

## Explorations of the Heteroatom Directed Photoarylation Reaction. A Review of the Photoinitiated Intramolecular Cycloaddition Reactions of Ylide Systems

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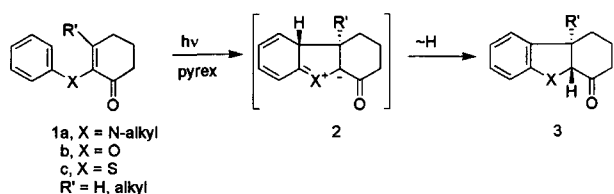
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The photoinitiated intramolecular ylide-olefin addition has been developed as an approach for the construction of one ring and two chiral centers, two rings and three chiral centers or three rings and six chiral centers in a single experimental operation from relatively simple starting materials. These investigations have uncovered several interesting and unusual reactions, which are sensitive to controls such as wavelength, temperature and solvent.

**key words:** Photochemistry, ylide, cycloaddition, photoarylation

### INTRODUCTION

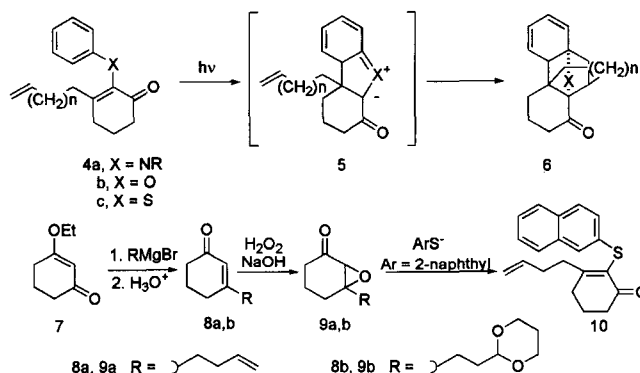
The photochemical six-electron heterocyclization reaction (1→3) reportedly proceeds via trans-fused ylide intermediates 2 [1]. Extensive studies have been carried out to elucidate the mechanism for this reaction. There is now substantial evidence, both chemical and spectroscopic, which supports the intermediacy of the ylide system 2 [2-4]. Surprisingly, very little attention has been focused on the reactions of these ylides.



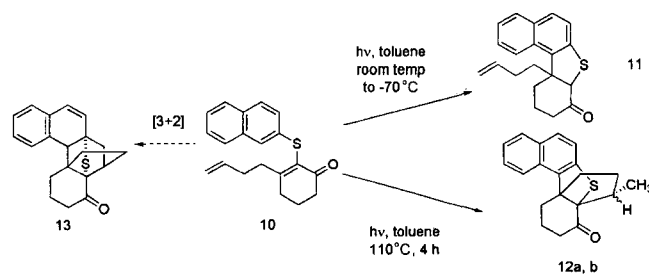
### RESULTS AND DISCUSSION

We initially chose to investigate intramolecular addition reactions involving the ylide species 5 generated on photocyclization of enone system 4 [5-7]. Preliminary investigations were carried out with the naphthyl vinyl sulfide 10 [8,9]. The preparation of 10 is representative of the methods used in the synthesis of photoprecursors.

Irradiation of 10 in toluene ( $2 \times 10^{-3}$  M) at temperatures ranging from  $-70^\circ\text{C}$  to  $25^\circ\text{C}$  provided the photocyclized product 11 in 81% isolated yield [8,10]. Conversely, high temperature photolysis of a solution of 10 in toluene ( $3 \times 10^{-3}$



M,  $110^\circ\text{C}$ ) for 3.5 h resulted in formation of the addition product 12 which was obtained as a mixture of diastereoisomers (79% isolated yield). We note that ring closure in the naphthyl vinyl sulfide 10 occurs only toward the 1-position of the naphthalene system. Control experiments demonstrate that both light and heat are required to effect the formation of 12. Thus, after heating a solution of 10 in toluene at reflux temperature for 6 h in the dark, only starting material was recovered. Likewise, 11 was stable toward refluxing toluene and under the reaction conditions (heat and light) used for formation of 12. None of the anticipated [3+2] adduct 13 was observed in any of these reactions.

