

by monitoring the growth in absorption of the peak at ~ 370 nm. Fluorescence spectra were measured with an excitation wavelength of 370 nm and scanned between 450 and 700 nm. The extent of cation formation was calculated either from the area under the fluorescence curve or from the height of the peak. Both methods of calculation gave identical results.

Acknowledgment. The continued financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We are also grateful to NSERC for

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Registry No. 1, 90-46-0; 1 cation, 261-23-4; 2, 5569-25-5; 2 cation, 46406-21-7; 3, 101169-00-0; 3 cation, 135074-99-6; 4, 4127-29-1; 4 cation, 135075-00-2; 5, 35666-57-0; 5 cation, 135075-01-3; 6, 596-38-3; 6 cation, 20460-07-5; 7, 112305-07-4; 7 cation, 112305-04-1; 8, 29903-57-9; 8 cation, 112304-98-0; 9, 29903-56-8; 9 cation, 119681-16-2; 10, 94465-25-5; 10 cation, 112305-00-7; 11, 42960-05-4; 11 cation, 119681-18-4.

Photochemistry of Phenyl Thioethers and Phenyl Selenoethers. Radical vs Ionic Behavior

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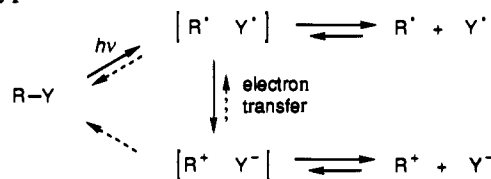
Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290. Received December 5, 1990.

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Abstract: In analogy with alkyl iodides and bromides, the phenyl thio- and selenoethers **2a,b**, **13a**, **21b,c** and **35** displayed competing radical and ionic photobehavior on irradiation in solution, via a mechanism thought to involve initial homolytic cleavage of the alkyl C-S or C-Se bond followed by electron transfer within the resulting radical pair cage (Scheme I). These are the first examples of ionic photobehavior to be recognized for the C-SAr and C-SeAr chromophores. The electronegatively substituted pentafluorophenyl analogues **2c**, **13b**, and **21d** displayed enhanced ionic photobehavior. By contrast, the 4-methoxyphenyl derivative **21a** exhibited almost exclusively radical behavior. The sulfoxide ($2R^*,R^*_S$)-**21f** displayed principally radical behavior, accompanied by epimerization at sulfur. The quantum yields for the disappearance of the 2-norbornyl ethers **21b** and **21c** were 0.53–0.64 in solution and rose to 0.89–0.95 in the presence of suspended fumed silica. Irradiation of the phenyl thioether **21b** on silica gel resulted in nucleophilic trapping by surface silanol groups to afford covalently bound material (**33**), which afforded chloride **34** on treatment with SOCl_2 . Irradiation of phenyl thioethers **2a** and **35**, phenyl selenoether **2b**, or $\text{C}_6\text{H}_5\text{SH}$ in allyl alcohol solution afforded acetal **11**, apparently via isomerization of some of the solvent to propanal (**44**) followed by acetalization. Irradiation of alcoholic solutions of aldehydes containing $\text{C}_6\text{H}_5\text{SH}$ is a useful means of generating acetals under neutral conditions.

Extensive studies from these laboratories and those of others have shown that alkyl iodides and bromides, which had traditionally been thought to exhibit only radical photobehavior,¹ in fact afford mixtures of radical and ionic products on irradiation in solution.^{2,3} We have proposed that the latter products arise via a previously unrecognized electron transfer within an initially formed radical pair cage (Scheme I, $\text{Y} = \text{I}$).⁴ This photobehavior is of both synthetic and mechanistic interest. Synthetically, it has proven to be a convenient and powerful method for the generation of a wide variety of carbocations, including many that are not readily available by classical, ground-state procedures, such as bridgehead cations,⁵ the 7-norbornyl cation,⁶ and small-ring cyclic and α -unsubstituted vinyl cations.⁷ Mechanistically, it represents one of the first, and most general, examples of electron transfer

Scheme I



within a radical pair to be recognized.^{4,8} We wish now to extend our studies to two additional systems that have traditionally been thought to exhibit only radical photobehavior, the C-SAr and C-SeAr chromophores.^{9,10}

(1) See, for example: (a) Steacie, E. W. R. *Atomic and Free Radical Reactions*, 2nd ed.; Reinhold: New York, 1958. (b) Majer, J. R.; Simons, J. P. *Adv. Photochem.* **1967**, *2*, 137–181. (c) Sammes, P. G. In *Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; Wiley: London, 1973; Chapter 11.

(2) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131–137.

(3) For a review of the photobehavior of alkyl halides in solution, see: Lodder, G. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: London, 1983; Chapter 29.

(4) Poindexter, G. S.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7142–7143.

(5) (a) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135–8144. (b) Kropp, P. J.; Worsham, P. R.; Davidson, R. I.; Jones, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 3972–3980. (c) Reddy, D. S.; Sollott, G. P.; Eaton, P. E. *J. Org. Chem.* **1989**, *54*, 722–723.

(6) Kropp, P. J.; Davidson, R. I.; Tise, F. P.; McCraw, G. L.; Underwood, G. A. Manuscript in preparation.

(7) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907–6915.

(8) For subsequent demonstrations of electron transfer within radical pairs, see: (a) Pokhodenko, V. D.; Khizhnyi, V. A.; Koshechko, V. G.; Samarskii, V. A. *Theor. Exp. Chem. (Engl. Transl.)* **1975**, *11*, 489–493; *Teor. Eksp. Khim.* **1975**, *11*, 579–584. (b) Pokhodenko, V. D.; Khizhnyi, V. A.; Samarskii, V. A. *Theor. Exp. Chem. (Engl. Transl.)* **1975**, *11*, 564–567; *Teor. Eksp. Khim.* **1975**, *11*, 674–678. (c) Lawler, R. G.; Barbara, P. F.; Jacobs, D. J. *Am. Chem. Soc.* **1978**, *100*, 4912–4914. (d) Arnett, E. M.; Molter, K. E.; Marchot, E. C.; Donovan, W. H.; Smith, P. J. *Am. Chem. Soc.* **1987**, *109*, 3788–3789. (e) Lee, S.-G. *J. Chem. Soc., Chem. Commun.* **1987**, 1115–1117. (f) DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948–8950.

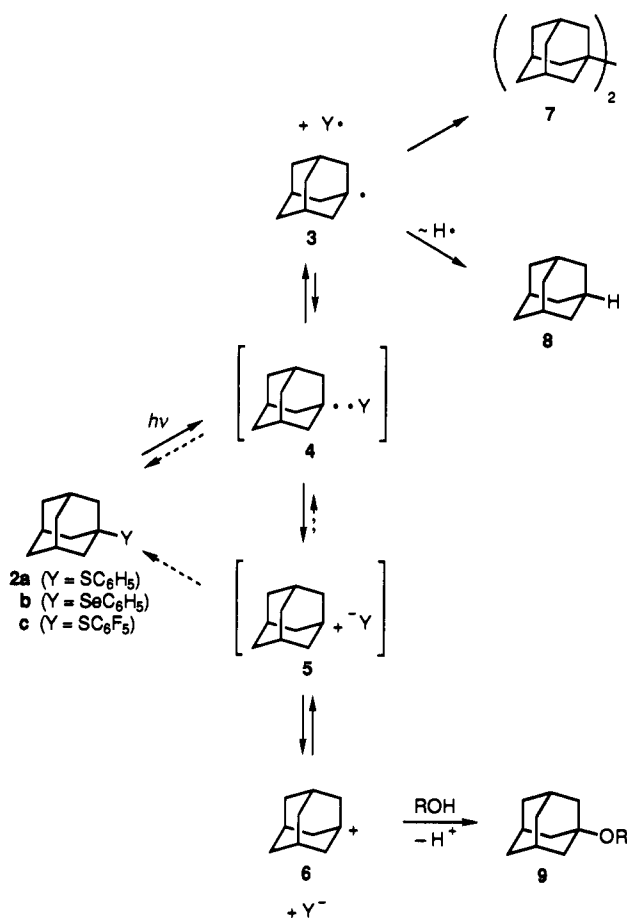
(9) For a review of the photochemistry of organosulfur compounds, see: (a) Block, E. *Q. Rep. Sulfur Chem.* **1969**, *4*, 237–351. (b) Dürr, H. In *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Georg Thieme: Stuttgart, 1975; Teil IV/5b, pp 1008–1076. (c) von Sonntag, C.; Schuchmann, H.-P. In *Supplement E. The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: Chichester, U.K., 1980; Part 2, Chapter 22. (d) Still, I. W. J. In *Organic Sulfur Chemistry*; Bernardi, F.; Csizmadia, I. G.; Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 11. (e) Still, I. W. J. In *The Chemistry of Sulphones and Sulfoxides*; Patai, S.; Rappoport, Z.; Stirling, C., Eds.; Wiley: Chichester, U.K., 1988; Chapter 18.

Table I. Irradiation of 1-Adamantyl Ethers 2a-c^a

2	Y	solvent	time, h	yield, % ^b				9/8	R
				2	8	9	10		
2a	SC ₆ H ₅	CH ₃ OH	32	36	26	21	c	0.8	CH ₃
		CH ₃ OH ^d	16	27	3	21	13	7	CH ₃
		CH ₂ =CHCH ₂ OH	16	17	21	17	c,e	0.8	CH ₂ CH=CH ₂
2b	SeC ₆ H ₅	CH ₃ OH	56	15	11	34	30 ^f	3.2	CH ₃
		CH ₂ =CHCH ₂ OH	32	37	5	16	36 ^{e,f}	3.2	CH ₂ CH=CH ₂
2c	SC ₆ F ₅	CH ₃ OH	12	13	1	60 ^g	60		CH ₃

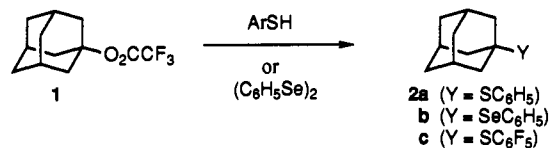
^a Conducted according to the standard small-scale procedure described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. Benzene or pentafluorobenzene, elemental sulfur or selenium, and 1,1'-biadamantane (7) were also obtained in varying amounts. ^c Trace. Diphenyl disulfide was also obtained. ^d 0.2 N NaOCH₃. ^e Acetal II was also obtained. ^f Diphenyl diselenide was also obtained. ^g (C₆F₅S)₂ was also obtained.

Scheme II



Results

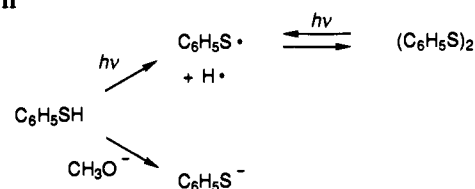
1-Adamantyl Ethers 2. Phenylalkyl thio- and selenoethers were chosen for study both to provide an easy means for the introduction of light through the phenyl absorption at 254 nm and to simplify product composition by limiting cleavage to the more easily broken alkyl-S or alkyl-Se bond. Initial studies involved the 1-adamantyl derivatives 2a-c, which are prepared from the trifluoroacetate 1.



As seen in Table I, irradiation of these ethers in methanol or allyl

(10) For a review of the photochemistry of organoselenium compounds, see: (a) Martens, J.; Praefcke, K. *J. Organomet. Chem.* 1980, 198, 321-351. (b) Goldschmidt, Z. In *The Chemistry of Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1987; Vol. 2, Chapter 5. (c) For an additional report on the photobehavior of several selenoethers, see: Windle, J. J.; Wiersema, A. K.; Tappel, A. L. *J. Chem. Phys.* 1964, 41, 1996-2002.

