

Photochemistry of Aryl Vinyl Sulfides and Aryl Vinyl Ethers: Evidence for the Formation of Thiocarbonyl and Carbonyl Ylides

James P. Dittami,* Yalin Luo, David Moss,[†] and W. Grant McGimpsey*

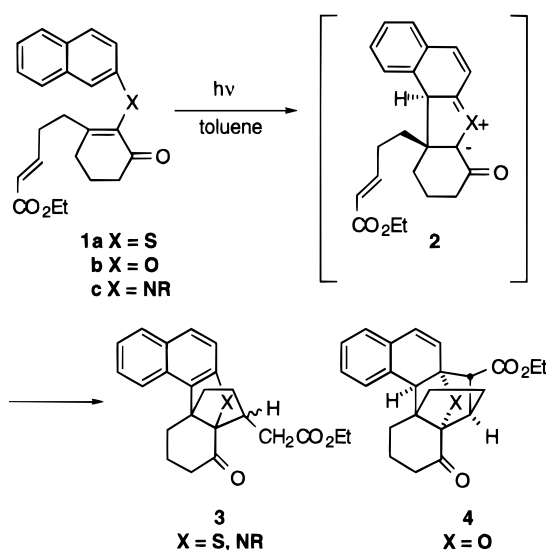
Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

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Aryl vinyl thioethers **5a** and **9a** and aryl vinyl ethers **5b** and **9b** form ylide intermediates following laser irradiation at 308 nm. In benzene, the ylides possess long-lived absorption bands in the 600–800 nm region with a second weaker band at ~460 nm. In methanol, a known quencher of zwitterionic species, the lifetimes are reduced significantly. The decay kinetics measured within the long wavelength absorption envelope vary with wavelength, indicating the presence of more than one ylide species. Formation of the ylides occurs *via* a naphthalene-like triplet state in the case of aryl vinyl ethers, while for the thioethers the multiplicity of the ylide precursor could be either singlet or triplet. Product formation in benzene for **5a** and **5b** involves ring closure of the ylide to produce dihydrothiophene and dihydrofuran products, respectively. For short periods of irradiation (either lamps or laser) a mixture of *cis*- and *trans*-fused products is observed, while for prolonged irradiation only the *cis*-fused compound is detected, suggesting a photoenolization mechanism for conversion of *trans* to *cis*. In addition to products derived from ring closure, **9a** provides intramolecular addition product **12**. Conversely, the ylide derived from **9b** gives rise to the [3 + 2] cycloaddition product **13**.