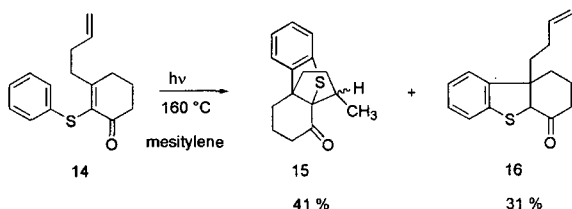


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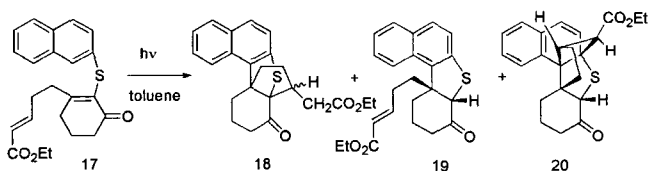
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The photochemistry of phenyl vinyl sulfide **14** was also explored. However, the conversion (**14**→**15**) requires a higher reaction temperature ( $4 \times 10^{-3}$  M, mesitylene,  $160^\circ\text{C}$ ) than the corresponding addition reaction **10**→**12**. Furthermore a significant amount of photocyclized “untrapped” product **16** was observed in the reaction mixture (31%). Again control experiments demonstrated that both heat and light are required to effect the transformation of **14** to **15**.

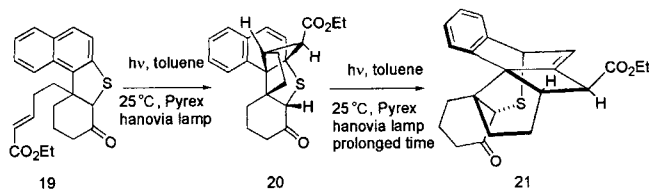


Incorporation of activating groups in the side chain markedly influences the facility and outcome of the intramolecular addition reaction [11-13]. Derivatives bearing an ethyl butenoate side chain were readily prepared from the corresponding acetal **9b** by i) phenolate or thiolate promoted epoxide opening ii) acetal hydrolysis and iii) Wittig olefination. Pyrex filtered irradiation of a solution of **17** in toluene ( $10^{-3}$  M) at room temperature provided predominantly intramolecular addition product **18** (84% isolated yield). Formation of **18** can even be observed at  $-70^\circ\text{C}$  (~60% isolated yield).

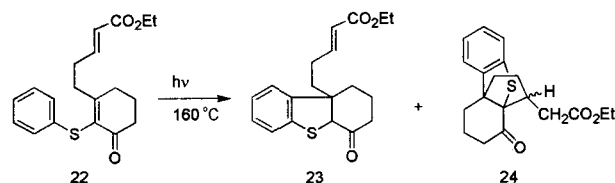


Two additional products were isolated from the room temperature photolysis of **17**. Formation of **19** is consistent with an intramolecular hydrogen shift from an intermediate thiocarbonyl ylide [2]. It has been reported by Schultz that ring closure products such as **3c** result from conrotatory ring closure to provide a trans-fused ylide **2c** followed by suprafacial hydrogen shift to yield the trans-fused dihydrothiophene. If this is indeed the case the observed cis-fused stereochemistry of dihydrothiophene can be rationalized on the basis of facile enolization of the initially formed trans dihydrothiophene. Other work in our laboratory supports this hypothesis. [2b] Compound **20** results from a photoinitiated intramolecular [2+2] cycloaddition of the dihydrothiophene **19** [14-16]. Thus irradiation of pure **19** in toluene with a Pyrex-Hanovia light source results in clean conversion to adduct **20** (major product) accompanied by the product of allylic rearrangement **21** [17]. Prolonged irradiation of **20** results in complete conversion to rearranged product **21**. Both structures **20** and **21** have been confirmed by X-ray crystallographic analysis. Notably if the

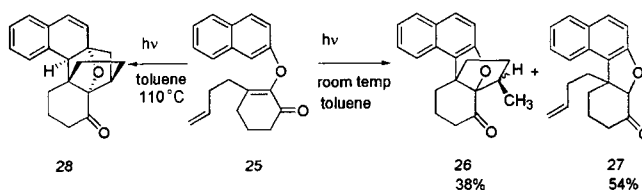
photolysis of **17** is carried out in methanol compound **19** is obtained almost exclusively. Thus it is possible to direct the course of the photoreaction to favor intramolecular addition product **18**, ring closed product **19**, [2+2] product **20** or [2+2]-allylic rearrangement product **21**.



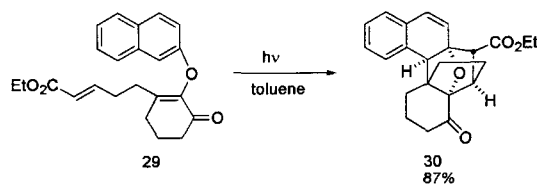
Consistent with earlier work, the intramolecular addition reaction is less favorable for systems which incorporate a phenyl group as the aromatic component. Thus photolysis of **22** must be carried out at elevated temperatures ( $160^\circ\text{C}$ ) before any appreciable intramolecular addition product **24** is observed.