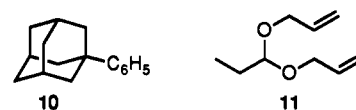
Scheme III

Table II. Irradiation of 2-Adamantyl Ethers 13a,b^a

13	Y	solvent	time, h	yield, % ^b			
				13	8	18	19
13a	SC ₆ H ₅	CH ₃ OH ^c	8	45	42	3	1
13a	SC ₆ H ₅	CH ₃ OH ^d	32	51	4	6	3 ^e
13b	SC ₆ F ₅	CH ₃ OH	32	17	20	18	21
13b	SC ₆ F ₅	CH ₃ OH ^d	12	20 ^f	14	10	6

^a Conducted according to the standard small-scale procedure described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. Benzene or pentafluorobenzene and elemental sulfur were also obtained in varying amounts. ^c Contained 20% 1,2-dimethoxyethane. ^d 0.2 N NaOCH₃. ^e Diphenyl disulfide was also obtained. ^f Thioether 13c (42% yield) and tetrafluorobenzene were also obtained.

alcohol solution afforded a mixture of the reduction product adamantane (8) and the nucleophilic substitution product 9 (R = CH₃ or CH₂CH=CH₂), which apparently arose via competing radical and ionic pathways (Scheme II).^{11,12} The ratio of ionic product 9 (R = CH₃) to radical product 8 obtained in methanol increased on going from the phenyl thioether 2a to the phenyl seleno analogue 2b, and then to the pentafluorophenyl thioether 2c. For either the thioether 2a or the selenoether 2b, the ratio of ionic product 9 to radical product 8 was the same in methanol as in the less nucleophilic solvent allyl alcohol, as expected for a mechanism in which the formation of ether 9 involves nucleophilic trapping of the 1-adamantyl cation (6). Varying amounts of 1-phenyladamantane (10), in which elemental sulfur or selenium had been extruded, were obtained from the phenyl ethers 2a,b, and in allyl alcohol the acetal 11 was formed as a byproduct. The

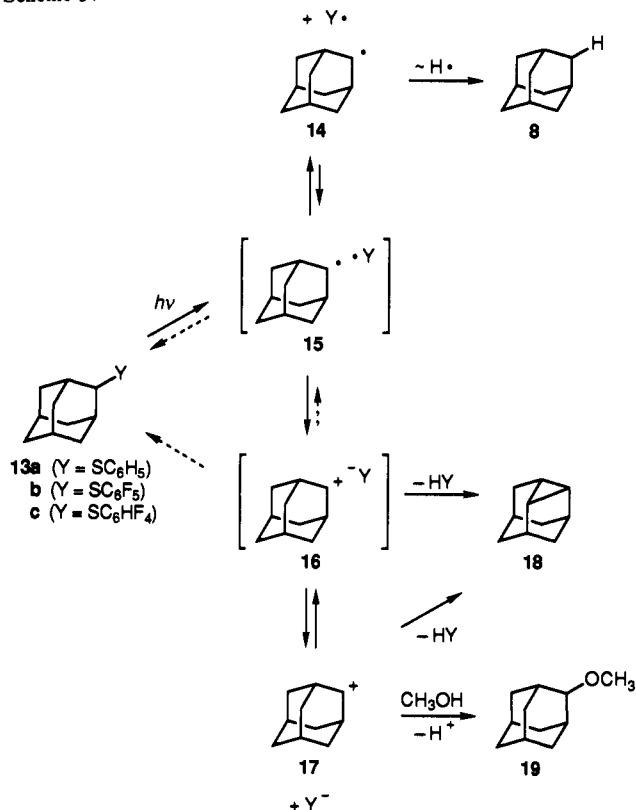


origin of these products is discussed below. Irradiation of phenyl thioether 2a in methanol was sluggish, due in part to blockage of the light by a precipitate of diphenyl disulfide. This product, which arises from secondary photolysis of the byproduct C₆H₅SH (Scheme III),¹³ could be eliminated by the use of a base scavenger.

(11) Also obtained was the radical coupling product 1,1'-biadamantane (7), which precipitated from solution and could not be readily analyzed.

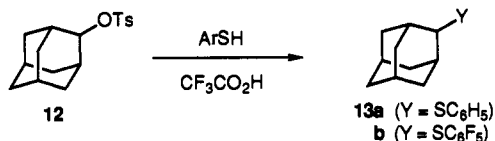
(12) Irradiation of thioether 2a in CH₃OD afforded ether 9 (R = CH₃) having no detectable C-D stretching absorption in the IR. Thus it does not arise via addition of methanol to a highly strained elimination product such as adamantene or 1,3-dehydroadamantane.

Scheme IV



In the absence of the strong hydrogen-atom donor C₆H₅SH, less of the reduction product adamantane (**8**) was also formed.

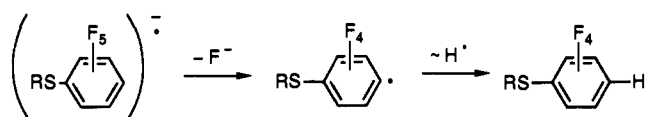
2-Adamantyl Ethers 13. The 2-adamantyl analogues **13a,b** were prepared from the corresponding tosylate **12**. On irradiation in methanol, thioethers **13a,b** slowly afforded a mixture of the reduction product adamantane (**8**) and the ionic products **18** and **19** (Table II), which apparently arose as shown in Scheme IV.¹⁴



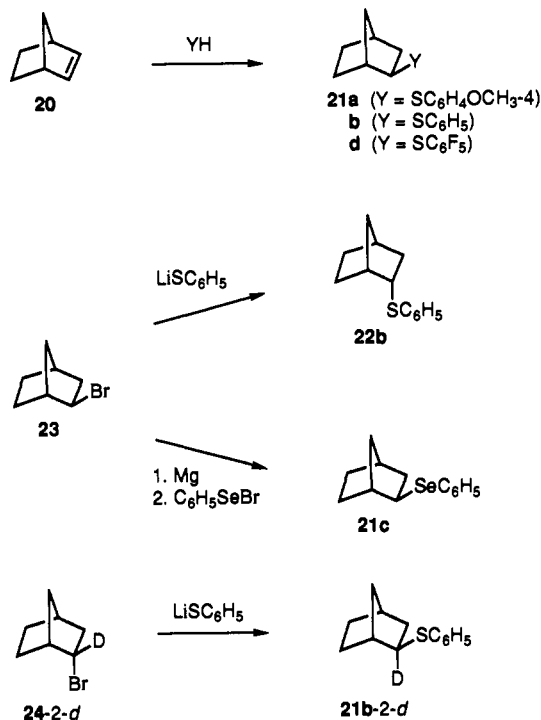
There is ample precedent for formation of the 1,3-elimination product **18** from the 2-adamantyl cation,¹⁵ but apparently none from the corresponding radical. In keeping with the greater ionization potential of the secondary 2-adamantyl radical,¹⁶ **13a,b** showed a lower degree of ionic behavior than their 1-adamantyl counterparts **2a** and **2c**. As expected, the pentafluoro derivative **13b** displayed a greater degree of ionic behavior than the phenyl analogue **13a**. Addition of sodium methoxide as a scavenger for the byproduct C₆H₅SH greatly reduced the formation of the reduction product adamantane (**8**) from **13a**. However, similar use of base with the pentafluoro derivative **13b** resulted in the formation of significant amounts of a tetrafluoro derivative (**13c**) that, as seen from the ¹H-¹⁹F coupling pattern in its ¹H NMR spectrum, had clearly lost the para fluorine atom. The loss of fluorine, which occurs in the absence of light, apparently follows initial electron transfer from the base (Scheme V).

2-Norbornyl Ethers 21a-e and 22b. Another secondary system studied was the 2-norbornyl. The exo thioethers **21a,b** and **21d**

Scheme V



were prepared by light-initiated addition of the corresponding thiol to 2-norbornene (**20**), and the seleno analogue **21c** by Grignard addition to benzeneselenenyl bromide. The endo phenylthio derivative **22b** was obtained by nucleophilic displacement on bromide **23**, and the deuterated derivative **21b-2-d** by displacement on the labeled bromide **24-2-d**.



Irradiation of the epimeric phenyl thioethers **21b** and **22b** afforded a mixture of the reduction product norbornane (**30**) and the 1,2- and 1,3-elimination products 2-norbornene (**20**) and nortricyclene (**31**) (Table III). Norbornane (**30**) was a major, if not the predominate, product in hydrocarbon solvents and in CH₂Cl₂, but was formed only in low yield in methanol containing sodium methoxide as a scavenger for C₆H₅SH. There was no detectable formation of **30** in the viscous solvent 1,2-ethanediol containing scavenger. Small amounts of nortricyclene (**31**) were formed under all conditions. The seleno analogue **21c** gave substantially higher yields of 2-norbornene (**20**) and lower yields of norbornane (**30**) under similar conditions. When either phenyl thioether **21b** or **22b** was irradiated to partial conversion, the recovered thioether was found to have undergone partial epimerization.

The products are presumably formed as shown in Scheme VI. The reduction product norbornane (**30**) clearly arises via abstraction of a hydrogen atom from the solvent or C₆H₅SH by the 2-norbornyl radical (**25**), whereas the 1,3-elimination product nortricyclene (**31**) is certainly ionic, originating from either the ion pair **27** or the 2-norbornyl cation (**28**).^{17,18} The origin of the 1,2-elimination product 2-norbornene (**20**) is less obvious, since it might arise via either hydrogen-atom transfer within the radical

(13) Fehér, T.; Gladden, T.; Kurz, D. *Z. Naturforsch. B* 1970, 25, 1215-1219.

(14) Phenyl thioether **13a** also afforded small amounts of a product having a retention time corresponding to the extrusion product 2-phenyladamantane.

(15) Sinnott, M. L.; Storesund, H. J.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* 1969, 1000-1001.

(16) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1986, 108, 2162-2169.

(17) Alternative generation of nortricyclene (**31**) via hydrogen-atom transfer from the 2-norbornyl radical (**25**) or within the radical pair **26** should be minor compared with formation of 2-norbornene (**20**) from these intermediates. For example, 1,2 elimination predominated over 1,3 elimination in the thermal decomposition of 2-methyl-2-norbornyl peroxy esters in cumene by ratios of 15-19:1; see ref 18.

(18) Bartlett, P. D.; Fickes, G. N.; Haupt, F. C.; Helgeson, R. *Acc. Chem. Res.* 1970, 3, 177-185.

Table III. Irradiation of 2-Norbornyl Ethers **21a-d** and **22b**^a

ether	Y	solvent	time, h	yield, % ^b			
				ether	30	20	31
21a	SC ₆ H ₄ OCH ₃	CH ₃ OH ^c	6	20	11	59	d,e
21b	SC ₆ H ₅	C ₉ H ₂₀	4	12	40	33	10
		C ₆ H ₁₂	4	23	29	35	6
		CH ₂ Cl ₂	4	19	42	24	9
		CH ₃ OH ^{c,f}	1	44	3	40	5
			2	17	4	58	8
		CH ₃ OH ^{c,g}	4	41 ^h	4	48	5
		(CH ₂ OH) ₂ ^{c,i}	8	12		42	14
		^j	16	1	2		2
		CH ₂ Cl ₂	4	5	47	4	15
		CH ₃ OH ^{c,f}	1	55	3	36	8
22b	SC ₆ H ₅		2	24	4	52	12
		CH ₃ OH ^{c,g}	6	33 ^k	7	48	9
		CH ₂ Cl ₂	4	14	18	44	10
21c ^l	SeC ₆ H ₅	CH ₃ OH ^c	4	18		62	7

^a Conducted at 254 nm according to the standard small-scale procedure described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. Benzene or anisole, elemental sulfur or selenium, and diphenyl disulfide or diselenide were also obtained in varying amounts. ^c 0.2 N NaOCH₃. ^d Trace. ^e Dimer **29** was also obtained in 8% yield. ^f Average of two runs. ^g Conducted according to the standard preparative-scale procedure described in the Experimental Section. ^h ¹H NMR analysis of recovered material showed it to be 84% **21b** and 16% **22b**. ⁱ Contained 10% 1,2-dimethoxyethane. ^j Adsorbed to dry silica gel. Chloride **34** was obtained in 61% yield by treatment of the silica gel with SOCl₂ after irradiation. ^k ¹H NMR analysis of recovered material showed it to be 24% **21b** and 76% **22b**. ^l Contained 18% **22c**.

Table IV. Isotopic Compositions and Deuterium Distributions in Thioether **21b-2-d** and Photoproducts^a

21b				30			20			31	
1	2x	2n	(%) ^b	1	2x	2n	1	2	(%) ^b	1,2,6	3
0	6	94	(0)	0	8	92	1	99	(2)	97	3
	(100% D ₁)				(100% D ₁)			(99% D ₁ , 1% D ₀)		(97% D ₁ , 3% D ₀)	

^a Irradiation was conducted according to the preparative procedure outlined in the Experimental Section. Deuterium distributions were determined by ¹H and ²H NMR analysis and isotopic compositions by mass spectral analysis. ^b Percent scrambling between C-1 and C-2.

pair **26** or proton transfer within the ion pair **27**.

