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# Evidence for a Nonradical Pathway in the Photoracemization of Aryl Sulfoxides[1]

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***Abstract:*** Photolysis of ($R_S$,$S_C$)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide provides mainly ($S_S$,$S_C$)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide at low conversion, though the other two stereoisomers are formed to smaller extents. Thus, the predominant process leading to sulfur inversion yields *only* sulfur inversion, without inversion of the adjacent CHD stereogenic center. This is taken as evidence for a mechanism for photochemical epimerization of sulfoxides that does not involve homolytic α-cleavage chemistry.

## Introduction

Sulfoxides undergo photochemically induced epimerization at sulfur[2−7] despite the ground-state barrier of approximately 40 kcal mol$^{-1}$. It is well established that carbon−sulfur bond homolysis (α-cleavage) is an extremely common photochemical reaction of sulfoxides,[8−12] and recombination of radical pairs or biradicals so-generated necessarily provides a mechanism for racemization. Nonetheless, it has been asserted that photochemical stereomutation occurs through a direct inversion of the sulfur center,[2,13−16] even though some results[3,4,7,17] demand that carbon−sulfur bond rupture occurs in the process of epimerization of the sulfur. Since α-cleavage is required in some instances of photochemical sulfoxide epimerization, and is known to occur from product and laser flash photolysis studies,[8,11,12,18,19] it is clear that positive evidence for a direct inversion mechanism is required to establish it as one of the primary photoprocesses of sulfoxides, even if it has been supposed by a series of authors. In this paper, we present such evidence for a nonhomolytic pathway.

Circumstantial evidence in favor of the existence of a nonhomolytic pathway for racemization has accumulated over the last several years. Sulfoxides with substituents that would form poorly stabilized radicals on α-cleavage have relatively high quantum yields for racemization despite low quantum yields for product formation.[12,15,16] Higher product yields are observed when the nascent radical is, for instance, benzyl.[12,14] Formation of sulfinyl radicals on the ns−$\mu$s time scale follows the same trend in that more stabilized alkyl radicals lead to higher yields of PhSO$^{\bullet}$ from phenyl sulfoxides.[11]

A second line of evidence is observed from the simple sulfoxide derivatives of several fluorescent chromophores.[15,16,20] In these compounds, the sulfoxide derivatives have decidedly lower fluorescence yields than the parent arenes. This is not accompanied by a rise in triplet yield or product formation and is unique to the sulfoxide, among sulfide, sulfoxide, and sulfone derivatives.[20] It was hypothesized that the racemization event was the source of the nonradiative decay. Finally, multireference ab initio methods have been used to demonstrate that, for DMSO, stationary points exist on excited-state energy surfaces that have $C_{2v}$ symmetry and are lower in energy than any geometry with $C_s$ symmetry.[21]

The underlying assumption in these works is that excitation of the sulfoxide is followed by geometric relaxation in the excited state. The excited state geometry is presumed to be one in which the sulfur is either no longer stereogenic or in which the potential for inversion is considerably lower than in the ground state. In this paper, we report evidence for just this sort of process, based on photolysis of a substrate with two adjacent

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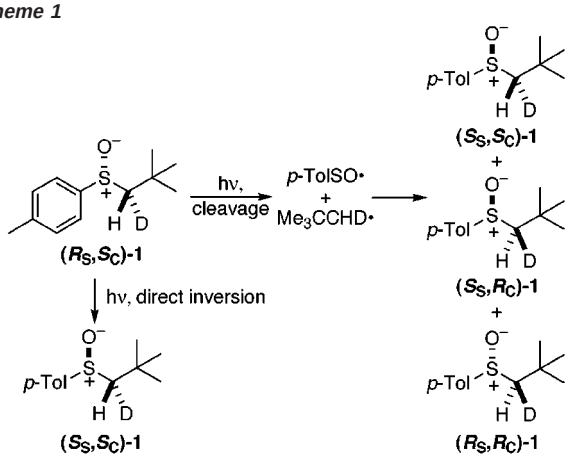
***Scheme 1***




stereogenic centers. Inversion of the sulfur center alone is the predominant process.