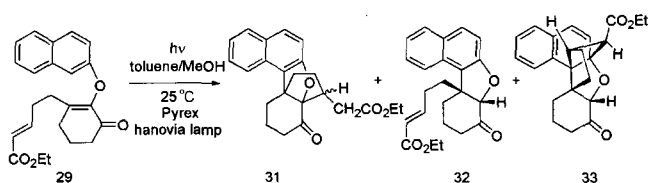
Replacement of sulfur with oxygen effects a dramatic change in reactivity. Photolysis of aryl vinyl ether **25** in toluene ( $3 \times 10^{-3}$  M) for 1 h at room temperature afforded the intramolecular addition product **26** (38%) along with photocyclized product **27** (54%). Notably, formation of the oxygen containing system **26** occurs at room temperature compared to  $110^\circ\text{C}$  for the sulfur analog. Furthermore high temperature photolysis of **25** provided a new product **28** resulting from [3+2] ylide alkene cycloaddition [11-12].



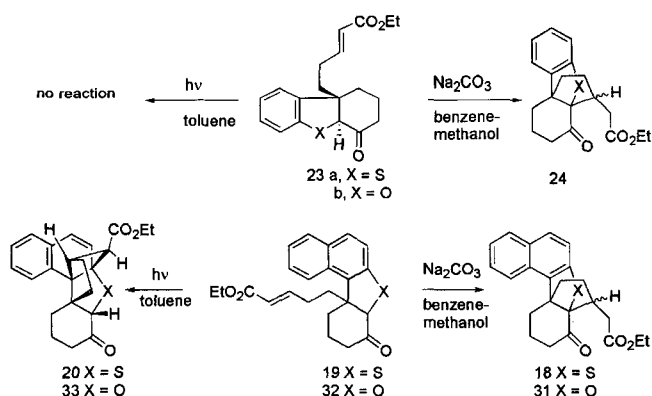
Naphthyl vinyl ether **29** bearing an ethyl butenoate side-chain ( $10^{-3}$  M, toluene) undergoes facile photoinitiated intramolecular [3+2] ylide alkene cycloaddition to give **30**. This reaction proceeds in high yield and can be carried out at  $-78^\circ\text{C}$ .



The influence of solvent on the photolysis of **29** is particularly dramatic. Thus photolysis of **29** in toluene/methanol did not give any of the usual [3+2] adduct **30**. Rather formation of **31** (45%), **32** (24%) and **33** (23%) was observed. As with the sulfur analog **20**, compound **33** results from ylide protonation to give the cis-fused dihydrofuran **32** followed by intramolecular [2+2] cycloaddition [15-16].

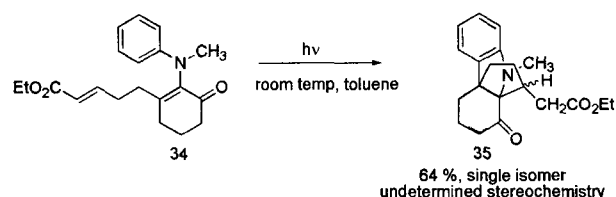


The preparation of some photoproducts has been carried out using dark reactions. Thus, it is possible to effect a base catalyzed conversion of compounds **23** to **24** in the absence of light. Control experiments demonstrate that compounds **23** are not converted to **24** under the normal conditions used for photolysis. We have also effected the base catalyzed conversions **19**→**18** and **32**→**31**. Note, however, that under the conditions of the photolysis **19** gives **20** and **32** gives **33**.