Further insight was gained from irradiation of the labeled derivative **21b-2-d** (Table IV). The resulting reduction product norbornane (**30**) was formed with deuterium predominantly in the 2-endo position, as expected for preferential transfer of a hydrogen atom to the exo side of the 2-norbornyl radical (**25**).¹⁹ The 1,2-elimination product 2-norbornene (**20**) was formed with only 2% of the scrambling between C-1 and C-2 that is characteristic of the 2-norbornyl cation. Thus **20** is formed principally from the radical pair **26** rather than the ion pair **27**. Due to symmetry, scrambling between C-1 and C-2 in the 1,3-elimination product nortricyclene (**31**) could not be detected. There was, however, some detectable scrambling of deuterium to C-3, as expected from its formation from the 2-norbornyl cation.²⁰⁻²²

Irradiation of a dry suspension of thioether **21b** on silica gel followed by extraction with CH₂Cl₂ afforded only small amounts of recovered thioether **21b** and the photoproducts norbornane (**30**) and nortricyclene (**31**). However, treatment of the extracted silica gel with SOCl₂ as a source of HCl²³ afforded chloride **34** in 70% yield. Apparently irradiation under these conditions afforded the 2-norbornyl cation (**28**), which was trapped nucleophilically by silanol groups on the silica surface (**33**).²⁴

(19) In contrast with the 2-norbornyl cation (**28**), which undergoes almost exclusive reaction from the exo face, the 2-norbornyl radical (**25**) has only a moderate preference for reacting in atom-transfer reactions from the exo face, with the degree of selectivity dependent on the atom donor involved; see ref 18.

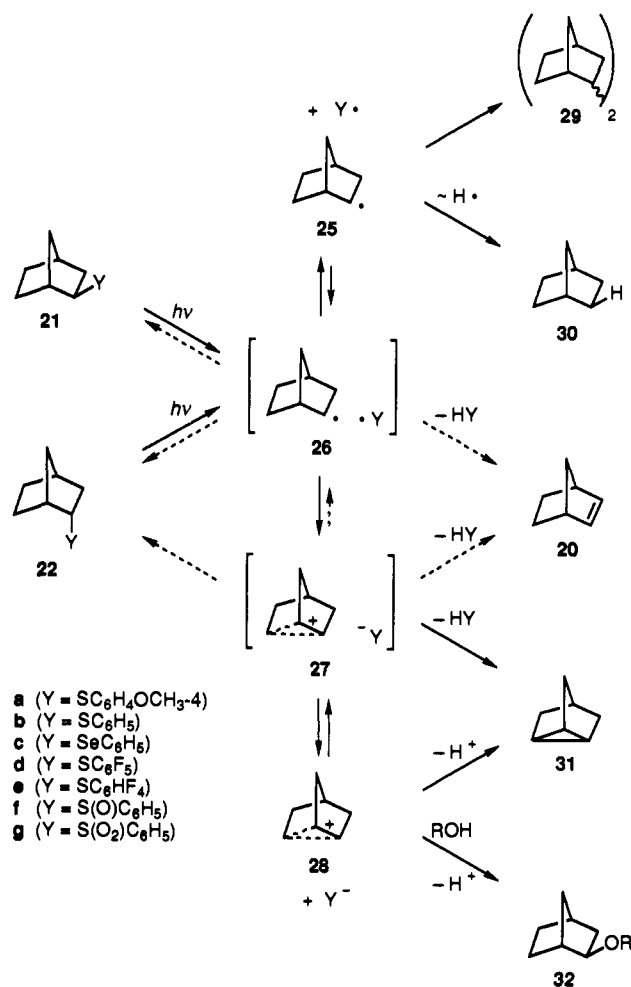
(20) The 2-norbornyl cation undergoes a 3,2 hydride shift with a rate of $2.5 \times 10^4 \text{ s}^{-1}$ at 25 °C; see ref 21.

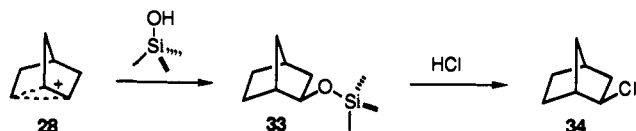
(21) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627-4640.

(22) The lack of any significant loss of deuterium in the formation of nortricyclene (**31**) indicates that it is not formed via a carbene intermediate arising from α elimination of C₆H₅SH. See: Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* **1984**, *49*, 1583-1589.

(23) For the reaction of thionyl chloride with silica surfaces, see: (a) Kropp, P. J.; Daus, K. A.; Crawford, S. D.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P. *J. Am. Chem. Soc.* **1990**, *112*, 7433-7434. (b) Kamitori, Y.; Hojo, M.; Masuda, R.; Kimura, T.; Yoshida, T. *J. Org. Chem.* **1986**, *51*, 1427-1431.

Scheme VI



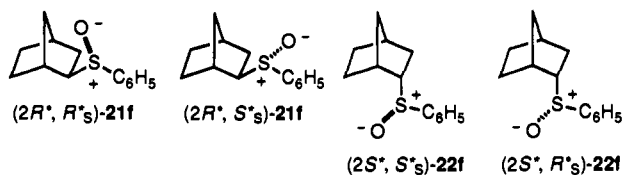


The effect of the electronegativity of the phenylthiyl group Y on the formation of ionic photoproducts was examined by studying the 4-methoxy and pentafluoro derivatives **21a** and **21d**. The 4-methoxy derivative **21a** afforded substantial amounts of the radical-derived products **20**, **29** and **30**, but only a trace of the ionic product nortricyclene (**31**). The electron-releasing 4-methoxy substituent apparently inhibits electron transfer.

By contrast, irradiation of the electronegatively substituted pentafluoro derivative **21d** in methanol afforded nortricyclene (**31**) in substantially higher yield than the unsubstituted phenyl thioether **21b** gave, along with some of the nucleophilic trapping product **32** (R = CH₃) (Table V). Thus the highly electronegative pentafluoro substitution apparently facilitates electron transfer. There was, however, competing disappearance of 2-norbornene (**20**) due to readdition of the byproduct C₆F₅SH. The use of sodium methoxide as a scavenger circumvented the disappearance of 2-norbornene (**20**), but was accompanied by competing conversion of the starting thioether **21d** to the tetrafluoro derivative **21e**, as had been observed previously with the 2-adamantyl analogue **13b**. Competing defluorination occurred to a lesser extent with ammonium hydroxide as the scavenger, which is a highly effective scavenger for irradiation of the corresponding bromide **23**,²⁵ but there was still some disappearance of 2-norbornene (**20**). The best compromise between minimal loss of fluorine and adequate scavenging was achieved using potassium *tert*-butoxide in *tert*-butyl alcohol as solvent.

Quantum Yields. Phenyl thioether **21b** and the phenyl selenoether **21c** underwent conversion to products in CH₂Cl₂ solution with quantum yields of 0.5–0.6 (Table VI). In gels of the same solvent containing fumed silica, the efficiencies dramatically increased to nearly unity.

2-Norbornyl Sulfoxides 21f. For a comparison of the ability of the more electronegative phenylsulfinyl group to undergo electron transfer, the photobehavior of the corresponding sulfoxides **21f** was studied. Oxidation of thioether **21b** afforded sulfoxide (2*R*^{*},*R*^{*}_S)-**21f** accompanied by the diastereomer (2*R*^{*},*S*^{*}_S)-**21f**.²⁶ Irradiation of the 2*R*^{*},*R*^{*}_S isomer in THF resulted in rapid epimerization about sulfur to give an approximately 0.7:1 photoequilibrium mixture of the 2*R*^{*},*R*^{*}_S and 2*R*^{*},*S*^{*}_S sulfoxides (Table VII).²⁷ Some competing epimerization about C-2 also occurred, as was observed for thioether **21b**, to give small amounts of the endo sulfoxides (2*S*^{*},*S*^{*}_S)- and (2*S*^{*},*R*^{*}_S)-**22f**. In addition, a



minor amount of disproportionation to the thioether **21b** and sulfone **21g** also occurred, along with the formation of norbornane (**30**) and 2-norbornene (**20**). Similar behavior was observed on

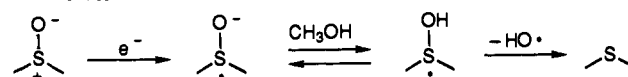
(24) For another recent example of nucleophilic trapping of a reactive intermediate by a silica surface, see: Quin, L. D.; Wu, X.-P. *Tetrahedron Lett.* **1990**, *31*, 6281–6282.

(25) Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709–2717.

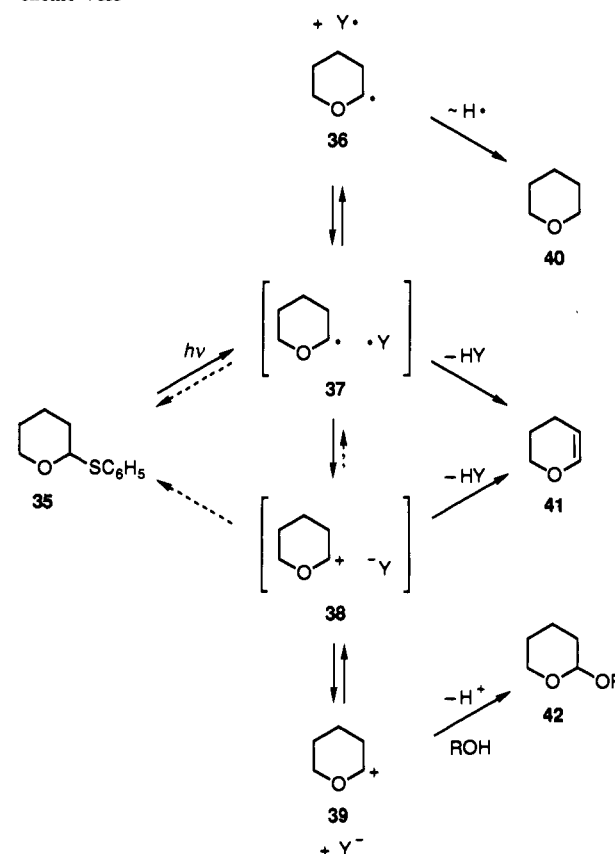
(26) The relative configurational assignments are based on the downfield shift of CH-1 in the 2*R*^{*},*R*^{*}_S isomer (δ 2.87) relative to the 2*R*^{*},*S*^{*}_S isomer (δ 2.52) induced by the adjacent oxygen atom: Goodridge, R. J.; Hambley, T. W.; Haynes, R. K.; Ridley, D. D. *J. Org. Chem.* **1988**, *53*, 2881–2889. These assignments are supported by a higher *R_f* for the 2*R*^{*},*R*^{*}_S isomer on silica gel and by the expected preferential formation of the less hindered 2*R*^{*},*R*^{*}_S isomer on silica gel and by the expected preferential formation of the less hindered 2*R*^{*},*R*^{*}_S isomer on oxidation of thioether **21b**: Glass, R. S.; Petsom, A.; Wilson, G. S. *J. Org. Chem.* **1987**, *52*, 3537–3541.

(27) Inversion of configuration at sulfur and disproportionation to sulfides and sulfones are known photochemical properties of sulfoxides; see ref 9a,d,e.

Scheme VII



Scheme VIII



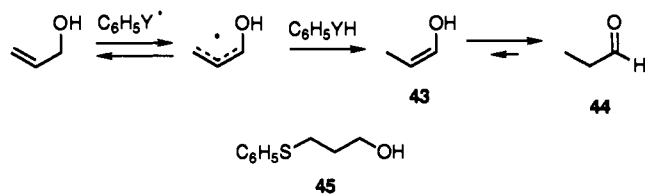
irradiation in methanol, except for the accompanying formation of small amounts of the 1,3-elimination and nucleophilic substitution products **31** and **32** (R = CH₃). In methanolic sodium methoxide substantial reduction to the thioether **21b** occurred, presumably via electron transfer to the sulfoxide (Scheme VII). Thus, only trace amounts of the ionic products **31** and **32** (R = CH₃) were obtained under the various conditions, partly because of other competing photobehavior characteristic of the sulfoxide chromophore.

2-Tetrahydropyranyl Ether 35. Irradiation of the phenyl thioether **35**, prepared by acid-catalyzed addition of C₆H₅SH to the dihydropyran **41**, in methanol or allyl alcohol afforded a mixture of the elimination product **41** and the nucleophilic substitution product **42** (R = CH₃ or CH₂CH=CH₂) (Table VIII). Only trace amounts of the reduction product **40** were obtained. The yield of the nucleophilic trapping product **42** (R = CH₂CH=CH₂) in allyl alcohol was greatly enhanced when the irradiation was conducted in the presence of a gel of fumed silica.