## Results and Discussion

Photolysis of ($R_S$,$S_C$)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide [**(*R*$_S$,*S*$_C$)-1**] was used to probe for a noncleavage pathway to sulfur inversion, as illustrated in Scheme 1. Because there is only a trivial diastereomeric preference on recombination of the radical pair produced by α-cleavage and because both radicals are inherently achiral, α-cleavage will provide all three new stereoisomers essentially without preference. In contrast, direct sulfur inversion of **(*R*$_S$,*S*$_C$)-1** provides **(*S*$_S$,*S*$_C$)-1** exclusively. The structure of **1** as an aryl primary-alkyl sulfoxide is known to reduce the quantum yield for α-cleavage chemistry.[12] The expected major product, a sulfenic ester, would be recognized easily.

Photolysis of **(*R*$_S$,*S*$_C$)-1** at 360 $\mu$M concentration in acetonitrile was followed by removal of samples as a function of time. The solvent was evaporated from each sample, and the residual material dissolved in $CDCl_3$. The two $R_S$ stereoisomers are separable by chiral chromatography from the two $S_S$ isomers and were quantified relative to one another. However, the stereogenic center at $C_1$ does not lend itself to chromatographic resolution. The $C_1$-proton of the ($R_S$,$S_C$) and ($S_S$,$R_C$) enantiomeric pair appears at 2.52 ppm and that of the ($R_S$,$R_C$) and ($S_S$,$S_C$) enantiomers appears at 2.81. Thus each pair of enantiomers was quantified in relation to the other. Use of a chiral shift reagent provides modest resolution within each enantiomeric pair, based again on the sulfur center. This allowed for direct quantification of the ratio of the ($S_S$,$S_C$) and ($R_S$,$R_C$) isomers (Figure 1), but the separation between enantiomers was not sufficient to allow quantification of the minor ($S_S$,$R_C$) isomer in the presence of the large quantity of **(*R*$_S$,*S*$_C$)-1**. However, estimates of the concentrations of all four isomers were obtained by using a combination of the three measurements. While very small quantities of products other than stereoisomers of **1** were undoubtedly formed, none was above the detection limit by HPLC or NMR.

Figure 1 shows the region of the NMR spectrum where the $C_1$-protons of the ($S_S$,$S_C$) and ($R_S$,$R_C$) isomers are observed as a function of photolysis time. The initial solution contained approximately 94% **(*R*$_S$,*S*$_C$)-1**, 5% **(*R*$_S$,*R*$_C$)-1**, and 1% **(*S*$_S$,*R*$_C$)-1**. As can be seen, **(*S*$_S$,*S*$_C$)-1** grows in preferentially. The signal-to-noise ratio was limited by the absolute concentrations of the

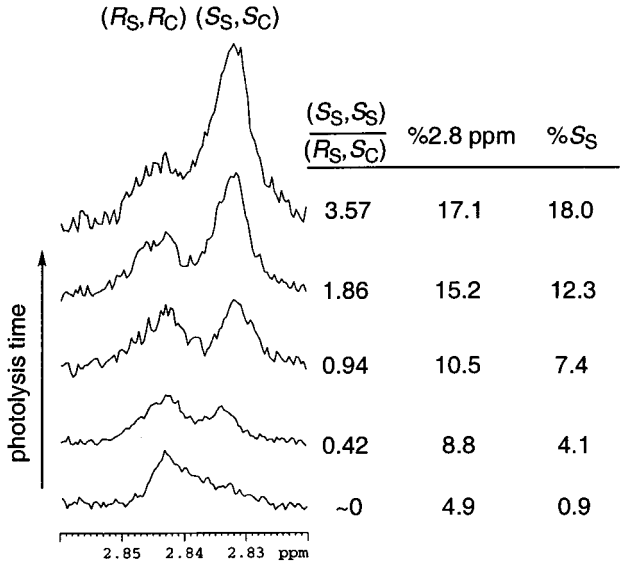



***Figure 1.*** $C_1$−proton resonances of **(*R*$_S$,*R*$_C$)-1** and **(*S*$_S$,*S*$_C$)-1** as a function of photolysis time. The spectra are normalized so that the height of the **(*R*$_S$,*R*$_C$)-1** peak is approximately constant. The ratios of **(*S*$_S$,*S*$_C$)-1** to **(*R*$_S$,*R*$_C$)-1** were determined by line shape fitting of the spectra. The % 2.8 ppm was determined by integration of the overall 2.8 and 2.5 regions of the spectra and represents the fraction of the total sulfoxide concentration that is **(*R*$_S$,*R*$_C$)-1** *or* **(*S*$_S$,*S*$_C$)-1**. The % $S_S$ was determined by chiral HPLC and represents the fraction of the total sulfoxide concentration that is **(*S*$_S$,*R*$_C$)-1** or **(*S*$_S$,*S*$_C$)-1**.