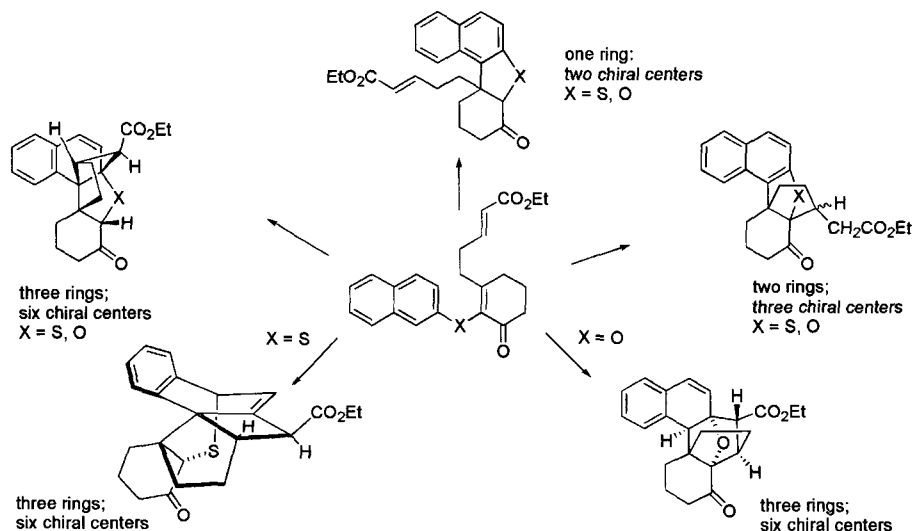
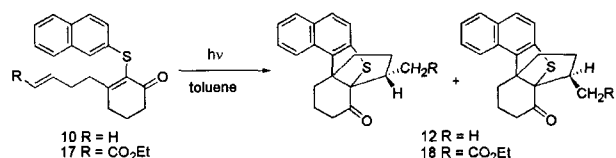
In summary product distribution in the tandem photocyclization-intramolecular ylide alkene cyclization is sensitive to temperature, solvent, electronic and structural features. Thus it is possible to direct formation of one ring and two chiral centers, two rings and three chiral centers or three rings and six chiral centers from a single starting material. Secondary photoprocesses which proceed in good yield and with excellent stereocontrol allow for formation of three rings and six chiral centers.

Preliminary studies in our laboratory demonstrate that aryl vinyl amines also function well in the photoinitiated ylide alkene cycloaddition reaction. Thus compound **34** provides **35** upon irradiation in toluene.



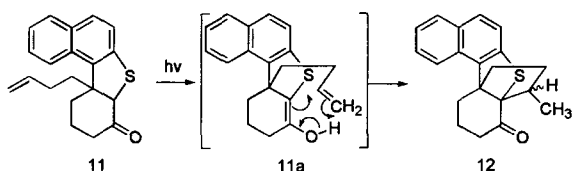
#### Tandem Photocyclization-Intramolecular Addition Reactions of Aryl Vinyl Sulfide. The Mechanism of Proton Shift

As noted earlier aryl vinyl sulfides **10** and **17** give rise to intramolecular addition products **12** and **18** respectively upon irradiation through Pyrex. Formation of these products requires photoarylation, carbon-carbon bond formation with the side chain and the addition of a hydrogen to the terminus of the side chain alkene. In an attempt to understand the mechanistic pathways underlying formation of these and other similar cycloaddition products a series of mechanistic studies were carried out [18].

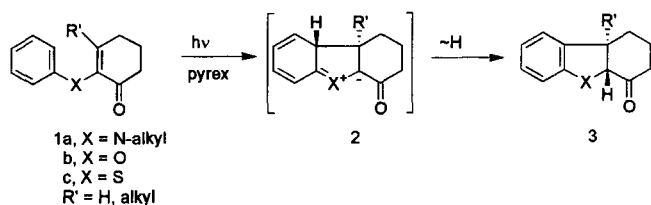


In order to ascertain if the hydrogen addition involved an intermolecular process such as abstraction from the solvent, the photolysis was conducted in toluene- $d_8$ . Irradiation of **10** with a Pyrex filtered light source at 110°C gave **12** with no observable deuterium incorporation. Likewise, irradiation of a solution of **17** in toluene- $d_8$  (room temperature) gave **18** which was free of deuterium. Thus hydrogen abstraction does not appear to involve the solvent. Dilution experiments were also carried out within the concentration range employed in our normal photolysis conditions to determine if hydrogen abstraction is an inter- or intramolecular process. The concentration profile for the photolysis of **17** showed that the formation of intramolecular addition product **18** is independent of the concentration of the starting material and supports an intramolecular hydrogen abstraction process.

One plausible intramolecular mechanism involves an initial formation of hydrogen shift product **11** followed by enolization to give **11a**. Subsequent ene-like reaction produces **12**. However, when **11** was prepared independently and subjected to the reaction conditions, only unchanged starting material was recovered.