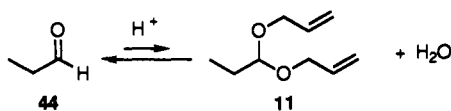
Acetal 11. Irradiation of the 1-adamantyl ethers **2a,b** and the tetrahydropyranyl ether **35** in allyl alcohol resulted in substantial amounts of acetal **11** as a byproduct. Similar irradiation of C₆H₅SH in allyl alcohol also afforded acetal **11**.²⁸ Thus, acetal formation on irradiation of ethers **2a,b** and **35** in allyl alcohol apparently involves the C₆H₅SH or C₆H₅SeH byproduct. Formation of **11** requires initial isomerization of some of the solvent to propanal (**44**), which presumably involves reversible hydrogen-atom abstraction by C₆H₅S^{*} to afford enol **43** followed by tautomeric equilibration.

The subsequent acetalization of propanal (**44**) under the irradiation conditions is remarkable. Although catalysis by acid

(28) In the absence of light the only product observed was the radical adduct 3-(phenylthio)-1-propanol (**45**).



impurities might be expected, treatment of a solution of propanal (44) in allyl alcohol in the presence of a catalytic amount of sulfuric acid afforded only a trace amount of acetal 11. Apparently the acid-catalyzed equilibrium between propanal (44) and acetal 11 favors the reactants without the accompanying removal of water. On the other hand, irradiation of a solution



of propanal (44) in allyl alcohol containing $\text{C}_6\text{H}_5\text{SH}$ effected rapid conversion to acetal 11. Indeed, irradiation of alcoholic solutions of aldehydes containing $\text{C}_6\text{H}_5\text{SH}$ is a synthetically useful method for the generation of acetals under neutral conditions.²⁹ The mechanism of acetalization is under further study.

Discussion

Ionic vs Radical Behavior. Ultraviolet absorption data for phenyl thioethers 2a, 21b, and 21d, as well as phenyl selenoether 21c, are summarized in Table IX. Simple alkyl thioethers display strong absorption in the range of 200–215 nm, as well as weaker absorption in the region of 230–240 nm, which has been assigned to the C–S $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions, respectively.^{9a,30} For phenyl thioethers, these bands are accompanied by a $\pi \rightarrow \pi^*$ transition in the range of 250–270 nm, which has an onset of absorption at ~ 310 nm. If the onset is taken as the 0,0 transition, S_1 lies ~ 390 kJ/mol above the ground state, well in excess of the alkyl C–S bond dissociation energy.³³ Phenyl selenoethers have two bands in the region 250–270 nm.³⁴ Again, if it is assumed that the onset of absorption at ~ 320 nm corresponds to the 0,0 transition, S_1 lies ~ 370 kJ/mol above the ground state, well in excess of the strength of an alkyl C–Se bond.³⁵ Thus it is not unexpected that phenyl thio- and selenoethers undergo dissociation on irradiation.

It is clear from the preceding results that the phenyl thio- and selenoethers 2, 13, 21, and 35 exhibit competing radical and ionic photobehavior, similar to that displayed by alkyl bromides and iodides.^{2,3,25} These are apparently the first examples of ionic behavior to be observed for the C–SAr and C–SeAr chromophores, which have traditionally been thought to exhibit only radical photobehavior.^{9,10} The data are consistent with a mechanism analogous to that proposed for alkyl halides,^{2,4} involving initial light-induced cleavage of the C–S or C–Se bond followed by

Scheme IX



electron transfer within the resulting radical pair (Scheme I).³⁶ Radical products arise via competing diffusion from the radical cage and, if structurally feasible, hydrogen-atom transfer within the cage. The electronegatively substituted $\text{C}_6\text{F}_5\text{S}^*$ fragment undergoes electron transfer more effectively than $\text{C}_6\text{H}_5\text{S}^*$ or $\text{C}_6\text{H}_5\text{Se}^*$, whereas 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{S}^*$ undergoes little or no electron transfer.

Although the overall photobehavior of phenyl thio- and selenoethers resembles that of analogous alkyl bromides and iodides, there are significant differences between the chalcogenides and halides. For examples, the 1-adamantyl derivatives 2 (Y = SC_6H_5 and SeC_6H_5) afforded somewhat lower yields of the nucleophilic trapping product 9 (R = CH_3) on irradiation in methanol (33% and 40%, respectively) than did the corresponding halides 2 (Y = Br and I) (53% and 99%, respectively).^{5a,37} In general, the phenyl thio- and selenoethers afforded lower yields of ionic products, particularly the nucleophilic trapping products 9, 19, and 32 (R = CH_3), than did the corresponding halides. However, the yield of ether 9 (R = CH_3) from the pentafluorophenyl derivative 2c (69%) was comparable with that obtained from the halides.

The deuterium labeling study with the 2-norbornyl thioether 21b in methanol showed that 2-norbornene (20) is formed almost exclusively (98%) via hydrogen-atom transfer within the radical pair 26. By contrast, the percent of 2-norbornene (20) arising from radical pair 26 vs ion pair 27 for the halide analogues 21 (Y = Br and I) is 33% and 63%, respectively.²⁵ The resulting ratio of in-cage radical product to total ionic product of 1:0.1 for thioether 21 (Y = SC_6H_5) compares with ratios of 1:3 and 1:8 for halides 21 (Y = Br and I), respectively. Thus, hydrogen-atom transfer competes much more effectively with electron transfer within the radical pair 26 when Y = $\text{C}_6\text{H}_5\text{S}^*$ than when Y = Br[•] or I[•], probably due to the greater ability of $\text{C}_6\text{H}_5\text{S}^*$ to abstract a hydrogen atom.³⁸ The absence of the nucleophilic trapping product 32 (R = CH_3) from the thioether 21 (Y = SC_6H_5) indicates that any ion pair 27b formed undergoes rapid proton transfer to give nortricyclene (31) accompanied by a trace amount of 2-norbornene (20), with no escape from the cage occurring to give the free 2-norbornyl cation 28.³⁹ By contrast, the halides 21 (Y = Br and I) afford substantial amounts of ether 32 (R = CH_3) from nucleophilic trapping of cation 28.²⁵ The difference undoubtedly lies in the much greater base strength of the counter ion $\text{C}_6\text{H}_5\text{S}^-$ compared with Br⁻ or I⁻, which leads to more efficient proton transfer.

Epimerization. The observed exo \rightleftharpoons endo interconversion of the 2-norbornyl epimers 21 and 22 (Y = SC_6H_5) is in marked

(29) The use of this technique with a number of other aldehydes and alcohols will be reported separately.

(30) Tagaki, W. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; pp 246–248.

(31) It is reasonable to assume that the onset of absorption is the 0,0 transition in these systems since there is little molecular distortion involved in the $\pi \rightarrow \pi^*$ transition and, hence, the ground-state and excited-state potential wells remain aligned.

(32) This is supported by the fluorescence of (methylthio)benzene, which displays an onset of emission at ~ 290 nm: Russell, P. G. *J. Phys. Chem.* 1975, 79, 1347–1352.

(33) D_0 for $\text{CH}_3-\text{SC}_6\text{H}_5$ is 251 kJ/mol: Back, M. H.; Sehon, A. H. *Can. J. Chem.* 1960, 38, 1076–1081.

(34) The assignment of these bands remains the subject of some controversy: Kuder, J. E. In *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley: New York, 1973; pp 867–868.

(35) C–Se bond strengths are ~ 40 kJ/mol below those of their sulfur analogues: Johnson, D. A. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 2, p 44.

(36) An alternative mechanism involving competing heterolytic and homolytic cleavage of the excited state is not rigorously excluded by the available data since those factors that favor electron transfer should also favor heterolytic over homolytic cleavage of the excited state. Competing heterolytic and homolytic cleavage of the excited state has been proposed for the photolysis of 9-fluorenone in methanol and of diphenylmethyl derivatives in acetonitrile: (a) Gaillard, E.; Fox, M. A.; Wan, P. *J. Am. Chem. Soc.* 1989, 111, 2180–2186. (b) Bartl, J.; Steenzen, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* 1990, 112, 6918–6928. On the other hand, excellent evidence for a mechanism involving homolytic cleavage followed by electron transfer has been presented for the photolysis of 1-naphthylmethyl esters; see ref 8f.

(37) Yields cited are normalized to complete conversion.

(38) It is conceivable that 2-norbornene (20) derived from the pentafluoro derivative 21d is formed to a larger extent from ion pair 27 than is that derived from the phenyl thioether 21b. However, attempts to test this were thwarted by a lack of success in preparing 21d-2-d due to loss of fluorine on treatment of 21d with base.

(39) Quenching of the 2-norbornyl cation 28 in methanolic sodium methoxide is reported to give a mixture of nortricyclene (31) and ether 32 (R = CH_3); see ref 21.

Table V. Irradiation of Pentafluorophenyl Thioether **21d**^a

solvent	base	time, h	yield, % ^b					
			21d	21e	30	20	31	32
CH ₃ OH		4	69			6	16	1
		16	22			c	41	4
CH ₃ OH	NH ₄ OH	6	37	16		14	13	2
		12	26	15		11	16	3
CH ₃ OH	CH ₃ ONa	6	12	37	5	27	16	3
		12	7	25	8	20	24	5
(CH ₃) ₃ COH	(CH ₃) ₃ COK	4	54	9		25	10	
		16	29	7		36	16	

^a Conducted according to the standard small-scale procedure described in the Experimental Section on solutions 0.2 N in the specified base.

^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. Pentafluoro- and tetrafluorobenzene and (C₆F₅S)₂ were also obtained in varying amounts. ^c None detectable.

Table VI. Quantum Yields for Disappearance of Starting Material

ether	Y	solvent	Φ ^a
21b	SC ₆ H ₅	CH ₂ Cl ₂	0.58
		CH ₂ Cl ₂ /SiO ₂ ^b	0.95
		C ₆ H ₁₂	0.64
21c	SeC ₆ H ₅	C ₆ H ₁₂ /SiO ₂ ^b	0.89
		C ₆ H ₁₂	0.53
		C ₆ H ₁₂ /SiO ₂ ^b	0.92

^a Determined at 254 nm as described in the Experimental Section. Values do not take into account any accompanying exo ⇒ endo interconversion. ^b 250 mg of Cab-O-Sil fumed silica added with thorough mixing.

contrast with the analogous bromides **21** and **22** (Y = Br), which do not interconvert on irradiation, but in agreement with the corresponding iodides **21** and **22** (Y = I), which do undergo isomerization.²⁵ Photoepimerization of alkyl iodides involves, at least principally, out-of-cage halogen-atom transfer between the corresponding alkyl radical and starting alkyl iodide, as shown in Scheme IX for the 2-norbornyl system.^{19,25,40} Halogen-atom transfer occurs readily for alkyl iodides ($k \sim 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), but slowly for alkyl bromides ($k \sim 6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$),⁴¹ allowing abstraction of a hydrogen atom from the solvent methanol ($k \sim 1 \times 10^4 \text{ s}^{-1}$)⁴² to compete with epimerization in the latter case.

Homolytic substitution of sulfides by attacking carbon radicals, while not common, has been observed.⁴³ Values of 1.7×10^5 to $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant for sulfur-atom transfer can be calculated from data reported for S_H2 attack of the 5-hexenyl radical on diphenyl disulfide.^{44,45} Although no data are currently available for similar attack on a phenyl thioether, rate constants of this magnitude would permit sulfur-atom transfer to compete with hydrogen-atom abstraction from the solvent.⁴⁶

(40) See also: Roth, R. C.; Binkley, R. W. *J. Org. Chem.* **1985**, *50*, 690–693.

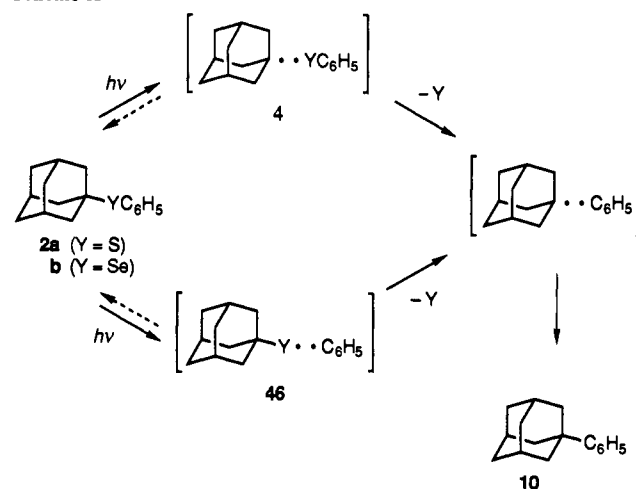
(41) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195–1199.