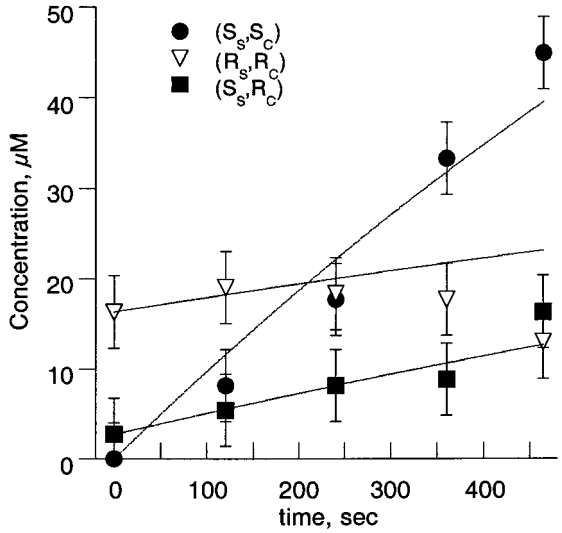



***Figure 2.*** Concentrations of the minor isomers as a function of photolysis time, along with the kinetic simulation.

isomers of **1** ($<10^{-4}$ M) in the presence of ca. 0.1 M shift reagent. The absolute concentration data are given in Figure 2.

The initial product of photolysis of **(*R*$_S$,*S*$_C$)-1** is largely **(*S*$_S$,*S*$_C$)-1**, though a smaller amount of **(*S*$_S$,*R*$_C$)-1** is also formed. Over the course of about 17% total conversion to the $S_S$ isomers, the initial quantity of **(*R*$_S$,*R*$_C$)-1** does not change significantly. We believe this is because while it is being drained largely to **(*S*$_S$,*R*$_C$)-1**, it is also being created by α-cleavage chemistry of the major isomer **(*R*$_S$,*S*$_C$)-1**. The kinetic data were simulated[22] by using two sets of rate constants that were each constrained to be internally identical. The first, $k_S$, connects **(*R*$_S$,*R*$_C$)-1** and **(*S*$_S$,*R*$_C$)-1** as one pair and **(*S*$_S$,*S*$_C$)-1** and **(*R*$_S$,*S*$_C$)-1** as the other.

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The second, $k_\alpha$, connects all isomers. Figure 2 illustrates the best fit to the data. The rate constants are functionally equivalent to the product of the photon flux and the quantum yield for each isomerization. Since the photon flux is the same for both processes, the rate constants are proportional to the quantum yields. While the fit is not perfect, we believe it captures the essence of the data.[23] The ratio of $k_S/k_\alpha$ is 6.2, and is then corrected by a factor of $^1/_2$ to account for the fact that any given stereoisomer can produce two products by the sulfur inversion ($k_S$) pathway, while the α-cleavage chemistry can produce any of four isomers, assuming both pathways have random outcomes. The resulting ratio of 3.1 thus represents at least a qualitative estimate of the ratio of quantum yields for the sulfur-only and α-cleavage stereochemical events.

The overall quantum yield of sulfur-center inversion [i.e., ($R_S$) to ($S_S$)], independently measured by HPLC analysis against azoxybenzene actinometry,[24] was 0.45. This approaches the expected maximum of 0.5, regardless of the mechanism.

The current results are the strongest evidence yet for a nonhomolytic photochemical stereomutation process in sulfoxides. Taken in combination with previous work, we believe that the scenario most consistent with all of the evidence is that the noncleavage mechanism of stereomutation is a geometrical relaxation of the electronically excited sulfoxide from its highly pyramidalized ground-state structure to one that is at least approximately trigonal at sulfur, followed by nonradiative decay to the ground state at or near a geometry that is planar at the sulfur center. This notion is analogous to the cis−trans isomerization of olefins.