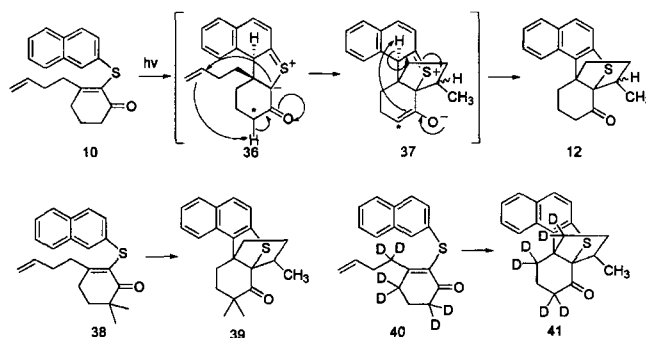


In view of the substantial evidence, both chemical and spectroscopic, that supports the intermediacy of an ylide system in the photochemical six-electron heterocyclization reaction (**1**→**3**) [2-4] we considered hydrogen transfer pathways that could proceed via these intermediates.



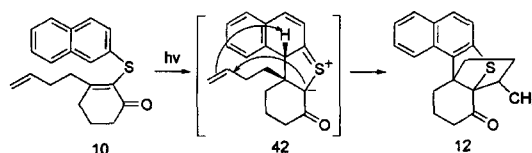
One possible mechanism for production of the intramolecular addition products **12** (and by similar mechanism **18**) involves initial formation of trans-fused ylide **36**, which can undergo an intramolecular ene-like reaction to provide **37** followed by an inter- or intramolecular enolate protonation to give **12**. In this case the hydrogen transfer occurs from the C\* center to the alkene terminus. Accordingly two experiments were carried out to test the viability of this process. In the first involving compound **38**, the two hydrogens on C\* which would be expected to transfer were replaced by methyl groups. However, the presence of these methyl groups did not prevent the formation of hydrogen transfer product **39**. In the second experiment, deuterium labeled substrate **40** was prepared in

an attempt to follow the course of the hydrogen transfer. However, the irradiation of hexadeuterated precursor **40** furnished product **41** in which all of the deuterium remained at the same positions as in the starting material. Consequently a mechanism involving hydrogen transfer from C\* was ruled out.

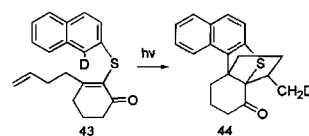


Next we considered the possible involvement of a cis-fused ylide. Orbital symmetry considerations favor a conrotatory cyclization of the aryl vinyl sulfide systems to provide trans-fused thiocarbonyl ylides. Formation of cis-fused ylide from excited state starting material is forbidden by the Woodward-Hoffmann rules. However, studies carried out by Schultz and Herkstroeter [2a] as well as in our own laboratory [2b] show that two transients are formed on laser flash photolysis of the aryl vinyl sulfide systems. Both exhibit properties characteristic of thiocarbonyl ylides and thus it is possible that both cis and trans-fused ylide are produced.

Ring closure of **10** to provide cis-fused ylide **42** can give rise to **12** via an ene-like pathway shown.

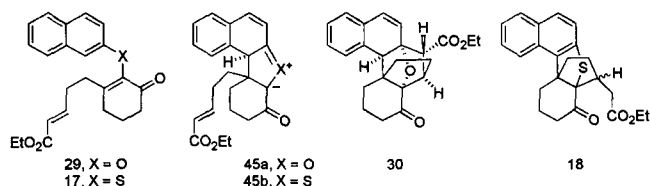


In order to test this hypothesis deuterio derivative **43** was prepared and subjected to the usual reaction conditions. Formation of **44** from **43** is consistent with a mechanism involving a cis-fused ylide (e.g. **42**). Although these results are contrary to the anticipated formation of a trans-fused ylide, they are supported in part by the observed formation of two ylide species in spectroscopic studies carried out by Shultz's group and our own.



*Tandem Photocyclization-Intramolecular [3+2] Cycloaddition of Aryl Vinyl Ether Systems. The Role of the Aromatic Component*

Studies in our laboratory demonstrate that structural modifications greatly influence the outcome of the photo-initiated intramolecular cycloaddition reaction. Thus aryl vinyl ethers **29**, which incorporate a naphthalene unit, undergo facile photocyclization to provide ylide **45a** and subsequent intramolecular [3+2] cycloaddition to afford adduct **30**. Conversely, aryl vinyl sulfides and phenyl vinyl ethers provide products arising from photocyclization and intramolecular ene-like addition (**17**→**18**). Finally, electron withdrawing groups on the dipolarophile greatly facilitate both intramolecular addition pathways. Herein we describe approaches to facilitate the intramolecular [3+2] cycloaddition for application to natural products synthesis.