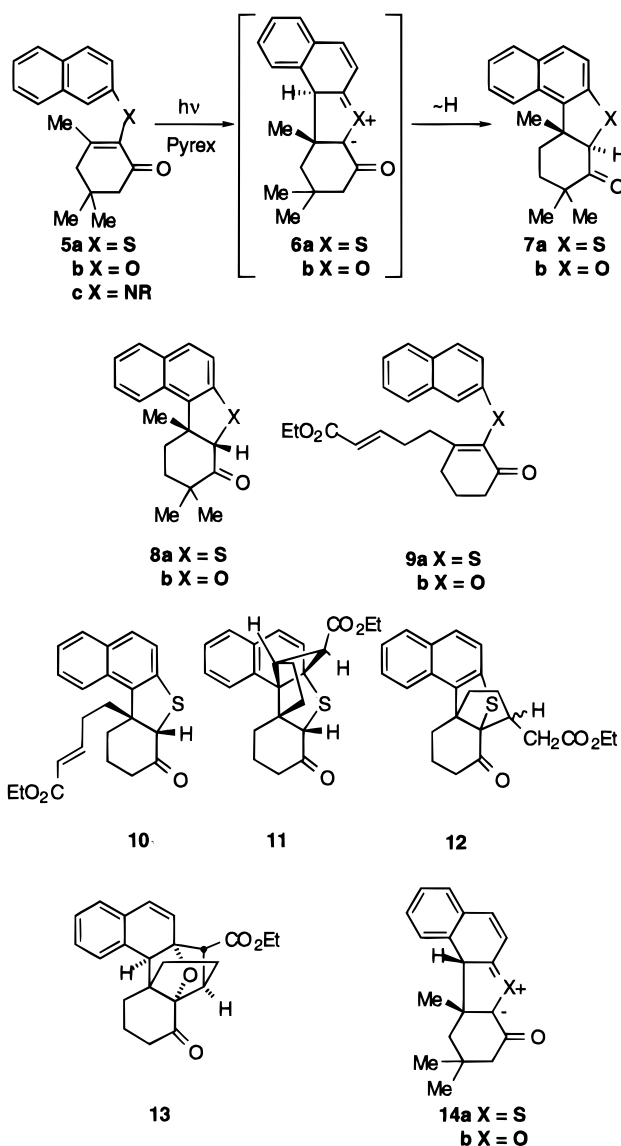
Introduction

The photoinitiated intramolecular ylide–alkene cycloaddition reaction provides a method for construction of up to three rings and six chiral centers in a single experimental operation from relatively simple starting materials.^{1–5} This one-step process involves photocyclization of aryl vinyl ether, aryl vinyl sulfide, or aryl vinyl amine systems **1** to generate ylide intermediates **2** that can undergo addition to a pendant alkene to provide **3** or **4**. The current study details the use of laser flash photolysis techniques to characterize these ylides and to probe the reactivities of excited state intermediates.



The photochemical six-electron heterocyclization reaction (**5** → **7**) reportedly proceeds via *trans*-fused ylide intermediates **6**.⁶ Extensive studies have been carried out to elucidate the mechanism for this reaction. There is now substantial evidence, both chemical and spectro-

scopic, that supports the intermediacy of the ylide system **6**.^{7–9}



[†] Permanent Address: Boston University, Boston, Massachusetts.

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Studies concerning intramolecular addition reactions of ylide systems such as **2** demonstrate that product distribution is influenced by reaction temperature, substrate structure, and wavelength of irradiation. It was of interest, therefore, to examine the properties of the ylide intermediates that are involved in these transformations. Four systems were selected for study. Aryl vinyl sulfide **5a** and aryl vinyl ether **5b** incorporate simple chromophores, and previous studies have shown that they efficiently provide products **7** and **8**, respectively, upon photolysis. Aryl vinyl sulfide **9a** and aryl vinyl ether **9b** incorporate more complicated functionality and, again, have been shown previously to give rise to products resulting from intramolecular ylide alkene addition. Laser flash photolysis data have been reported previously for **5b**.^{7,8b} However, there are no reports on transients derived from **5a**, **9a**, or **9b**.

Results and Discussion

One-Laser Flash Photolysis. (i) Aryl Vinyl Sulfides. Laser flash photolysis of the sulfur-containing compound **5a** in nitrogen-saturated benzene yielded a long-lived transient with broad absorption maxima in the 600–800 nm region and a second, weaker band with λ_{max} 450 nm (Figure 1, Table 1). These absorptions are assigned to a thiocarbonyl ylide produced by cyclization of the naphthalene and vinyl moieties. A *trans* ring-fusion as shown in **6a** is inferred from an expected conrotatory cyclization¹⁰ and has been demonstrated for related dipole systems via ylide trapping experiments.^{4,9} However, the possibility of *cis*-fused system **14a** has not been ruled out.

Several spectroscopic and kinetic characteristics lead to the identification of the transient as a thiocarbonyl ylide: (i) the absorption spectrum closely resembles that of the corresponding carbonyl ylide reported by Wolff,^{8b} several structurally related thiocarbonyl ylides described by Herkstroeter and Schultz,⁷ and a variety of carbene-derived sulfur and oxygen ylides;¹¹ (ii) the observed lifetime is typical of carbonyl and thiocarbonyl ylides in solution—for example, both Wolff and Schultz reported lifetimes on the millisecond time scale; (iii) the addition of MeOH, a known quencher of zwitterionic species via proton transfer, significantly decreased the observed lifetime (thus, the decay rate constant increased by 1 order of magnitude when photolysis was carried out in 50:50 MeOH:benzene).