The issue of the state multiplicity from which this occurs is slightly ambiguous, but we suggest the predominance of evidence favors stereomutation from the singlet, with possible involvement of the triplet. Previous product and flash photolysis studies with phenyl-based sulfoxides produced no evidence for long-lived triplet states at room temperature, and the product study data were most consistent with α-cleavage occurring at least largely from a singlet state.[10−12,14,25] To be competitive with α-cleavage, it is at least reasonable to speculate that the geometrical relaxation would also occur from the singlet state, though short triplet lifetimes are also compatible with nonradiative relaxation and decay.

With larger aromatic chromophores such as pyrene and naphthalene, two groups have shown that the usual fluorescence is quenched by sulfinyl substitution.[10,15,16,20] This was not accompanied by any systematic increase in triplet yield, as determined by flash photolysis experiments.[20] These results are consistent with geometric relaxation providing a nonradiative deactivation pathway from the singlet. Furthermore, fluorescence yields of the larger aromatic systems went up when samples were constrained in glassy matrices at 77 K, again suggestive that fairly large geometry changes might be associated with the nonradiative decay.[20] If intersystem crossing were to occur simultaneously with or after geometric relaxation, triplets would be formed that would also end up giving racemized starting material upon decay to ground state. However, triplet sensitization and isoprene-quenching experiments on the larger aromatics suggested that nearly all the isomerization occurred from a singlet state.[20]

In very early experiments on methyl tolyl sulfoxide, Hammond and co-workers used extremely high concentrations of piperylene and lowered the yield of racemization of methyl tolyl sulfoxide.[26] However, subsequent careful experiments involving inter- and intramolecular sensitization by naphthalene showed that piperylene quenched naphthalene fluorescence with a rate constant ($7 \times 10^7$ $M^{-1}$ $s^{-1}$) consistent with interference with the *singlet* chemistry rather than triplet.[27] It is not straightforward to show that piperylene quenches short-lived nonfluorescent singlets, but it must be seen as at least plausible that these early experiments do not demonstrate triplet involvement as surely as once thought.

Further supporting the argument for geometric relaxation are calculations carried out for DMSO.[21] Using full valence[28] CASSCF methodology, with energy corrected with MCQDPT second-order perturbation theory,[29,30] energies were obtained for DMSO in multiple singlet and triplet states at the ground-state equilibrium geometry and at the inversion transition state. Additional stationary points in excited $^1A'$ and $^1A''$ states were found in both $C_s$ and $C_{2v}$ symmetry. In the ground state, of course, the lowest energy $C_{2v}$ structure is the transition state for inversion. However, in the two lowest singlet excited states ($^1A'$ and $^1A''$ symmetry), the stationary points with $C_{2v}$ symmetry ($^1B_1$ and $^1B_2$, respectively) are the lowest energy structures found. The $^1B_1$ stationary point is only 6 kcal $mol^{-1}$ above the ground electronic state at its own optimized geometry, which suggests that transitions to the ground electronic state would be facile. Because the entry point onto the ground-state surface is at a geometry where the sulfur center is planar, random stereomutation is expected. It must be noted that these calculations do not include the type of conjugated aromatic chromophore used here, but there is ample evidence from absorption, emission, and chiroptical spectroscopy that the sulfinyl group is a strong perturber of the aromatic chromophore.[20,25,31−33]

## Conclusions

By showing that sulfur-only inversion predominates over stereomutation of the adjacent stereogenic sites in **1**, we have provided the strongest evidence yet for a noncleavage mechanism for photochemical stereomutation in sulfoxides. Given the low quantum yield of product formation, the only remaining argument against a noncleavage mechanism relies on the confluence of (a) a nearly unity quantum yield for α-cleavage regardless of the alkyl substituent structure, (b) a fraction of recombination of the geminate sulfinyl−alkyl radical pairs that is near unity for the neopentyl radical but much smaller for the benzyl[14] radical, (c) a pathologically high selectivity of the neopentyl radical for reaction at the sulfur center of the sulfinyl

(23) The curvature of the data relative to the kinetic plots is probably reflective of the fact that the sample size was depleted during the measurement, which increases the effective photon flux to some degree. Any unaccounted for systematic error due to product formation would decrease the amount of **($S_S$,$R_C$)-1** from its apparent values and increase the value of $k_S/k_\alpha$.