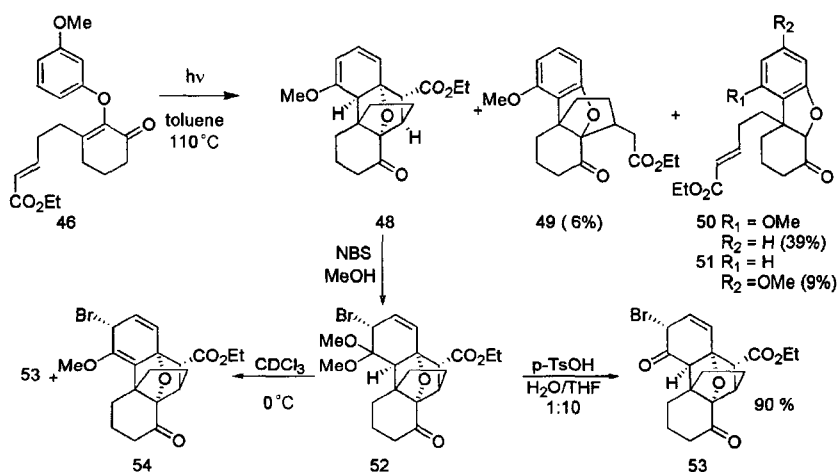
Two factors account for the high reactivity of the naphthalene photoprecursors. i) Frontier Molecular Orbital (FMO) theory predicts that dipolar cycloadditions of thiocarbonyl ylides and carbonyl ylides are controlled by the HOMO (1,3-dipole)-LUMO (dipolarophile) interaction [6]. Thus factors which raise the HOMO of the dipole, such as conjugating and electron donating substituents, and/or lower the LUMO of the dipolarophile, such as electron withdrawing groups, will favor [3+2] cycloaddition. ii) Ylides derived from naphthalene systems benefit from extended conjugation and preservation of aromatic character. Thus they may have longer lifetimes than ylides derived from phenyl substituted systems in which

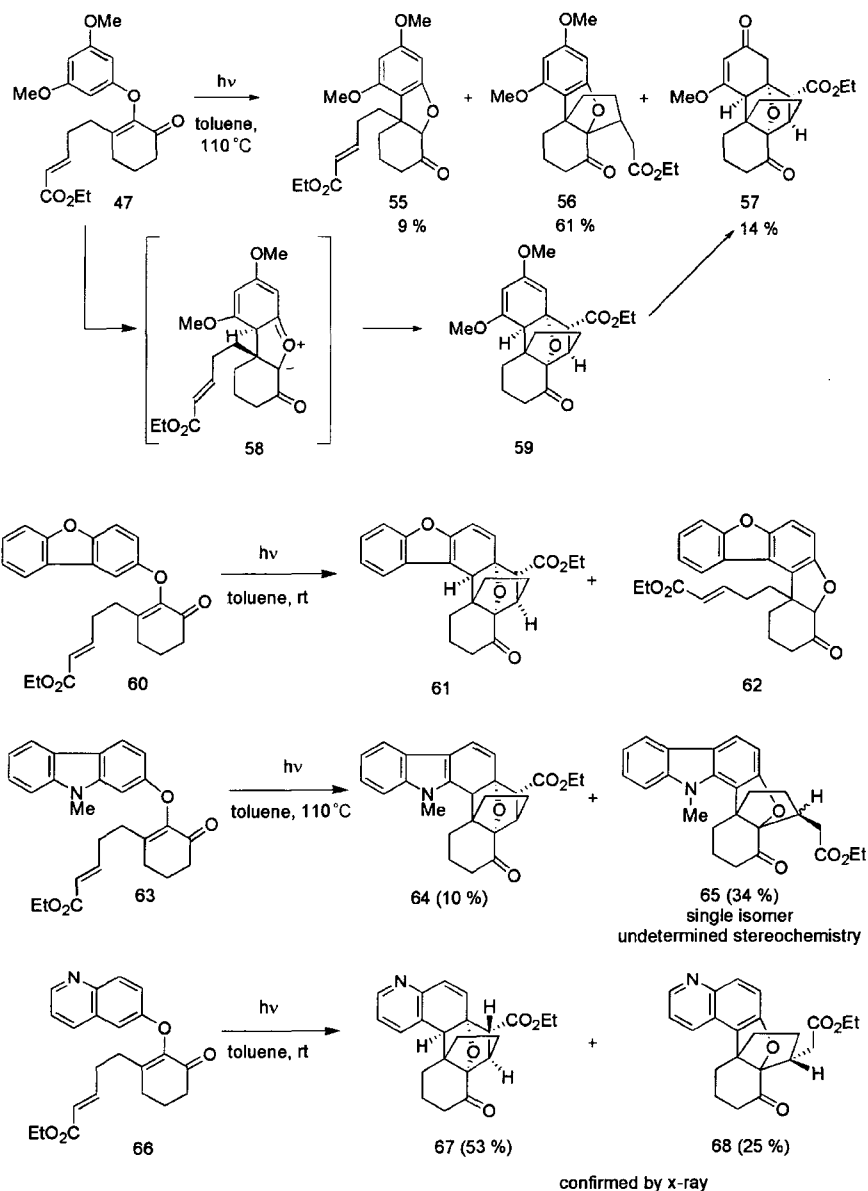
aromaticity is lost. Consequently, electron rich aromatic systems or bicyclic heteroaromatic systems (similar to naphthalene electronically) should perform well in the photoinitiated intramolecular ylide alkene [3+2] cycloaddition.