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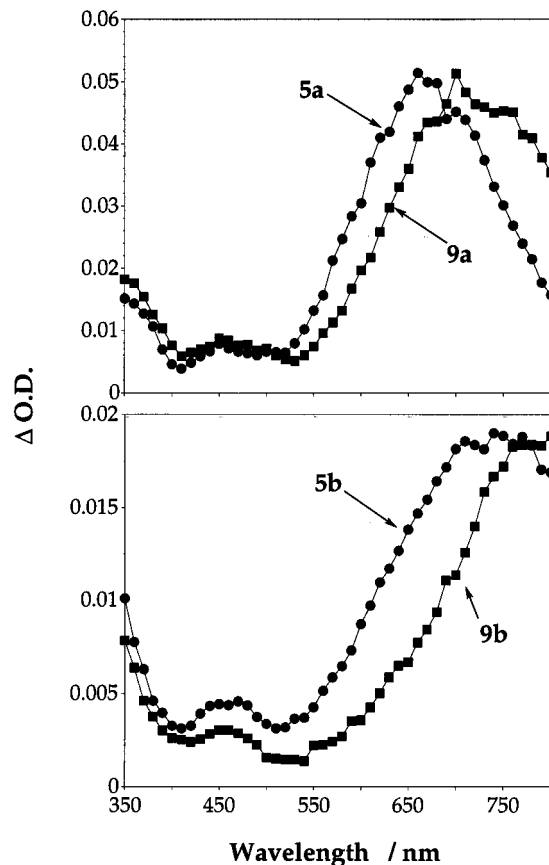
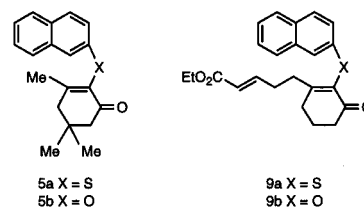


Figure 1. Transient absorption spectra of ylides derived from **5a** and **9a** (top) and **5b** and **9b** (bottom) following 308 nm photolysis in nitrogen-saturated benzene. Spectra were obtained 1 μ s after the laser pulse.

Table 1. Lifetimes (μ s) of Carbonyl and Thiocarbonyl Ylides Produced on Photolysis of the Indicated Starting Materials in Benzene and Methanol^a

solvent	compd 5a		compd 5b	
	750 nm	600 nm	830 nm	630 nm
C ₆ H ₆	60	260	52	64
CH ₃ OH	1.6	1.6	<0.1	<0.1
solvent	compd 9a		compd 9b	
	750 nm	600 nm	830 nm	630 nm
C ₆ H ₆	52	280	10	8.3
CH ₃ OH	0.46	0.63	<0.1	<0.1

^a Lifetimes were measured at two different absorption wavelengths within the ylide absorption band.

Kinetic analysis of decay lifetimes at various wavelengths within the long wavelength absorption band revealed that, while first-order behavior was observed, the lifetimes calculated were dramatically dependent on the monitoring wavelength within the band. For example, at 600 nm, the lifetime was 260 μ s versus 60 μ s at 750 nm. Schultz also found two first-order decays within the long wavelength absorption envelope of several similar thiocarbonyl ylides.⁷ In those systems the