(42) Estimated from the rate constant for abstraction of a hydrogen atom from tetrahydrofuran: Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1988**, *29*, 3449–3450.

(43) (a) Ingold, K. U.; Roberts, B. P. *Free-Radical Substitution Reactions*; Wiley-Interscience: New York, 1971; pp 218–219. (b) Poutsma, M. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, pp 138–139.

(44) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398–1399. The value of $1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was obtained by correcting the originally reported value of $7.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ by using the currently accepted rate constant for unimolecular cyclization of the 5-hexenyl radical: Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742. The value of $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ was calculated from the reported observation that a primary alkyl radical abstracts a hydrogen atom from C₆H₅SH ~ 20 times as readily as undergoing S_H2 attack on diphenyl disulfide. The rate constant for hydrogen-atom abstraction from C₆H₅SH by a primary radical is $\sim 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268–275.

(45) These values are consistent with the report that trapping by diphenyl disulfide competes with self-trapping of an alkyl radical with its *N*-hydroxy-pyridine-2-thione (PTOC) ester precursor at a ratio of disulfide to ester of 30/1: Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron Lett.* **1984**, *25*, 5777–5780. The rate constant for self-trapping of a primary radical with a PTOC ester is $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615–1618.

Scheme X

It is interesting to note that at short irradiation times, the endo thioether **22** (Y = SC₆H₅) underwent photoconversion in methanol somewhat less efficiently than the exo epimer **21** (Y = SC₆H₅). A similar, but larger, difference observed previously for the analogous bromides **21** and **22** (Y = Br) was suggested to be a photochemical example of steric departure control arising from steric interaction of the departing endo substituent with the adjacent endo hydrogen atoms.²⁵

Extrusion of Sulfur or Selenium. The 1-adamantyl ethers **2a,b** underwent some loss of sulfur or selenium to give the corresponding phenyl derivative **10**, in competition with the formation of photoproducts 7–9.⁴⁷ Loss of sulfur or selenium on irradiation is common for organosulfur and organoselenium compounds^{9,10} and probably occurs via extrusion of elemental sulfur or selenium from a radical pair, followed by recombination (Scheme X). Although extrusion from **2a,b** could, in principle, occur from radical pair **4**, it more likely occurs from radical pair **46** arising from competing cleavage of the C₆H₅-S or C₆H₅-Se bond since C₆H₅S[•] and C₆H₅Se[•] are stable radicals.^{48,49} The more prominent extrusion from ethers **2a,b** than from the others studied probably reflects the greater stability of the tertiary 1-adamantyl radical, which facilitates extrusion from radical pair **46**. Not surprisingly, extrusion occurred more readily with the selenoether **2b**.

Surface Effects. Suspensions of fumed silica in solvents having a refractive index close to that of silica form translucent gels that

(46) As with iodides **21** and **22** (Y = I), phenyl thioethers **21** and **22** (Y = SC₆H₅) afforded little or none of the out-of-cage radical products **29** and **30**. By contrast, bromides **21** and **22** (Y = Br), which do not undergo transfer with the 2-norbornyl radical (**25**), afford substantial amounts of these products; see ref 25.

(47) Small amounts of the corresponding extrusion products were also obtained from ethers **13a**, **21b,c** and **22b**.

(48) Thyron, F. C. *J. Phys. Chem.* **1973**, *77*, 1478–1482.

(49) Although the alkyl-chalcogenide bond cleaves more readily, some competing cleavage of the phenyl-chalcogenide bond clearly occurs since benzene was observed as a minor product from irradiation of each of the phenyl ethers.

Table VII. Irradiation of Sulfoxide (2R*,R*s)-21f^a

solvent	time, h	yield, % ^b							
		21f ^c	21f ^d	22f ^e	22f ^f	21b	30	20	31
THF	15	25	40	g	4	1 ^h	18	4	g
	30	23	33	g	4	2 ^h	15	12	g
	45	15	22	g	3	8 ^h	20	5	g
CH ₃ OH	15	48	29	g	g	g	13	g	1 ⁱ
	15					64	2	18	2

^a Conducted with 66 mM solutions containing 145 mg of sulfoxide (2R*,R*s)-21f. ^b Determined by gas chromatographic or HPLC analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. ^c 2R*,R*s. ^d 2R*,S*s. ^e 2S*,S*s. ^f 2S*,R*s. ^g Trace. ^h Sulfone 21g was also obtained. ⁱ Ether 32 (R = CH₃) was also obtained in 3% yield. ^j 0.2 N NaOCH₃.

Table VIII. Irradiation of 2-Tetrahydropyranyl Ether 35^a

solvent	yield, % ^b				R
	35	40	41	42	
CH ₃ OH	24	67	9	CH ₃	
CH ₂ =CHCH ₂ OH ^c	14	12	50	24	CH ₂ CH=CH ₂
CH ₂ =CHCH ₂ OH/SiO ₂ ^{c,d}	e	6	51	43	CH ₂ CH=CH ₂

^a Conducted for 4 h according to the standard small-scale procedure described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. ^c Acetal 11 was also obtained. ^d 250 mg of Cab-O-Sil fumed silica was added with thorough mixing. ^e Trace.

Table IX. Ultraviolet Absorption Data

ether	Y	solvent	λ_{\max} , nm ^a		onset, nm ^b
			$n \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$	
2a	SC ₆ H ₅	CH ₂ Cl ₂	234 (3.44)	264 (3.26)	305
			228 (3.62)	270 (3.11)	
21b	SC ₆ H ₅	CH ₂ Cl ₂	234 (3.66)	260 (3.85)	315
			222 (3.36)	256 (3.72)	
21c	SeC ₆ H ₅	CH ₂ Cl ₂	234 (3.89)	256 (3.90)	320
			272 (3.85)		
			222 (3.82)	252 (3.60)	
21d	SC ₆ F ₅	CH ₂ Cl ₂	234 (3.38)	268 (3.47)	310
			274 (3.50)		
			226 (3.53)	268 (3.54)	

^a log ϵ given in parentheses. ^b Estimated from wavelength at which there was a perceptible rise from the base line.

transmit light sufficiently well so that they can be used as media for photochemical reactions.⁵⁰ Under these conditions several interesting surface effects were observed. The presence of fumed silica afforded substantially improved quantum yields for the conversion of the phenyl thio- and selenoethers 21b,c to products. This is presumably due to adsorption of the byproducts C₆H₅SH and C₆H₅SeH to the highly polar surface, thereby inhibiting their readdition to the unsaturated product 2-norbornene (20). The silica surface thus affords a convenient means of scavenging C₆H₅SH and C₆H₅SeH in nonhydroxylic media. It also provides a highly polar local environment that can facilitate electron transfer, as seen by the enhanced formation of the nucleophilic trapping product 42 (R = CH₂CH=CH₂) from the phenyl thioether 35 in the presence of fumed silica, and by the apparent formation of the nucleophilic trapping product 33 when phenyl thioether 21b was irradiated on dry silica gel.⁵¹

Concluding Remarks. The use of photochemically generated radical pairs to afford ionic products is both mechanistically interesting and synthetically useful. Phenyl thio- and selenoethers join the ranks of alkyl halides as suitable precursors for radical pairs capable of undergoing electron transfer to cationic intermediates, as does the irradiation of aldehydes in the presence of C₆H₅SH or C₆H₅SeH. The balance of radical vs ionic product formation from radical pairs clearly depends on both the identity

of the component radicals and the environment in which they are created, and can be controlled by varying these parameters. Our studies continue on the generation of radical pairs from other precursors, as well as on the effects of environmental changes on their behavior.

Experimental Section

General Procedures. Infrared spectra were obtained on a Beckman 4250 spectrophotometer (spectra reported to nearest 5 cm⁻¹) or a Nicolet 20 DX FTIR spectrophotometer (spectra reported to nearest 2 cm⁻¹). Ultraviolet absorption spectra were obtained on a Hewlett-Packard 8451A diode array spectrophotometer in the solvent specified. Proton NMR spectra were determined in CDCl₃ solution on a Bruker AC 200 spectrometer, and deuterium spectra were obtained on a Varian XL-400 spectrometer in CCl₄ solution. Mass spectra were obtained on a Micromass 7070F instrument. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument equipped with a 12 ft × 0.125 in. stainless steel column containing either 20% SF-96 or 20% β,β -oxydipropionitrile on 60–80-mesh Chromosorb W. Preparative gas chromatography was performed on a Varian Aerograph 90-P instrument equipped with a 10 ft × 0.25 in. stainless steel column packed as described above. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected.

Irradiations. Irradiations were conducted in 200 × 14 mm quartz tubes made of 1-mm wall thickness General Electric type 204 clear fused-quartz tubing, and placed in a water-cooled quartz immersion well that was either suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 (254 nm) or F8T5-BL (350 nm) lamps or positioned 6 cm from a 450-W Hanovia medium-pressure mercury arc lamp and reflector. All solvents employed in irradiations were used as received except for those treated as follows: *tert*-butyl alcohol, distillation from CaH₂; CH₂Cl₂, stirring over concentrated H₂SO₄ followed by Na₂CO₃ and then distillation from P₂O₅; methanol, distillation from Mg and storage over 3-Å molecular sieves.

In a typical small-scale irradiation, either 50 μ L or 50 mg of the substrate and 50 μ L of tetradecane (internal standard) were added to an oven-dried tube along with 5 mL of purified solvent. The tube was then fitted with a rubber stopper pierced with two hypodermic needles, one of which was attached to a section of polyethylene capillary tubing for the introduction of N₂ into the solution and for the withdrawal of aliquots. The solution was deaerated by bubbling for at least 5 min, an aliquot was removed for gas chromatographic analysis, and irradiation was commenced. The temperature of the solution was maintained at 10 °C with water cooling. Aliquots were removed periodically during the course of the irradiation and analyzed by gas chromatography. There was no reaction in the absence of light.

Preparative-scale irradiations were conducted with 0.05 M solutions containing 0.2–2.0 g of substrate. The resulting mixture was poured into an equal volume of water and extracted with three portions of 2-methylbutane. The combined organic layers were washed with water and saturated NaCl solution and then dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation and the products were collected by preparative gas chromatography.

Preparation of Ethers 2a–c. A. 1-(Phenylthio)tricyclo[3.3.1.1^{3,7}]decane (2a). A modification of the general procedure of Perkins and Turner was used.⁵² Into a 50-mL round-bottomed flask was placed 3.0 g (20 mmol) of tricyclo[3.3.1.1^{3,7}]decane-1-ol, and 4.0 mL (28 mmol) of trifluoroacetic anhydride was added slowly. The addition was somewhat exothermic. The contents were stirred under a calcium chloride drying tube for 15 min, 5.0 mL (50 mmol) of benzenethiol was added, and the mixture was stirred at room temperature overnight. The reaction was quenched with 100 mL of 10% NaOH solution and extracted with two

(50) Fumed silica consists of aggregated spheres, which are nonporous and amorphous, formed by hydrolysis of SiCl₄ vapor in a flame of H₂ and O₂.

(51) Analysis of silica surfaces with use of solvatochromic indicators has shown that they have a much higher polarity/polarizability than even the most polar solvents: Lindley, S. M.; Flowers, G. C.; Leffler, J. E. *J. Org. Chem.* 1985, 50, 607–610.

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75-mL portions of ether. The combined extracts were dried over saturated NaCl solution followed by anhydrous Na₂SO₄. Removal of the ether afforded a colorless oil that crystallized on standing. Recrystallization from petroleum ether afforded 3.4 g (69% yield) of thioether **2a** as colorless needles: mp 72–73 °C; IR (CH₂Cl₂) 3085, 3070, 2965, 2940, 2860, 1590, 1490, 1450, 1350, 1035, 740, 695 cm⁻¹; ¹H NMR δ 7.42 (dd, *J* = 6.8, 4.0 Hz, 2 H, CH-3', -5'), 7.27 (m, 3 H, CH-2', -4', -6'), 1.95 (br s, 3 H, CH-3, -5, -7), 1.75 (br d, *J* = 3.0 Hz, 6 H, CH₂-2, -9, -10), 1.56 (br s, 6 H, CH₂-4, -6, -8); lit.⁵³ mp 71.5–72 °C; ¹H NMR δ 7.0–7.6 (m, 5 H), 1.62–2.2 (m, 15 H).

