ylamine. Recrystallization from benzene gave colorless crystals: mp 65–69 °C; IR (KBr) 1692 cm^{-1}; ^{19}F NMR (ether) δ –83.9 (q, 3 F), –124.0 (t, 2 F). Anal. Calcd for C$_3$H$_2$F$_5$NO$_2$: C, 20.12; H, 1.13; F, 53.05; N, 7.82. Found: C, 19.91; H, 1.11; F, 52.87; N, 7.71.

Trifluoroacetohydroxamic acid[3] was prepared in a similar manner from ethyl trifluoroacetate and hydroxylamine. Recrystallization from methylene chloride gave colorless plates: mp 49–51 °C; ^{19}F NMR (ether) δ –75.2 (s). Anal. Calcd for C$_2$H$_2$F$_3$NO$_2$: C, 18.61; H, 1.56; F, 44.14; N, 10.86; Found: C, 19.13; H, 1.62; F, 43.51; N, 10.58.

Methoxycarbonyl 2,2,3,3,4,4,4-Heptafluoro-*N*-hydroxybutanimidate (3). Methanol (18 mL, 0.43 mol) was added dropwise to 54.5 g (0.21 mol) of **1b** cooled in a water bath to keep the temperature below 40 °C. The reaction mixture was evaporated to dryness under reduced pressure, and the resulting solid was collected on a filter and washed with hexane to give 51.13 g (85%) of **3** as colorless crystals: mp 42–43 °C; ^{19}F NMR (CDCl$_3$) δ –82.2 (t, J = 9 Hz, 3 F), –121.4 (m, 2 F), –127.5 (m, 2 F); ^{1}H NMR (CDCl$_3$) δ 3.96 (s, 3 H), 9.8 (NOH). Anal. Calcd for C$_6$H$_4$F$_7$NO$_4$: C, 25.10; H, 1.40; F, 46.33; N, 4.88; Found: C, 25.24; H, 1.48; F, 46.46; N, 4.98.

Registry No. **1a**, 87050-94-0; **1b**, 87050-95-1; **1c**, 87050-97-3; **2** (R$_f$ = CF$_3$), 1514-45-0; **2** (R$_f$ = CF$_3$(CF$_2$)$_2$), 87050-96-2; **2** (R$_f$ = CF$_3$(CF$_2$)$_6$), 15435-88-8; **2** (R$_f$ = CF$_3$CF$_2$), 87051-00-1; **3**, 87051-03-4; **5a**, 460-49-1; **5b**, 424-62-4; **5c**, 335-91-1; **6a**, 87050-98-4; **6b**, 87050-99-5; **6c**, 87051-01-2; **7**, 87051-02-3; COCl$_2$, 75-44-5; SOCl$_2$, 7719-09-7; CF$_3$CF$_2$CN, 422-04-8; CF$_3$CF$_2$NCO, 356-74-1; CF$_3$COCl, 354-34-7; PCl$_5$, 10026-13-8; CF$_3$(CF$_2$)$_6$CO$_2$Et, 3108-24-5; CF$_3$-(CF$_2$)$_2$CO$_2$Et, 356-27-4; CF$_3$CF$_2$CO$_2$Et, 426-65-3; CF$_3$CO$_2$Et, 383-63-1.

(3) Knunyants, I. L.; Sokol'skii, G. A. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 602.

Photochemistry of Benzyl Sulfite

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Photoextrusion reactions have been the subject of considerable recent attention. In addition to posing interesting mechanistic questions, photoextrusions are occasionally of preparative value.[1] A functional group that offers the potential for such reactions is the sulfite ester (e.g., benzyl sulfite (1)). Examination of the photochemical literature

PhCH$_2$OS(O)OCH$_2$Ph
1
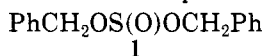
reveals little information regarding sulfite photochemistry. Kobayashi et al. suggested that the photochemical fragmentation of *n*-butyl sulfite occurred via homolysis of the S–O bond.[2] A low-temperature ESR study of several acylic sulfites including **1** reported by Gilbert et al. appears to confirm this suggestion.[3] The photochemistry of cyclic sulfite esters of some 1,2-diols has also been examined, and pathways involving photoextrusion of both SO$_2$ and SO$_3$ have been observed.[4,5] To date, however, no systematic study of the products and mechanism of the photolysis of benzyl sulfite has been reported. We describe here the results of such a study.