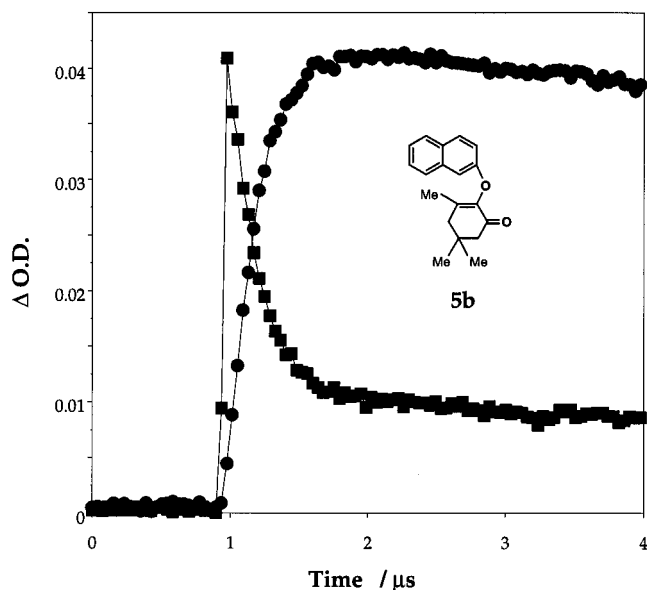


Figure 2. Transient decay obtained at 440 nm (square symbols) and 750 nm (round symbols) following 308 nm photolysis of compound **5b** in nitrogen-saturated benzene.

lifetimes differed by as much as 2 orders of magnitude depending on the absorption wavelength monitored. Similar spectroscopic and kinetic behavior was observed for **9a**.

(ii) Aryl Vinyl Ethers. Intermediates derived from aryl vinyl ethers **5b** and **9b** exhibited behavior different from those produced from the aryl vinyl thioethers. Photolysis of **5b** yielded two major transient absorption bands (λ_{max} 750, 440 nm) exhibiting dramatically different lifetimes and a third minor absorption band (λ_{max} 460 nm) that decays at roughly the same rate as the long-lived major band at 750 nm (see Figures 1 and 2). The long-lived species absorbing at 750 nm was identified as the ylide and correlates well with data reported by Wolff.^{8b} The second band (λ_{max} 440 nm) was produced concurrently with the laser pulse and exhibits fast and slow decaying components. The short-lived component decayed by first order kinetics with $\tau = 200$ ns. Figure 2 displays the resolvable growth of the ylide absorption at 750 nm and the corresponding decay of the 440 nm band. The similarity in kinetics for growth of the 750 nm species and the concomitant decay of the short-lived 440 nm transient was not observed in the sulfur series of compounds. We tentatively assign the major (short-lived) component of the low wavelength band to a localized naphthalene triplet-triplet absorption. Support for this assignment is given by the transient behavior in the presence of oxygen. In air-saturated solutions, the decay rate of the short-lived 440 nm absorption and the growth rate of the long wavelength band were significantly enhanced (behavior also noted by Wolff).^{8b} Phosphorescence measurements carried out at low temperatures in methylcyclohexane glasses yielded spectra that were nearly identical in shape and wavelength position to that of naphthalene itself ($E_{0-0} = 60.7$ kcal/mol for **5b** versus 60.9 kcal/mol for naphthalene).¹² Additional triplet quenching experiments were attempted using 1,3-cyclohexadiene as a quencher. However, permanent chemical reaction led to complex transient behavior.

A transient absorption spectrum obtained following decay of the short-lived species (1 μ s after the laser pulse) exhibits a peak at λ_{max} 750 nm and a minor absorption band at λ_{max} 460 nm. Both bands display similar decay kinetics and are attributed to absorption by the ground state ylide. The ylide absorption at 460 nm is responsible for the slow decay observed at 440 nm. Like the corresponding aryl vinyl thioether systems, kinetic analysis of **5b** points to two ylide bands within the same long wavelength absorption envelope. However, there is a much smaller difference in their lifetimes (52 μ s at 830 nm versus 64 μ s at 630 nm) than in the corresponding thioether systems (60 μ s at 750 nm versus 260 μ s at 600 nm). Similar behavior was noted for aryl vinyl ether **9b**. Decay rates measured for each of the aryl vinyl ether-derived ylides were faster than for the corresponding thioethers. Thus, the ylides produced from **5b** decayed faster than those from **5a** and **9b** faster than **9a**. Reaction with added MeOH was also more efficient for the ether-derived ylides. While the lifetimes of the sulfur ylides for **5a** and **9a** decreased to 1.6 μ s in neat MeOH, the ylide lifetimes for the oxygen systems **5b** and **9b** in MeOH were less than 100 ns.