B. 1-(Phenylseleno)tricyclo[3.3.1.1^{3,7}]decane (2b). A solution of 2.0 g (13 mmol) of tricyclo[3.3.1.1^{3,7}]decane-1-ol and 25 mL (325 mmol) of trifluoroacetic acid in 50 mL of benzene was heated under reflux for 24 h. The reaction mixture was concentrated to ca. 25 mL by rotary evaporation, washed with 50 mL each of saturated NaHCO₃ and NaCl solutions, and dried over anhydrous Na₂SO₄. Rotary evaporation afforded 1.1 g of trifluoroacetic acid, tricyclo[3.3.1.1^{3,7}]dec-1-yl ester (**1**) as a pale yellow oil.

To a solution of 1.0 g (4.0 mmol) of trifluoroacetate **1** in 20 mL of trifluoroacetic acid and 50 mL of CH₂Cl₂ contained in a 100-mL round-bottomed flask were added 2.2 g (7.0 mmol) of diphenyl diselenide and 0.85 g (13 mmol) of zinc powder. The mixture was allowed to stir for 36 h at 25 °C. It was then cooled in an ice bath, washed with 50 mL of saturated NaHCO₃ solution, and dried over saturated NaCl solution followed by anhydrous Na₂SO₄. Concentration by rotary evaporation gave 0.88 g of an off-white solid, which on recrystallization from methanol afforded 0.63 g (54% yield) of selenoether **2c** as small, colorless needles: mp 44–45 °C; ¹H NMR δ 1.65 (s, 6 H), 1.97 (s, 9 H), 7.3 (m, 3 H, CH-2', -4', -6'), 7.6 (m, 2 H, CH-3', -5'); lit.⁵² mp 35 °C; lit.⁵³ mp 35 °C; lit.⁵⁴ mp 34–35 °C; lit.⁵⁵ ¹H NMR δ 1.58–2.05 (m, 15 H), 7–7.8 (m, 5 H).

C. 1-[(Pentafluorophenyl)thio]tricyclo[3.3.1.1^{3,7}]decane (2c). A modification of the general procedure of Perkins and Turner was used.⁵² Into a 50-mL round-bottomed flask was placed 3.0 g (20 mmol) of tricyclo[3.3.1.1^{3,7}]decane-1-ol, and 4.0 mL (28 mmol) of trifluoroacetic anhydride was added slowly. The addition was somewhat exothermic. The contents were stirred under a calcium chloride drying tube for 15 min, 5.0 mL (50 mmol) of pentafluorobenzenethiol was added, and the mixture was stirred at 25 °C for 24 h. The reaction was quenched with 50 mL of saturated NaHCO₃ solution and extracted with a 50-mL portion of ether. Removal of the ether afforded a colorless oil that crystallized on standing. Recrystallization from a mixture of hexanes afforded 5.0 g (75% yield) of thioether **2b** as colorless needles: mp 120–122 °C; IR 2920, 2899, 2853, 1636, 1513, 1482, 1092, 980, 861 cm⁻¹; ¹H NMR δ 1.62 (s, 6 H), 1.83 (d, 6 H), 2.03 (s, 3 H); MS *m/z* (M⁺) calcd for C₁₆H₁₅SF₅ 334.0815, found 334.0800.

Irradiation of Ethers 2a–c. From preparative-scale irradiations conducted as described above the following products were isolated by preparative gas chromatography. 1,1'-Bitricyclo[3.3.1.1^{3,7}]decane (**7**) was isolated as a colorless solid: ¹H NMR δ 2.0 (br s, 6 H), 1.6 (m, 24 H); lit.⁵⁵ no spectral data given. Tricyclo[3.3.1.1^{3,7}]decane (**8**) was obtained as an amorphous solid that was identified by comparison with a commercial sample. 1-Methoxytricyclo[3.3.1.1^{3,7}]decane (**9**, R = CH₃) was isolated as a colorless liquid, which had spectral data in agreement with those of a sample prepared as described previously.⁵⁶ A sample obtained from irradiation in CH₃OD had a similar IR spectrum. Ether **9** (R = CH₂CH=CH₂) and acetal **11** were isolated as colorless liquids that were identified by comparison with samples prepared independently as described below. 1-Phenyltricyclo[3.3.1.1^{3,7}]decane (**10**) was isolated as a colorless solid: mp 81–82.5 °C; ¹H NMR δ 1.66 (s, 6 H), 1.90 (d, 6 H), 2.07 (s, 3 H), 7.22 (m, 5 H); lit.⁵⁷ mp 82 °C; lit.⁵⁸ mp 87–89 °C.

Independent Synthesis of 1-(2-Propenyloxy)tricyclo[3.3.1.1^{3,7}]decane (9, R = CH₂CH=CH₂). Sodium hydride (0.56 g of a 50% suspension in oil, 11 mmol) was placed in an N₂-flushed 300-mL Schlenk flask and washed three times with small portions of anhydrous THF, which were subsequently removed with a disposable pipet. The washed hydride was then suspended in 75 mL of anhydrous THF. To this mixture were added 1.0 g (6.6 mmol) of tricyclo[3.3.1.1^{3,7}]decane-1-ol (**1**) and 1.0 mL (11 mmol) of 3-bromopropene, and the mixture was stirred at reflux overnight. Excess sodium hydride was then destroyed by the careful, dropwise addition of water. The reaction mixture was poured into 300 mL

of water and extracted with two 200-mL portions of 2-methylbutane. The combined organic layers were washed with 300 mL of water and 100 mL of saturated NaCl solution and then dried over anhydrous Na₂SO₄. The 2-methylbutane was removed by distillation and the product was distilled under reduced pressure to give 0.82 g (65% yield) of ether **9** (R = CH₂CH=CH₂) as a colorless liquid: bp 112 °C (2.6 mmHg); IR (neat) 3080, 2910, 2860, 1650, 1460, 1360, 1310, 1115, 1090, 915 cm⁻¹; ¹H NMR δ 5.9 (m, 1 H, =CH), 5.0 (m, 2 H, =CH₂), 3.92 (dt, *J* = 7.0, 1.5 Hz, 2 H, -CH₂O-), 2.12 (br s, 3 H, CH-3, -5, -7), 1.73 (br d, *J* = 3.0 Hz, 6 H, CH₂-2, -9, -10), 1.59 (br s, 6 H, CH₂-4, -6, -8); MS *m/z* (M⁺) calcd for C₁₃H₂₀O 192.1514, found 192.1517.

Independent Synthesis of 3,3'-(Propylidenebis(oxy))bis-1-propene (11). Preparation as described previously⁵⁹ afforded acetal **11** as a colorless liquid: IR (neat) 3085, 3020, 2975, 2940, 2885, 1655, 1470, 1425, 1390, 1345, 1130, 1085, 1040, 995, 920 cm⁻¹; ¹H NMR δ 5.8 (m, 2 H, 2 × =CH), 5.1 (m, 4 H, 2 × =CH₂), 4.39 (t, *J* = 5.2 Hz, 1 H, CH-1), 3.90 (m, 4 H, 2 × -CH₂O-), 1.49 (dq, *J* = 8.0, 5.2 Hz, 2 H, CH₂-2), 0.75 (t, *J* = 8.0 Hz, 3 H, CH₃-3); lit.⁵⁹ no spectral data.

Preparation of Ethers 13a,b. A. 2-(Phenylthio)tricyclo[3.3.1.1^{3,7}]decane (13a). To a solution of 1.5 mL (1.5 mmol) of benzenethiol in 10 mL of CF₃CO₂H that had been stirred for 15 min was added 3.06 g (10.0 mmol) of tricyclo[3.3.1.1^{3,7}]decane-1-ol, 4-methylbenzenesulfonate (**12**).⁶⁰ The resulting solution, which immediately turned yellow, was vigorously stirred at 25 °C for 4 days and then poured into 60 mL of water and extracted with two 100-mL portions of ether. The combined ether layers were washed with four 60-mL portions of 1 N KOH solution and two 60-mL portions of saturated NaCl solution and then dried over anhydrous Na₂SO₄. Removal of the solvent gave a yellow oil, which was subsequently purified by chromatography over alumina to afford, on elution with 2-methylbutane, 1.15 g (47% yield) of thioether **13a** as a colorless oil: IR (neat) 3070, 3055, 2910, 2855, 1585, 1485, 1470, 1450, 1440, 1100, 1025, 730, 685 cm⁻¹; ¹H NMR δ 7.3 (m, 5 H, C₆H₅-), 3.57 (br s, 1 H, CH-2), 1.9 (m, 14 H); MS *m/z* (M⁺) calcd for C₁₆H₂₀S 244.1286, found 244.1286.

B. 2-[(Pentafluorophenyl)thio]tricyclo[3.3.1.1^{3,7}]decane (13b). To a solution of 2.0 mL (2.0 mmol) of pentafluorobenzenethiol in 10 mL of CF₃CO₂H that had been stirred for 15 min was added 3.06 g (10.0 mmol) of tosylate **12**.⁶⁰ The resulting solution, which immediately turned yellow, was vigorously stirred at 25 °C for 4 days and then poured into 60 mL of water and extracted with two 100-mL portions of ether. The combined ether layers were washed with four 60-mL portions of 1 N KOH solution and two 60-mL portions of saturated NaCl solution and then dried over anhydrous Na₂SO₄. Removal of the solvent afforded a pale yellow oil, which was subsequently purified by recrystallization to yield 2.27 g (70% yield) of thioether **13b** as a colorless solid: mp 83.5–85 °C; ¹H NMR δ 1.56 (d, 3 H), 1.72 (s, 3 H), 1.90 (br s, 6 H), 2.28 (d, 2 H), 3.51 (s, 1 H); IR (melt) 2929, 2909, 2858, 1514, 1489, 1450, 1089, 863 cm⁻¹; MS *m/z* (M⁺) calcd for C₁₆H₁₅SF₅ 334.0815, found 334.0807.

Irradiation of Ethers 13a,b. From preparative-scale irradiations conducted as described above the following products were isolated by preparative gas chromatography. Tricyclo[3.3.1.1^{3,7}]decane (**8**) was obtained as an amorphous solid that was identified by comparison with a commercial sample. 2-[(2,3,5,6-Tetrafluorophenyl)thio]tricyclo[3.3.1.1^{3,7}]decane (**13c**) was obtained as a colorless liquid: ¹H NMR δ 7.01 (tt, *J* = 9.6, 7.3 Hz, 1 H, CH-4'), 3.62 (s, 1 H, CH-2), 2.31 (br s, 1 H), 2.25 (br s, 1 H), 1.9 (m, 6 H), 1.73 (br s, 4 H), 1.59 (br s, 1 H), 1.52 (br s, 1 H). Octahydro-2,4-methano-1H-cycloprop[*cd*]indene (**18**) was isolated as a colorless, amorphous solid: ¹H NMR δ 2.21 (s, 2 H, 2 × CH), 2.10 (m, 1 H, CH), 1.80 (s, 3 H, CH₂ and CH), 1.35 (m, 7 H, 2 × CH₂ and 3 × CH), 1.15 (t, *J* = 8 Hz, 1 H, CH); lit.⁶¹ ¹H NMR (CCl₄) δ 2.4–1.0 (m, 14 H). 2-Methoxytricyclo[3.3.1.1^{3,7}]decane (**19**) was isolated as a colorless liquid: ¹H NMR δ 3.32 (br s, 4 H, CH-2 and CH₃O-), 2.0 (m, 4 H), 1.7 (m, 8 H), 1.5 (m, 2 H); lit.⁶² ¹H NMR (CCl₄) δ 3.30 (CH-2), 2.3–1.2 (14 H).