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radical to form sulfoxides over sulfenic esters despite a much lower selectivity for the benzyl radical, and (d) the selective rotation of the *p*-Tol−SO$^{\bullet}$ bond over the $Me_3C-CHD^{\bullet}$ bond in the geminate radical pair. We do not find this combination of requirements credible and conclude that photochemical stereomutation of sulfoxides is accomplished both by α-cleavage and by a noncleavage pathway, which we believe derives from geometric relaxation in an electronically excited state.

## Experimental Section

**General Methods.** Commercially available compounds were used without purification except as noted. THF was distilled under Ar from the sodium benzophenone ketyl and diisopropylamine was distilled from $CaH_2$. NMR spectra were obtained on either a Varian VXR-300 or a Bruker Avance DXR 400. HPLC data were collected using a HP 1050 instrument equipped with a diode array UV/vis detector and an Astec Chirobiotic V (Vancomycin stationary phase) column. Mass spectra were collected on a VG Magnum ion trap GC-MS operating in EI mode.

The NMR chiral shift reagent of choice was (*R*)-(−)-*N*-(3,5-dinitrobenzoyl) α-phenylethylamine[34] in $CDCl_3$. Best results were obtained when the shift reagent was near 100 mM, given a sulfoxide concentration of ca. 1 mM. Several other conditions were evaluated and found inferior, including use of other solvents and use of α-methoxyphenylacetic acid[35] as a shift reagent. Spectra for analysis were obtained at 400 MHz with deuterium decoupling.

**(*R*)-Neopentyl *p*-Tolyl Sulfoxide**.[36] The procedure of Rieke[37] was used to generate the organometallic reagent. $MgCl_2$ (2.75 g, 29.1 mmol), KI (2.07 g, 53.0 mmol), and K (2.23 g, 13.2 mmol) were placed in a flame-dried 250 mL round-bottom flask equipped with a condenser and stir bar under argon. THF (70 mL) was added and the mixture was held at reflux for 2 h, then at room temperature for 30 min. Neopentyl bromide (1.67 mL, 13.2 mmol) was added and the system was brought to reflux again for 20 min with vigorous stirring. (1*R*,2*S*,5*R*)-(−)-Menthyl (*S*)-*p*-toluenesulfinate[38] (3.18 g, 10.8 mmol) in THF (10 mL) was added at room temperature and the system was brought to reflux. After 4 h, the system was cooled, quenched with saturated $NH_4Cl$(aq), and extracted with ether. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (silica, 5% EtOAc in $CH_2Cl_2$) gave 0.50 g of sulfoxide (22%). Typical enantiomeric ratios after initial workup were 95:5. Multiple recrystallizations from hexane gave samples with >99% of the (*R*)-sulfoxide. $^1$H NMR ($CDCl_3$) $\delta$ 1.20 (s, 9H); 2.42 (s, 3H); 2.52 (d, $J = 13.5$ Hz, 1H); 2.81 (d, $J = 13.5$ Hz, 1H); 7.33 (d, $J = 8$ Hz, 2H); 7.52 (d, $J = 8$ Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ 142.6, 141.3, 130.1, 124.0, 74.1, 32.1, 30.0, 21.6. UV−vis ($\lambda_{max}$ 248.2 nm). Ion trap MS *m*/*e* (relative abundance) 211 (M + 1, 100), 194 (10), 140 (38), 92 (14). HPLC (90:10, MTBE:acetonitrile, 1 mL/min) retention times were 18.4 and 19.7 min for (*S*) and (*R*) sulfoxides, respectively. Racemic sulfoxide was obtained by *m*-CPBA oxidation (1 equiv, −78 °C, $CH_2Cl_2$) of the neopentyl tolyl sulfide, obtained from sodium *p*-toluenethiolate and neopentyl tosylate.[39]