Compounds **46** and **47** were prepared from 3-ethoxy-cyclohexenone by the usual procedure [12] to evaluate the impact of electron rich 1,3-dipole systems on the intramolecular [3+2] cycloaddition. Photolysis of **46** at 110°C provided a mixture of regioisomers **48-51** resulting from ylide alkene addition (**49**), hydrogen migration (**50**, **51**) and intramolecular [3+2] ylide-alkene cycloaddition (**48**). Support for the formation of **48** is given by the following conversions. Treatment of **48** with *N*-bromosuccinamide in methanol provides the bromoketal **52**. Axial addition of Br to the enol ether is expected to provide product with the stereochemistry shown. Acid hydrolysis of **52** (*p*-TsOH, THF, H<sub>2</sub>O) provides bromo ketone **53**. Similarly, **52** is converted to a mixture of **53** and **54** on standing in CDCl<sub>3</sub>.

Photolysis of **47** at 110°C in toluene provides hydrogen shift product **55**, intramolecular addition product **56**, and a third product assigned by NMR analysis as **57**. Presumably, **57** forms via photocyclization and intramolecular [3+2] cycloaddition to the intermediate carbonyl ylide **58** and subsequent hydrolysis of the resulting enol ether **59** by adventitious water to provide **57**. Notably **57** was not detected in the crude NMR spectrum.

Photoprecursors which incorporate bicyclic heteroaromatic components were also examined. Thus **60**, **63**, and **66** were prepared by coupling the commercially available hydroxyl substituted aromatic component with cyclohexane epoxide **9b** and subsequent elaboration of the side chain as described previously. Photolysis of **60** in toluene at room temperature provided [3+2] adduct **61** accompanied by hydrogen shift product **62**. Irradiation of **63** at 110°C yielded both [3+2] adduct **64** and intramolecular addition product **65**. Similarly photolysis of **66** (r.t. in toluene) yielded [3+2] adduct **67** and intramolecular addition product **68**. Products **61**, **62**, **64** and **65** provide spectral

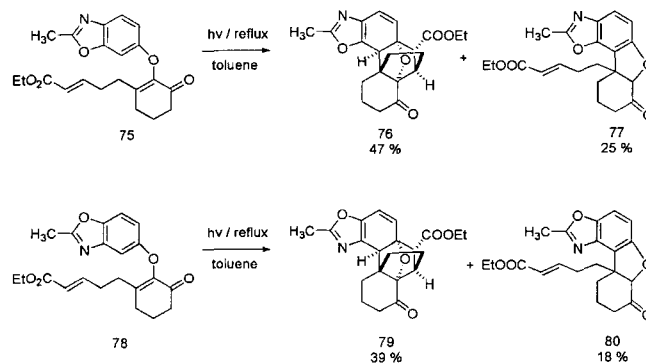
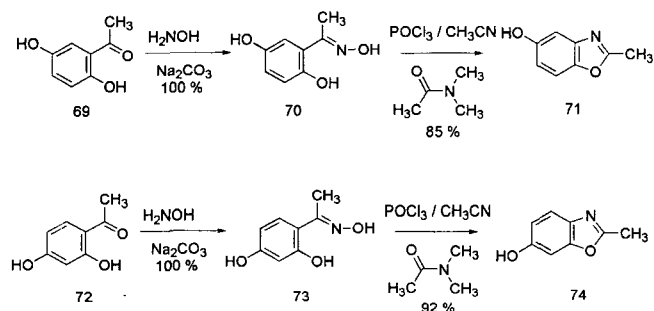




data comparable to compounds for which structures have been confirmed by single crystal X-ray analysis. Assignments for **67** and **68** were confirmed by single crystal X-ray analysis.