Preparation of Ethers 21a–d. A. exo-2-[(4-Methoxyphenyl)thio]bicyclo[2.2.1]heptane (21a). To a solution of 3.9 g (42 mmol) of bicyclo[2.2.1]hept-2-ene (**20**) in 100 mL of purified pentane contained in a 250-mL round-bottomed flask was added 5.27 g (37.6 mmol) of 4-methoxybenzenethiol. The mixture was degassed and stirred for 2 days in the presence of fluorescent room light. Removal of the pentane by distillation afforded 9.86 g of a colorless oil, which was shown to contain

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a small amount of excess bicyclo[2.2.1]hept-2-ene (20) by gas chromatographic analysis. Further purification by preparative gas chromatography afforded thioether **21a** as a colorless oil: IR (neat) 3065, 2950, 2870, 2830, 1590, 1570, 1490, 1455, 1440, 1285, 1240, 1175, 1090, 1025, 820 cm^{-1} ; $^1\text{H NMR}$ δ 7.31 (dt, $J = 9.2, 3.5$ Hz, 2 H, CH-2', -6'), 6.83 (dt, $J = 9.2, 3.5$ Hz, 2 H, CH-3', -5'), 3.78 (s, 3 H, CH₃O-), 3.03 (ddd, $J = 8.1, 5.0, 2.0$ Hz, 1 H, CH-2n), 2.22 (br s, 2 H, CH-1 and -4), 1.0 (m, 8 H); MS m/z (M^+) calcd for C₁₄H₁₈OS 234.1078, found 234.1085.

B. *exo*-2-(Phenylthio)bicyclo[2.2.1]heptane (21b). The procedure used was a modification of that employed by Brown et al.⁶³ To a solution of 10.0 g (0.106 mol) of bicyclo[2.2.1]hept-2-ene (20) in 50 mL of pentane contained in a 100-mL round-bottomed flask was added 10.0 mL (0.097 mol) of benzenethiol. The flask was fitted with a reflux condenser, deaerated under N₂, and irradiated for 4 h with a 450-W mercury arc lamp. The solvent was removed by distillation and the product was distilled under reduced pressure to give 19.6 g (99% yield) of thioether **21b** as a colorless liquid: bp 118–125 °C (4 mmHg); IR (neat) 3085, 3070, 2960, 2880, 1585, 1480, 1435, 730, 680 cm^{-1} ; $^1\text{H NMR}$ δ 7.3 (m, 5 H, C₆H₅-), 3.22 (ddd, $J = 2.0, 4.5, 7.5$ Hz, 1 H, CH-2n), 2.32 (br s, 2 H, CH-1, -4), 1.5 (m, 8 H); lit.⁶⁴ IR (film) 2955, 2870, 1585, 735, 685 cm^{-1} ; lit.⁶³ $^1\text{H NMR}$ (CCl₄) δ 3.11 (ddd, $J = 1.5, 4.9, 7.5$ Hz, 1 H).

C. *exo*-2-(Phenylseleno)bicyclo[2.2.1]heptane (21c). A modification of the procedure of Liotta and Waykole was used.⁶⁵ Into a 100-mL round-bottomed flask containing 0.85 g of magnesium turnings and 50 mL of diethyl ether was slowly added 5.25 g (30.0 mmol) of *exo*-2-bromobicyclo[2.2.1]heptane (23). The resulting mixture was heated under reflux for 0.5 h and then cooled to 0 °C. A solution of benzene-selenenyl bromide, prepared from 2.4 g (15 mmol) of Br₂ and 4.68 g (15.0 mmol) of diphenyl diselenide,⁶⁶ in 25 mL of THF was added over 0.75 h. The dark red mixture was warmed to 25 °C over 20 min, stirred an additional 30 min, carefully diluted with 25 mL of water, and then extracted with 100 mL of ether. The ether layer was washed with two 100-mL portions of 10% sodium thiosulfate solution and dried over saturated NaCl solution followed by anhydrous Na₂SO₄. Removal of the ether by distillation afforded 5.3 g of an orange liquid, which was further purified by chromatography on silica gel to afford 1.38 g (18% yield) of an 82/18 mixture of selenoethers **21c** and **21e** as a pale yellow oil: $^1\text{H NMR}$ δ 7.3 (m, 5 H, C₆H₅-), 3.66 (m, 0.18 H, CH-2x), 3.34 (m, $J = 2.1, 5.6, 10.6$ Hz, 0.82 H, CH-2n), 2.35 (m, 2 H, CH-1, -4), 1.7 (m, 10 H).

D. *exo*-2-[(Pentafluorophenyl)thio]bicyclo[2.2.1]heptane (21d). To a solution of 1.0 g (10.6 mmol) of bicyclo[2.2.1]hept-2-ene (20) in 5 mL of purified pentane contained in a Pyrex round-bottomed flask was added 1.3 mL (9.8 mmol) of pentafluorobenzenethiol. The solution was warmed to a gentle reflux. The mixture was degassed and irradiated for 3 h with a 450-W mercury arc lamp. Distillation afforded 2.94 g (99% yield) of thioether **21d** as a colorless, crystalline solid: bp 100–102 °C (4 mmHg); mp 44 °C; IR 2970, 2885, 1795, 1635, 1505, 1475, 1370, 970, 900, 850 cm^{-1} ; $^1\text{H NMR}$ δ 3.18 (m, 1 H, CH-2n), 2.30 (br s, 1 H, CH-1), 2.03 (br s, 1 H, CH-4), 1.4 (m, 8); MS m/z (M^+) calcd for C₁₃H₁₁F₅S 294.0502, found 294.0498.

Preparation of *endo*-2-(Phenylthio)bicyclo[2.2.1]heptane (22b). The procedure used was a modification of that of Brown et al.⁶³ A solution of 1.0 mL (10 mmol) of benzenethiol in 25 mL of anhydrous ether was degassed with N₂ and cooled in a dry ice/2-propanol bath. Methyl-lithium (7.5 mL of a 1.63 M solution in ether, 12 mmol) was injected over a period of 3 min and the mixture was allowed to warm to 25 °C over a period of 2 h. Removal of the ether under reduced pressure afforded the lithium salt as a crystalline, white solid. To a solution of the salt in 10 mL of dimethylformamide was injected 0.65 mL (5 mmol) of *exo*-2-bromobicyclo[2.2.1]heptane (23), and the mixture was stirred at 25 °C for 3 days. The mixture was poured into 50 mL of water and extracted with three 50-mL portions of ether. The combined ether layers were then washed with 75 mL each of water and saturated NaCl solution and dried over anhydrous Na₂SO₄. Removal of the solvent by distillation afforded 0.9 g (90% yield) of a pale yellow oil, which was purified by preparative gas chromatography to give thioether **22b** as a colorless liquid: IR (neat) 3080, 3065, 2960, 2875, 1590, 1485, 1455, 1445, 1095, 1030, 745, 690 cm^{-1} ; $^1\text{H NMR}$ δ 7.3 (m, 5 H, C₆H₅-), 3.56 (m, 1 H, CH-2x), 2.2 (m, 4 H), 1.4 (m, 6 H); lit.⁶⁷ $^1\text{H NMR}$ (CCl₄) δ 3.50 (ddd, $J = 11, 6, 4$ Hz, 1 H).

Preparation of *exo*-2-(Phenylthio)bicyclo[2.2.1]heptane-2-*d* (21b-*d*). Treatment of 1.65 g (15 mmol) of benzenethiol with 12.3 mL (16.0 mmol) of 1.3 M methyl-lithium in 50 mL of ether followed by removal of the solvent, and the addition of 50 mL of dimethylformamide and 1.75 g (10.0 mmol) of *endo*-2-bromobicyclo[2.2.1]heptane-2-*d* (**24-2-*d***)²⁵ as described above for the preparation of thioether **22b** afforded 1.98 g (100% yield) of thioether **21b-2-*d*** as a colorless liquid: $^2\text{H NMR}$ (CCl₄) δ 3.50 (s, 0.06 D, CD-2x), 3.15 (s, 0.94 D, CD-2n).

Irradiation of Ethers 21a–e and 22b. From preparative-scale irradiations conducted as described above the following products were isolated by preparative gas chromatography. Bicyclo[2.2.1]hept-2-ene (20) and bicyclo[2.2.1]heptane (30) were identified by comparison with commercial specimens. *exo*-2-[(2,3,5,6-Tetrafluorophenyl)thio]bicyclo[2.2.1]heptane (21e) was isolated as a colorless liquid: IR (neat) 2948, 2865, 2905, 1632, 1628, 1490, 1478, 1452, 1440, 1430, 1258, 1248, 1236, 1226, 1168, 944, 906, 884, 836, 704 cm^{-1} ; $^1\text{H NMR}$ δ 7.03 (tt, $J = 9.6, 7.2$ Hz, 1 H, CH-4'), 3.32 (m, 1 H, CH-1), 2.33 (br s, 1 H, CH-1), 2.08 (br s, 1 H CH-4), 1.8 (m, 2 H), 1.6 (m, 2 H), 1.4 (m, 1 H), 1.2 (m, 1 H), 1.1 (m, 2 H). 2,2'-Bicyclo[2.2.1]heptane (29) was isolated as a colorless liquid, which was identified by comparison with a sample prepared as previously described.⁶⁸ $^1\text{H NMR}$ δ 2.13 (m, 4 H, CH-1, -4, -1', -4'), 1.58 (s, 2 H, CH-2, -2'), 1.43 (m, 4 H), 1.25 (m, 6 H), 1.08 (m, 6 H). Tricyclo[2.2.1.0^{2,6}]heptane (31) was isolated as a colorless, amorphous solid: $^1\text{H NMR}$ δ 1.97 (s, 1 H, CH-4), 1.20 (s, 6 H, CH₂-3, -5, -7), 0.97 (s, 3 H, CH-1, -2, -6); lit.⁶⁹ $^1\text{H NMR}$ (CCl₄) δ 1.88 (s, 1 H, CH-4), 1.19 (s, 6 H, 3 × CH₂), 0.98 (s, 3 H, CH-1, -2, -6). *exo*-2-Methoxybicyclo[2.2.1]heptane (32, R = CH₃) was isolated as a colorless liquid: $^1\text{H NMR}$ δ 3.15 (s, 3 H, CH₃O-), 3.11 (s, 1 H, CH-2), 2.28 (s, 1 H, CH-1), 2.13 (s, 1 H, CH-4), 1.39 (m, 5 H, CH₂-3, CH-5x, -6x, CH-7_{syn}), 0.94 (m, 3 H, CH-5n, -6n, CH-7_{anti}); lit.⁷⁰ $^1\text{H NMR}$ (CCl₄) δ 3.20, 3.15, (m, s, 4 H), 2.25 (m, 2 H), 0.90–1.77 (m, 8 H).

Irradiation of Ether 21b on Silica Gel. To a solution of 50 μL of ether **21b** and 50 μL of tetradecane in 5 mL of CH₂Cl₂ was added 300 mg of Merck 10181 silica gel. The solvent was removed by rotary evaporation, and the silica gel was transferred to a quartz tube connected to a rotary evaporator motor and placed in a cooling well at such an angle that it could be spun. Dinitrogen was passed over the silica gel for 10 min, after which it was irradiated for 16 h with a 450-W lamp and then washed with CH₂Cl₂. The silica gel was added to 5 mL of CH₂Cl₂, 1.0 mL of SOCl₂ was added, and the mixture was stirred for 20 min. The organic layer was separated, washed with water, and analyzed by gas chromatography. Isolation by preparative gas chromatography afforded chloride **34** as a colorless liquid, which was identified by comparison with a specimen prepared independently as described below.

Independent Preparation of *exo*-2-Chlorobicyclo[2.2.1]heptane (34). A solution of 0.94 g of 2-bicyclo[2.2.1]heptene (20) in 6 mL of anhydrous ether was saturated with HCl by bubbling the gas through the stirred solution for 15 min. The solution was stirred for an additional hour and then resaturated with HCl. After another 30 min, the solution was saturated once more and stirred for one more hour. Gas chromatographic analysis at this point revealed only trace amounts of **20** remaining. The ether solution was washed with 10 mL each of water and saturated NaHCO₃ and NaCl solutions and then dried over anhydrous Na₂SO₄. Removal of the ether by distillation afforded chloride **34** as a colorless liquid, which was further purified by preparative gas chromatography: IR (neat) 2960, 2875, 1455, 1440, 1310, 1300, 1255, 1045, 945, 890, 830, 795, 755, 660 cm^{-1} ; $^1\text{H NMR}$ δ 3.89 (m, 1, CH-2n), 2.36 (m, 2, CH-1, -4), 1.5 (m, 8); lit.⁷¹ $^1\text{H NMR}$ (CCl₄) δ 3.82 (CH-2n).