(iii) Multiplicity of the Ylide Precursors. Kinetic analysis suggests that the transformation of aryl vinyl sulfides and aryl vinyl ethers to ylide systems occurs via states with different multiplicity. As noted earlier, photolysis of **5b** yielded two major transient absorption bands exhibiting dramatically different lifetimes. Growth kinetics for the long wavelength band correlate well with the decay kinetics of the 440 nm band, which we have assigned to a localized naphthalene triplet-triplet absorption. Ylides derived from **9b** exhibit similar kinetic behavior. Thus, for these aryl vinyl ethers, ylide formation is clearly via the triplet manifold.

On the other hand, ylides derived from **5a** and **9a** were produced concurrently with the laser pulse. This observation, coupled with the lack of an observable naphthalene triplet absorption, suggests involvement of a short-lived singlet state in ylide formation. This result is consistent with data reported by Schultz in which the majority of aryl vinyl sulfide systems examined provided ylides via the singlet manifold. However, Schultz also reports that substrates that incorporate the vinyl substituent in a ring, precluding free rotation in the excited state, react through a combination of singlet and triplet state manifolds. In addition, Schultz was able to show ylide formation following triplet sensitization of several naphthyl vinyl sulfides.^{7,9}

The lack of observation of a triplet absorption does not preclude a triplet route, since it is possible that reaction from the triplet is faster than the time resolution of our instrumentation. In fact, phosphorescence measurements indicate that the triplet states of **5a** and **9a** are formed following excitation although apparently in low yield. However, since the triplet energies of the naphthalene groups in the sulfur and oxygen compounds differ only slightly, it is difficult to rationalize a large difference in triplet reactivity on the basis of energy arguments alone. Alternatively, production of the triplet may be less efficient in the sulfur compounds than in the oxygen analogs reflecting a greater contribution to ylide formation from the short-lived singlet.

(iv) Ylide Lifetimes. It is reasonable to expect a difference in lifetimes for ylides derived from systems **5** versus those derived from **9**. Ylides derived from either **5a** or **5b** are expected to exhibit decay kinetics which

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reflect the efficiency of the intramolecular hydrogen shift whereas ylides derived from **9a** and **9b** can decay by either intramolecular hydrogen shift or an intramolecular ylide-alkene addition process. Indeed, ylide lifetimes for **9b** are considerably shorter than for **5b**. Compound **9b** provides exclusively compound **13**. The structure of **13** is consistent with intramolecular six-electron conrotatory cyclization occurring from **9b** to provide ylide **2b** and subsequent intramolecular [3 + 2] dipolar cyclization to the side chain olefin. Conversely, sulfur-containing systems show little difference in ylide lifetime regardless of the available modes for decay. Compound **9a** provides three products, **10–12**. Both **10** and **11** occur as products of intramolecular hydrogen shift. Compound **10**, which is formed initially, is converted to **11** by a secondary photoprocess involving intramolecular [2 + 2] cycloaddition. The mechanism for formation of compound **12** is not known. However, previous work indicates that it may involve an intramolecular ylide olefin addition process. Furthermore, neither **10** nor **11** is involved in the formation of **12**.⁵ Considering the additional pathways that are available to **9a** it is surprising that the lifetimes for the ylides derived from **5a** and **9a** are so similar. The reason for this similarity is unclear at this time.