**($R_S$,$S_C$)-1-Deuterio-2,2-dimethylpropyl *p*-Tolyl Sulfoxide (1).** Diisopropylamine (0.11 mL, 0.81 mmol) and THF (10 mL) were charged to a flame-dried 25 mL flask equipped with an argon inlet. After the mixture was cooled to 0 °C, *n*-BuLi (1.78 M in hexane, 0.42 mL, 0.76 mmol) was added with stirring over 20 min. The mixture was then cooled to −78 °C. (*R*)-Neopentyl *p*-tolyl sulfoxide (0.10 g, 0.48 mmol) in 1 mL of THF was then added to the cold reaction mixture over 5 min. After an additional 5 min, the reaction was quenched with excess $D_2O$ (2 mL). Ether (20 mL) and water (20 mL) were added and the organic layer was separated. The ether layer was washed with brine and dried ($MgSO_4$) and solvent was removed. The crude product was recrystallized three times from ethanol to obtain 30 mg (30%) of highly purified material, which was a mixture of 94% ($R_S$,$S_C$), 5% ($R_S$,$R_C$), and 1% ($S_S$,$S_C$) isomers. No sulfoxide containing two α-protons was observed by NMR. The peaks at 2.81 and 2.52 ppm changed from 13.5 Hz doublets to 2 Hz triplets (deuterium coupling).

The relative chemical shifts of the $C_1$-protons of the $R_S$ and $S_S$ isomers in the presence of the shift reagent were determined from a sample of nondeuterated neopentyl tolyl sulfoxide that was of a known $R_S$:$S_S$ ratio of about 90:10. The resonance is slightly downfield for the $R_S$ isomers. The absolute stereochemistry at the sulfur center was determined from the sense of the CD spectrum.[31]

**Photolyses for NMR Analysis.** A solution of **1** (340 $\mu$M) in $CH_3CN$ (100 mL) was prepared in a septum-sealed quartz tube equipped with a stir bar. The solution was purged with Ar to remove $O_2$. It was irradiated at 254 nm using a low-pressure Hg lamp in a Rayonet minireactor equipped with a magnetic stirrer and a fan. Only a 15 mm gap of a single 4 W bulb was not covered with foil in order to slow the reaction. At 2 min intervals, about 25 mL of the solution was removed by syringe. No photoproducts aside from stereoisomers of **1** were observed by HPLC or NMR. The solvent was evaporated, and the residue was dissolved in $CDCl_3$ such that the concentration was about 1 mM. The samples were split into two NMR tubes and then analyzed. Spectra were obtained after adding successive 200 $\mu$L aliquots of saturated (≤200 mM) shift reagent in $CDCl_3$. Typically, 256 scans were obtained. The S/N ratio in Figure 1 is limited by the low concentration of the ($R_S$,$R_C$) and ($S_S$,$S_C$) isomers (ca. $10^{-4}$ M) in the presence of approximately $10^{-1}$ M shift reagent. The ratio of [**($R_S$,$R_C$)-1** + **($S_S$,$S_C$)-1**] to [**($R_S$,$S_C$)-1** + **($S_S$,$R_C$)-1**] was determined by ordinary integration of the 2.81 and 2.52 ppm peaks, and the ratios of **($R_S$,$R_C$)-1** to **($S_S$,$S_C$)-1** were obtained using the line shape analysis feature of WinNMR. The error bars in Figure 2 are best-estimate error limits, based on estimates of systematic error and reproducibility of the three measurements. The HPLC measurements do not contribute significantly to the error.

**Quantum Yields.** Duplicate 4.0 mL solutions of (*R*)-neopentyl *p*-tolyl sulfoxide (5 mM) in acetonitrile contained in 1 cm square fluorescence cells were degassed by purging with Ar. Excitation was provided by a 75 W Xe lamp filtered through a monochromator set to 254 nm with ±12 nm linear dispersion. The stirred sample was held in a fixed sample holder mounted at the monochromator exit, which ensures complete absorption of the exiting light. Samples of a few microliters each were periodically removed and analyzed by chiral HPLC. Conversion from the $R_S$ isomers to $S_S$ isomers was linear with time up to at least 10% conversion. The photon flux was determined by azoxybenzene actinometry.

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