), and 343 nm for **14** $(\lambda_{ex}$ 310 nm).

Fluorescence of the Sulfones 7, 9, and 10. The spectra were obtained in cyclohexane at excitation wavelength of 310 nm (Table V).

Phosphorescence of the Sulfones 7, 9, and 10. The phosphorescence spectra were observed in chloroform glass at 77 °C. The emission maxima were found at 468 (onset 405) nm for **7** (broad), 480 nm for **9**, and 475 nm for **10**. (Table VI).

Phosphorescence of the Sulfones 8, 13, and 14. The phosphorescence spectra were observed in EPA glass at 77 K. The emission maxima were found at 410, 433, and 460 nm for **8** $(\lambda_{ex}$ 254 nm), 495, 530, 570, and 620 nm for **13** $(\lambda_{ex}$ 310 nm), and 484, 518, 557, and 602 nm for **14** $(\lambda_{ex}$ 310 nm) (Table VI).

F. CIDNP Investigations. All CIDNP measurements were performed on a Bruker WP 80-MHz FT NMR spectrometer with a ^{1}H probe modified for irradiation of the sample through a lens–fiber optic light pipe arrangement (see Figure 3).

The unfiltered light of a Varian 300 W ElMAC V1X 300 UV Xe–Hg lamp irradiated the sample. The spectra were obtained from Fourier transformations of 5–10 free induction decays recorded at ca. 20°–60° flip angles and 2-s pulse delay.

Approximately 10 mg of the sample to be analyzed was dissolved in 0.5 mL of a deuterated solvent, usually C_6D_6 and placed in either a Pyrex or a quartz NMR tube. Certain additives were used to elucidate the nature of the photochemical mechanism. Tri-*n*-butyltin hydride and bromotrichloromethane were added as radical scavengers. Benzophenone $(E_T = 68.6$ kcal/mol),[16] acetophenone $(E_T = 73.7$ kcal/mol),[16] and xanthone $(E_T = 74.0$ kcal/mol)[16] were added as triplet sensitizers. The results are listed in Table VII and in Figures 1 and 2.

(27) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 800.
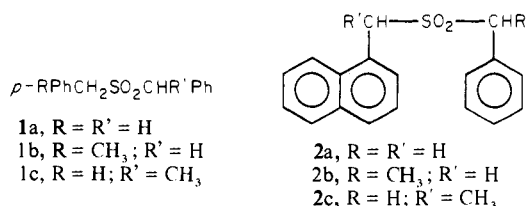
Mechanistic Studies of the Photodecomposition of Arylmethyl Sulfones in Homogeneous and Micellar Solutions

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Abstract: The mechanism of photodecomposition of aryl sulfones has been investigated by using both steady-state and time-resolved techniques. Direct evidence for radical and triplet-state intermediates is provided. A correlation is found between the dynamics of reaction of the intermediate triplet states with the stabilities of the intermediate radicals.

The photoactivity of aryl sulfones was first reported by Cava et al.[1] who found that upon irradiation these compounds efficiently lose molecular sulfur dioxide and yield products typical of radical coupling reactions. The quantum yields for reaction of a series of aryl sulfones have been determined under both direct photolysis and triplet-sensitized reaction conditions.[2] It was found that both the singlet and triplet states of these compounds are photoreactive and that the relative amount of reaction from each state was structure dependent. For example, the photocleavage of dibenzyl sulfone (DBS) **1a** was found to occur both from singlet and triplet states. For the naphthyl benzyl sulfone **2a** reaction was found

p-RPhCH$_2$SO$_2$CHR'Ph

1a, R = R' = H
1b, R = CH$_3$; R' = H
1c, R = H; R' = CH$_3$

R'CH—SO$_2$—CHR

2a, R = R' = H
2b, R = CH$_3$; R' = H
2c, R = H; R' = CH$_3$

to occur mainly from the triplet state; however, for the β-naphthyl sulfone **3a** the singlet state was determined to be the more pho-

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