(1) For a recent review of photoextrusion reactions, see: Givens, R. S. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 227 ff.
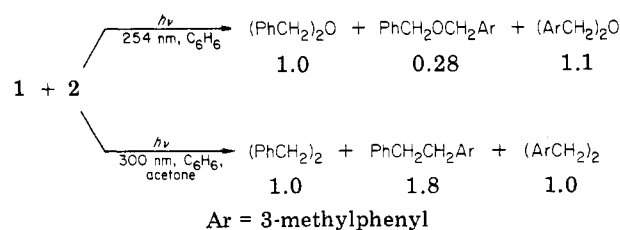(2) Kobayashi, M.; Minato, H.; Miyaji, Y.; Yoshioka, T.; Tanaka, K.; Honda, K. *Bull, Chem. Soc. Jpn.* **1972**, *45*, 2817.
(3) Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *J. Chem. Res., Synop.* **1977**, 173.
(4) Griffin, G. W.; Manmade, A. *J. Org. Chem.* **1972**, *37*, 2589.
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Scheme I

Ar = 3-methylphenyl

Results and Discussion

The UV spectrum of **1** is nearly identical with that of benzyl alcohol, indicating that the benzyl groups are acting as the chromophore. In contrast, aliphatic sulfites are essentially transparent in the near UV[6] region.

The photochemistry of **1** was examined in a variety of aprotic solvents (acetonitrile, benzene, cyclohexane, dioxane, and ethyl acetate). Both direct irradiations (0.095 M, 254 nm) and acetone–sensitized irradiations (0.095 M, 4.5 M acetone, 300 nm) were performed. Results were similar in all solvents, and the outcome in benzene is reported in Table I.

Direct irradiation resulted in the efficient decomposition of **1**; the quantum yield for the disappearance of **1** in cyclohexane was found to be 0.39 ± 0.04 by using potassium ferrioxalate actinometry. Photolysis produced benzyl alcohol, benzyl ether, and the rearrangement product, benzyl phenylmethanesulfonate along with trace amounts of bibenzyl, toluene, and benzaldehyde. Isolation of the rearranged product indicates that at least part of the photochemistry proceeds via C–O bond cleavage and was unexpected on the basis of Kobayashi's work with benzyl *p*-toluenesulfinate.[2] When the reaction was sensitized with acetone, the yield of sulfonate decreased, only a trace of benzyl ether was produced, and bibenzyl emerged as a major product. Of the photoproducts that were observed, only the rearranged product was photolabile, some photodecomposition being observed after prolonged irradiation (>80% conversion of **1**).

A point of interest bearing on the mechanism of the reaction is the magnitude of the solvent-cage effects in the recombination reactions that produce the benzyl ether and bibenzyl. For examination of this, equimolar mixtures of benzyl sulfite and 3-methylbenzyl sulfite (**2**) were irradiated under conditions identical with those above. The benzyl ethers in the direct irradiation and bibenzyls in the sensitized irradiation were separated from the other products by column chromatography, and the product ratios were determined by NMR spectroscopy. The results are shown in Scheme I. The formation of only a minor amount of unsymmetrical ether in the direct irradiation indicates a large cage effect (ca. 85%) in the ether-forming reaction. The nearly statistical distribution of bibenzyls obtained in the sensitized reaction is consistent with recombination after escape from the solvent cage and argues against the extrusion of SO$_3$.

A final point that must be considered is the high yield of benzyl alcohol obtained under both direct and sensitized irradiation conditions. A similar results was reported by Kobayashi in the direct irradiation of *n*-butyl sulfite.[2] A possible route to benzyl alcohol involves cleavage of the S–O bond followed by extrusion of SO. Hydrogen abstraction by the resulting benzyloxy radicals could produce benzyl alcohol. Precedent for a sulfinyl photoextrusion

(6) "Atlas of Spectral Data and Physical Constants for Organic Compounds", 2nd Ed.; Grasselli, J. G., Ritchey, W. M., Eds.; CRC Press, Cleveland, 1975; Vol. IV, p 575.

Notes

Table I. Products of the Photolysis of Benzyl Sulfite in Benzene

conditions	conversion, %	product, mol/mol of sulfite			
		PhCH$_2$OH	PhCH$_2$SO$_3$CH$_2$Ph	(PhCH$_2$)$_2$O	(PhCH$_2$)$_2$
direct	54	0.48	0.30	0.20	trace
acetone sensitized	68	0.68	0.09	trace	0.32

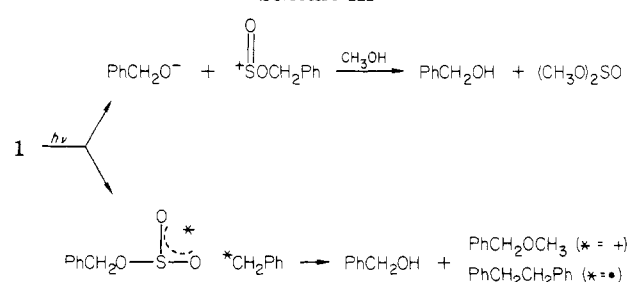### Table II. Products of the Photolysis of Benzyl Sulfite in Methanol

conditions	conversion, %	product, mol/mol of sulfite			
		PhCH$_2$OH	PhCH$_2$OCH$_3$	(PhCH$_2$)$_2$	(CH$_3$O)$_2$SO
direct	100	1.4	0.17	0	0.40
acetone sensitized	94	0.71	trace	0.21	0.11