Laser and Lamp Product Studies. Product studies were carried out to correlate preparative-scale photochemistry with our time-resolved data. Pyrex-filtered Hg lamp irradiation of **5a** in benzene provided exclusively *cis*-fused product **8a** at concentrations ranging from 10^{-3} to 10^{-4} M. Interestingly, analysis of mixtures produced by 308 nm laser irradiation of **5a** showed evidence of both *cis*- and *trans*-fused products **8a** and **7a**. The ratio of **8a** to **7a** increased with increasing number of laser pulses. Previous studies support initial formation of *trans*-fused ylide intermediates that undergo suprafacial hydrogen migration to provide *trans*-fused dihydrofuran and dihydrothiophene systems. These are readily converted to the corresponding *cis*-fused isomers with mild base treatment.

Photolysis of aryl vinyl ether **5b** provided mixtures of *cis* and *trans* products in both the laser and lamp studies. Pyrex-filtered Hg lamp irradiation of **5b** in benzene provided a mixture of *cis*-fused and *trans*-fused products that varied with the concentration. Thus, photolysis of **5b** at 3.5×10^{-4} M gave a mixture of **8b** to **7b** in a ratio of 3.6:1. Photolysis of **5b** at 9×10^{-3} M, however, provided **8b** and **7b** in a ratio of 6.4:1. Finally, photolysis of **5b** in methanol provided exclusively *cis*-fused product **8b**.

The observation of exclusively *cis*-fused products in the preparative-scale work and mixtures of *cis*- and *trans*-fused in the laser photolysis mixtures of **5a** supports a mechanism involving photoenolization of the initial cycloadducts. In order to confirm this, the following experiment was carried out. A sample of **5a** was irradiated in benzene with 1500 pulses from the 308 nm laser source. Product analysis by NMR showed the presence of both **7a** and **8a**. The sample was then resubjected to photolysis, this time under preparative-scale conditions (25 min, Pyrex-filtered Hg lamp irradiation). Product analysis of the resulting mixture by NMR showed only *cis*-fused product **8a**. Thus, disparity in *cis*-*trans* product ratios that were observed between the preparative-scale and time-resolved work can be rationalized in terms of photoenolization of the initially formed *trans*-fused products.¹³

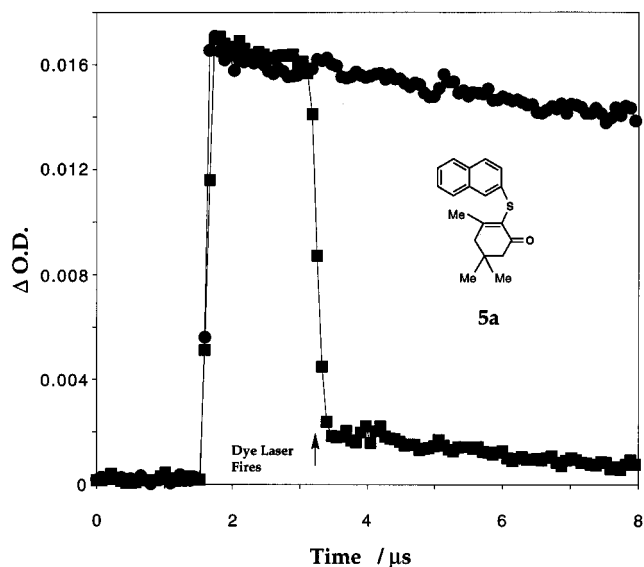


Figure 3. Transient decay obtained at 600 nm following one-laser (308 nm; round symbols) and two-laser (308 + 640 nm; square symbols) photolysis of compound **5a** in nitrogen-saturated benzene.