Quantum Yields. The actinometer consisted of a 0.050 M solution of (*E*)-2-octene in benzene that had been purified by washing with concentrated H₂SO₄ followed by fractional distillation from K₂CO₃.⁷² The phenyl thio- or phenyl selenoether solution was 0.050 M in substrate. These solutions were irradiated according to the standard small-scale procedure in a Rayonet photochemical reactor equipped with a merry-go-round apparatus and placed in a cold room maintained at 5–7 °C. The temperature of the cavity within the reactor stayed below 10 °C. Aliquots were taken at 15-min intervals and subjected to gas chromatographic analysis. Conversions were 9–13%. No curvature of the kinetic plot was observed due to absorption by the photoproducts under the conditions used.

Preparation of *exo*-2-(Phenylsulfinyl)bicyclo[2.2.1]heptane (21f). A solution of 10 g (5.0 mmol) of thioether **21b** in 150 mL of CH₂Cl₂ was

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cooled to 5 °C and 10 g (5.0 mmol) of 85% 3-chloroperoxybenzoic acid was added. The mixture was stirred at 5 °C for 4 h and then washed with saturated Na₂CO₃ solution, which was back-extracted with 2-methylbutane. The combined organic fractions were dried over saturated NaCl solution followed by anhydrous Na₂SO₄ and concentrated by rotary evaporation. Flash chromatography of the resulting yellow oil on silica gel gave sulfoxides **21f** in two fractions on elution with 10% ethyl acetate in hexane. Recrystallization from hexane of the first isomer eluted gave (2*R**,*S**₅)-*exo*-2-(phenylsulfinyl)bicyclo[2.2.1]heptane [(2*R**,*S**₅)-**21f**] as a colorless prisms: mp 61–62 °C; IR (melt) 3057, 2960, 2946, 2871, 1477, 1444, 1298, 1089, 1052, 1034, 749, 696 cm⁻¹; ¹H NMR δ 7.6 (m, 2 H, CH-3', -5'), 7.5 (m, 3 H, CH-2', -4', -6'), 2.52 (m, 2 H, CH-1, -2), 2.37 (br s, 1 H, CH-4), 2.1 (m, 1 H), 1.6 (m, 4 H), 1.18 (m, 3 H); MS *m/z* (M⁺) calcd for C₁₃H₁₆OS 220.0922, found 220.0920.⁷³

Recrystallization of the second isomer from hexane gave (2*R**,*R**₅)-*exo*-2-(phenylsulfinyl)bicyclo[2.2.1]heptane [(2*R**,*R**₅)-**21f**] as fine, colorless prisms: mp 71–72 °C; IR (melt) 3054, 2955, 2912, 2873, 1477, 1441, 1312, 1299, 1086, 1044, 999, 749, 697 cm⁻¹; ¹H NMR δ 7.6 (m, 2 H, CH-3', -5'), 7.5 (m, 3 H, CH-2', -4', -6'), 2.87 (br d, *J* = 4.2 Hz, 1 H, CH-1), 2.74 (ddd, *J* = 11.1, 5.1, 1.5 Hz, 1 H, CH-2), 2.31 (br s, 1 H), 1.6 (m, 3 H), 1.2 (m, 5 H); MS *m/z* (M⁺) calcd for C₁₃H₁₆OS 220.0922, found 220.0922.⁷³

Irradiation of Sulfoxide (2*R,*R**₅)-**21f**.** From the irradiations outlined in Table VII the following products were isolated by column chromatography. Sulfoxide (2*R**,*S**₅)-**21f** was identified by comparison with the material described above. *exo*-2-(Phenylsulfonyl)bicyclo[2.2.1]heptane (**21g**) was obtained as colorless prisms on recrystallization from pentane: mp 80.5–81.5 °C; UV λ_{max} (heptane) 218 nm (ε 6455), 270 nm (ε 1120); ¹H NMR δ 7.9 (m, 2 H, CH-3', -5'), 7.6 (m, 3 H, CH-2', -4', -6'), 2.96 (br dd, 1 H, CH-2), 2.64 (br s, 1 H, CH-1), 2.36 (br s, 1 H, CH-4), 1.9 (m, 2 H), 1.5 (m, 3 H), 1.2 (m, 3 H); MS *m/z* (M⁺) calcd for C₁₃H₁₆O₂S 236.0871, found 236.0872. (2*S**,*R**₅)-*endo*-2-(Phenylsulfonyl)bicyclo[2.2.1]heptane [(2*S**,*R**₅)-**22f**] was obtained as a colorless oil: IR (neat) 3057, 2959, 2874, 1478, 1444, 1312, 1085, 1040, 996, 752, 695 cm⁻¹; ¹H NMR δ 7.6 (m, 2 H, CH-3', -5'), 7.5 (m, 3 H, CH-2', -4', -6'), 2.94 (m, 1 H, CH-2), 2.37 (br s, 1 H, CH-1), 2.15 (br s, 1 H, CH-4), 1.9 (m, 3 H), 1.5 (m, 5 H). (2*S**,*S**₅)-*endo*-2-(Phenylsulfonyl)bicyclo[2.2.1]heptane [(2*S**,*S**₅)-**22f**] was obtained as pale yellow prisms: mp 100–102 °C; IR (melt) 3084, 3050, 3018, 2959, 2874, 1475, 1456, 1444, 1087, 1070, 1033, 999, 757, 713 cm⁻¹; ¹H NMR δ 7.7 (m, 2 H, CH-3', -5'), 7.5 (m, 3 H, CH-2', -4', -6'), 3.10 (m, 1 H, CH-2), 2.82 (br s, 1 H, CH-1), 2.27 (br s, 1 H, CH-4), 2.1 (m, 1 H), 1.5 (m, 6 H), 0.92 (ddd, *J* = 2.3, 5.5, 13.2 Hz, 1 H, CH-3n).

Tetrahydro-2-(phenylthio)-2*H*-pyran (35). A. Preparation. A modification of Parham's procedure was employed.⁷⁴ To a mixture of 10 mL (0.10 mol) of 3,4-dihydro-2*H*-pyran (**41**) and 10 mL (0.10 mol) of benzenethiol was added two drops of concentrated HCl and the mixture, which turned pale yellow with time, was heated at 80 °C overnight. Three pellets of KOH were added and the product was distilled under reduced pressure to give 16.5 g (85% yield) of thioether **35** as a colorless liquid: bp 106–107 °C (0.3 mmHg); UV λ_{max} (cyclohexane) 226 nm (ε 3970), 252 nm (ε 5390); IR (neat) 3060, 2940, 2850, 1585, 1480, 1440, 1190, 1100, 1075, 1035, 1005, 735, 685 cm⁻¹; ¹H NMR δ 7.5 (m, 2 H, CH-3', -5'), 7.3 (m, 3 H, CH-2', -4', -6'), 5.25 (dd, *J* = 8.7, 4.2 Hz, 1 H, -OCHS-), 4.21 (m, 1 H, CH-6_{ax}), 3.62 (m, 1 H, CH-6_{eq}), 1.8 (m, 6 H, CH₂-3, -4, -5); lit.⁷⁴ bp 100–102 °C (0.9 mmHg).

B. Irradiation. From preparative-scale irradiations conducted as described above the following products were isolated by preparative gas chromatography. Tetrahydropyran (**40**) and 3,4-dihydro-2*H*-pyran (**41**) were identified by comparison with commercial specimens. Acetals **42** (R = CH₃) and **42** (R = CH₂CH=CH₂) were identified by comparison with samples prepared independently as described below.

Independent Preparation of Tetrahydro-2-methoxy-2*H*-pyran (42, R = CH₃). To a mixture of 10 mL (0.11 mol) of 3,4-dihydro-2*H*-pyran (**41**) in 50 mL of dry methanol was added two drops of concentrated HCl. The mixture became warm after an induction period of 3–4 min. The solution was allowed to cool to 25 °C and was then neutralized with Na₂CO₃. The solvent was removed by distillation and the product dis-

tilled from a single pellet of KOH to afford 12.4 g (88% yield) of acetal **42** (R = CH₃) as a colorless liquid: bp 123–125 °C; IR (neat) 2940, 1440, 1385, 1195, 1125, 1080, 1065, 1035, 955, 900, 875, 810 cm⁻¹; lit.⁷⁵ bp 128–129 °C.

Independent Preparation of Tetrahydro-2-(2-propenyloxy)-2*H*-pyran (42, R = CH₂CH=CH₂). A similar procedure afforded 9.53 g (56% yield) of acetal **42** (R = CH₂CH=CH₂) as a colorless liquid: bp 167–170 °C; IR (neat) 3185, 2940, 2865, 1650, 1445, 1380, 1355, 1340, 1325, 1265, 1205, 1185, 1120, 1025, 920, 900, 870, 815 cm⁻¹; lit.⁷⁶ bp 165–167 °C.

Control Studies on the Formation of Acetal 11. A. Treatment of 2-Propen-1-ol with Acid. Two drops of concentrated H₂SO₄ was added to 10 mL of anhydrous 2-propen-1-ol. The solution, which immediately turned a clear, dark brown on addition of the acid, was saturated with N₂. An aliquot was removed, transferred to a vial wrapped with aluminum foil, and placed in the dark for 4 h. In accord with previous findings,⁷⁷ the only product observed by gas chromatographic analysis was propanal (**44**), found to be present in 35 mM concentration (0.175 mmol). The remainder of the solution was irradiated at 254 nm as described above for 4 h. It became charcoal-gray colored. The only product observed by gas chromatographic analysis was propanal (**44**), present in 25 mM concentration (0.125 mmol).

B. Attempted Acid-Catalyzed Formation. Similar treatment of 10 mL of 2-propen-1-ol containing 50 μL (0.19 mmol) of propanal (**44**) produced only a trace of acetal **11** by gas chromatographic analysis.

C. Irradiation of Benzenethiol in 2-Propen-1-ol. A solution of 25 μL (0.24 mmol) of C₆H₅SH in 5 mL of anhydrous 2-propen-1-ol was saturated with N₂. An aliquot was removed, placed in a vial wrapped with aluminum foil, and placed in the dark for 4 h. The only product observed by gas chromatography was the thioether **45**, prepared independently as described below. The remainder of the solution was irradiated at 254 nm in the usual way for 4 h. Gas chromatographic analyses revealed the presence of acetal **11** in 52 mM concentration (0.26 mmol).

D. Irradiation of Benzenethiol in 2-Propen-1-ol Containing Propanal (44). A solution of 50 μL (0.49 mmol) of C₆H₅SH and 50 μL (0.69 mmol) of propanal (**44**) in 5 mL of anhydrous 2-propen-1-ol was saturated with N₂ and irradiated at 254 nm for 4 h. Gas chromatographic analysis of the reaction mixture revealed that 0.12 mmol (25%) of the C₆H₅SH remained, and that 0.17 mmol (35%) of the thioether **45** and 0.63 mmol of the acetal **11** had been formed (90% yield based on starting propanal (**44**) or 171% based on consumed C₆H₅SH).

E. Irradiation of 3-(Phenylthio)-1-propanol (45) in 2-Propen-1-ol Containing Propanal (44). A solution of 50 μL (0.35 mmol) of thioether **45** in 5 mL of anhydrous 2-propen-1-ol was saturated with N₂ and irradiated for 4 h at 254 nm. Gas chromatographic analysis of the resulting product mixture revealed 72% (0.25 mmol) of thioether **45** remaining, as well as the presence of 0.28 mmol of the acetal **11** (280% yield based on thioether **45** consumed).

Independent Preparation of 3-(Phenylthio)-1-propanol (45). Boustany's method was used.⁷⁸ A solution of 10 mL (97 mmol) of benzenethiol in 25 mL of anhydrous 2-propen-1-ol contained in a Pyrex tube was saturated with N₂ and irradiated for 4 h at 300 nm. The solution was a light apricot color after the irradiation. Distillation gave 5.5 g (39% yield) of thioether **45** as a colorless liquid: bp 135–138 °C (2 mmHg); IR (neat) 3380, 3085, 3070, 2955, 2900, 1585, 1480, 1440, 1045, 1025, 900, 730, 685 cm⁻¹; ¹H NMR δ 7.2 (m, 5 H, C₆H₅-), 3.62 (t, 2 H, *J* = 6.5 Hz, -CH₂O-), 2.92 (t, 2 H, *J* = 6.5 Hz, -SCH₂-), 2.72 (br s, 1 H, -OH), 1.75 (q, 2 H, *J* = 6.5 Hz, CH₂-2); lit.⁷⁹ bp 130 °C (2 mmHg).

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