Scheme II
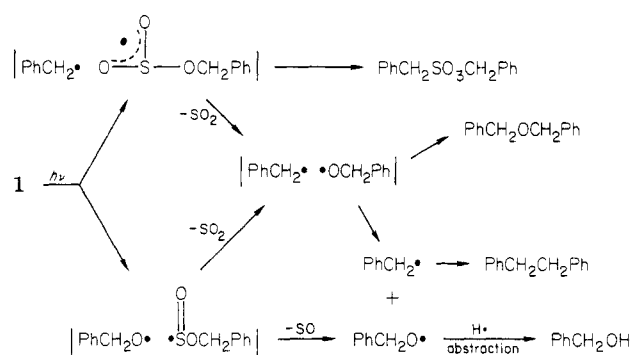
Scheme III

has been reported,[7] and partial evidence for a radical abstraction pathway was obtained when direct irradiations of 1 and 2 were performed with toluene as a cosolvent. In both cases, bibenzyl appeared as a significant product (approximately 32% of theoretical), suggesting that H-atom abstraction from the toluene is occurring. In view of our inability to detect products resulting from the reactions of benzyloxy radicals with benzene (biphenyl, benzyl phenyl ether), however, this mechanism must be considered as tentative. This pathway, along with a C–O cleavage process necessary to account for sulfonate formation, is presented in Scheme II. We propose that direct irradiation yields singlet radical pairs, giving the observed cage recombination products as well as benzyl alcohol via SO extrusion. Sensitized irradiation gives triplet radical pairs, most of which escape from the solvent cage to yield benzyl alcohol and bibenzyl.

In methanol, the photochemistry of 1 is altered dramatically. The disappearance quantum yield increases to 0.74, and the products that are obtained suggest competition between ionic and free-radical pathways (Table II). Both S–O and C–O cleavage processes are indicated. Direct irradiation affords benzyl alcohol and methyl sulfite as major products along with some benzyl methyl ether. These products could form from ion pairs generated by cleavage of both S–O and C–O bonds. Under acetone-sensitized conditions only a trace of benzyl methyl ether is formed, and bibenzyl appears as a significant product, indicating homolytic C–O cleavage. We propose the mechanism outlined in Scheme III.

In summary, our experiments indicate that benzyl sulfite can undergo photochemical fragmentation by both S–O and C–O bond cleavage. Both homolysis and heterolysis may occur in these reactions, and the partitioning between these pathways is highly multiplicity and solvent dependent.

Experimental Section

Benzyl sulfite and 3-methylbenzyl sulfite were prepared by the method of Theobald et al.[8] NMR spectra were recorded on a

Varian T-60 spectrometer with Me$_4$Si as an internal standard. IR spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. UV spectra were recorded on a Beckman Model DU-8 spectrophotometer. All solvents were reagent grade and were fractionally distilled and stored over molecular seives prior to use. Acetone was fractionally distilled from potassium permanganate.

Irradiations were performed with a Rayonet RPR-100 photochemical reactor equipped with either 8 RPR 2537-Å (direct irradiations) or 8 RPR 3000-Å (sensitized irradiations) lamps.

General Procedure. A solution of 0.15 g (0.57 mmol) of 1 in 6 mL of solvent in an oven-dried 12 × 100 mm quartz tube was sparged with nitrogen for 0.5 h. The solution was then irradiated for either 5 h (direct irradiations) or 10 h (sensitized irradiations). The solvent was evaporated, and the products were analyzed by NMR and/or GC and separated by preparative TLC (silica gel) or column chromatography (alumina). Benzyl alcohol, benzyl ether, and bibenzyl were identified by comparison of spectral data and chromatographic behavior with commercial samples. Benzyl phenylmethanesulfonate, benzyl methyl ether, and methyl sulfite were identified by comparison with samples prepared by literature procedures.[9–11]

Quantum Yields. Quantum yields were measured with potassium ferrioxalate actinometry.[12] Disappearance of starting material was followed by NMR with p-dimethoxybenzene as an internal standard. Conversions were held below ca. 20%, and the result reported was the average of three runs extrapolated to 0% conversion.

Mixed Photolyses. A solution of 0.91 g (3.5 mmol) of 1 and 1.0 g (3.5 mmol) of 2 in 50 mL of solvent was irradiated in the usual way. The mixture of ethers in the direct irradiation and bibenzyls in the sensitized irradiation was isolated by column chromatography (alumina, 0–5% ether/petroleum ether) and analyzed by NMR. In the case of the ethers, Eu(fod)$_3$ was added to separate the benzylic methylene singlets.

Registry No. Benzyl sulfite, 35506-85-5.

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(8) Theobald, J. M.; Williams, M. W.; Young, G. T. J. Chem. Soc. 1963, 1927.
(9) King, J. F.; Lewars, E. G.; Danks, L. J. Can. J. Chem. 1972, 50, 866.
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(12) Hatchard, T. C.; Parker, C. A. Proc. R. Soc. London, Ser. A. 1956, 235, 518.