Two-Laser Photolysis. Theoretical studies predict that carbonyl ylides may undergo fragmentation following photoexcitation,^{14,15} and numerous experimental examples exist that support this prediction.¹⁶ Direct time-resolved evidence for ylide photochemistry was obtained by addition of fluorenylidene with acetone.¹⁷ In this case, 590 nm irradiation resulted in efficient bleaching of the ylide absorption, indicating the occurrence of photochemistry. Interestingly, it was found that ylide photolysis merely accelerated the thermal decay process, i.e., ring closure to form the oxirane. Given the reported photo-reactivity of carbonyl ylides, we have carried out two-laser studies on each of the sulfur and oxygen systems. Figure 3 shows the one- and two-laser decays of ylide **5a**. It is clear that the second laser pulse (640 nm dye laser) causes extensive, irreversible depletion of the ylide absorption. In fact, this behavior was observed for each of the four ylides studied. This result is interesting in view of Schultz and Herkstroeter's observation⁷ that the transients produced from 2-naphthyl-1-indenyl sulfide decay with a rate that is independent of the monitoring light intensity. However, we note that the intensity of the second laser used in this two-laser experiment was much higher than the monitoring lamp in Schultz and Herkstroeter's study and, therefore, would be expected to greatly enhance any photochemical reactions of the ylide. Transient absorption spectra obtained following the second laser pulse failed to show any new transient absorptions. For this reason, two-laser product-oriented studies were carried out in which samples of **5a** were subjected to several hundred pairs of laser pulses. The samples were concentrated and analyzed by NMR. How-

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ever, preliminary results indicate that no products other than those observed following one-laser irradiation were formed (dihydrothiophenes). While these results are preliminary and more quantitative experiments are in progress, at this point it is tempting to conclude that the H-transfer responsible for thermal ylide decay in **5a** may also occur photochemically.

Analogous two-laser behavior has been reported for the carbonyl ylide formed by the reaction of acetone and fluorenylidene. While the long wavelength absorption of this ylide was efficiently depleted by a second laser pulse, no new product formation was observed.¹⁷

Experimental Section

Chemicals. Compounds **5a**,¹⁸ **5b**,^{8b} **9a**,⁵ and **9b**⁴ were prepared according to previously published procedures. Aldrich spectrophotometric grade solvents were employed for time-resolved laser experiments and were used as received. Spectrophotometric grade benzene used for photochemical product studies was purified by distillation from CaH₂ under nitrogen.

Laser Flash Photolysis. The time-resolved laser flash photolysis apparatus has been described in detail elsewhere.¹⁹ Briefly, for kinetic studies and transient absorption spectra, solutions of the aryl vinyl compounds were prepared at concentrations sufficiently large to give optical densities in the

range 0.6–0.8 at the excitation wavelength (~0.3 mM). Unless otherwise noted, the solutions were continuously purged with a stream of nitrogen and were caused to flow through a specially constructed quartz cell (7 mm × 7 mm) by means of a peristaltic pump. This ensured that a fresh volume of solution was exposed to each laser pulse, thus avoiding accumulation of photoproducts. Samples were irradiated with the pulses of a Lumonics EX 510 excimer laser (308 nm; ~20 mJ/pulse; 8 ns pulse duration). In the two-laser studies, the 308 nm pulse was followed, after a period of 1–2 μs, by the pulse from a flashlamp-pumped dye laser (640 nm; ~150 mJ; 350 ns).

Laser Product Studies. Concentrations were increased to approximately 1 mM for these studies. Typically, 3 mL of a nitrogen-purged sample in a 1.0 cm quartz cell was irradiated with as many as 1800 laser pulses or pairs of pulses in the two-laser experiments. A magnetic stirrer provided agitation in order to ensure that the entire sample was exposed to the laser radiation. Product mixtures were analyzed by ¹H and ¹³C NMR.

Lamp Product Studies. Experiments were conducted using a 450-W Canrad-Hanovia medium-pressure quartz mercury-vapor lamp. The lamp was placed in a water-cooled Pyrex immersion well. Reaction solutions were saturated with argon prior to irradiation.

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