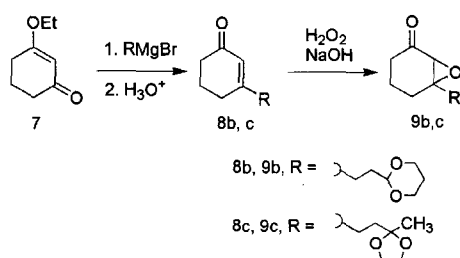
Compounds **71** and **74** were prepared via standard procedures for the synthesis of **75** and **78**.

Irradiation of both **75** and **78** proceeded as expected to provide [3+2] adducts **76** and **74** respectively.



*Tandem Photocyclization Intramolecular Addition Reactions of Aryl Vinyl Ethers, Sulfides and Amines. Addition of the Photochemically Generated Ylide Systems to Heterodipolarophiles*

In continuation of our studies [18] on the Heteroatom Directed Photoarylation we examined intramolecular addition reactions of photochemically generated ylide systems to pendant heterodipolarophiles. Photoprecursors bearing an aldehyde functional group **81**, **82**, **86**, **88**, **90**, **91** and **96** in the side chain were prepared from **9b** via phenolate, thiolate or aryl amine promoted epoxide opening followed by acetal hydrolysis. Compounds **99a,b** and **103** which bear a methyl ketone side chain were prepared by a similar procedure from **9c** via **8c**. Compound **8c** is available from **7** via methyl ketal Grignard addition followed by acid catalyzed hydrolysis and elimination.

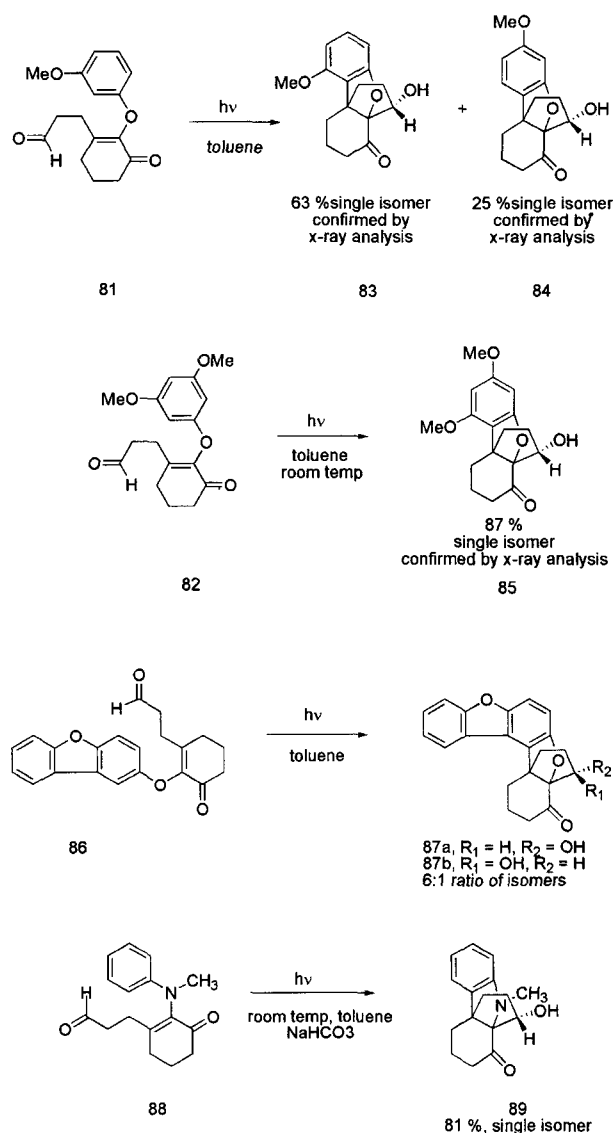


Each of these systems were evaluated as substrates for the photoreaction and all provided products consistent with photoarylation and subsequent ylide-dipolarophile addition. It is of interest to examine the kinds of products formed as well the stereoselectivity as a function of structural features in the starting material.

Photolysis of aryl vinyl ether **81** provided regioisomeric products **83** (63%) and **84** (25%) resulting from initial ring closure to the 2- or 6-position of the aromatic system followed by stereospecific addition to the side chain aldehyde. In like manner, photolysis of **82** provided **85** as a single diastereoisomer (87%). The observed stereoselectivity in the side chain addition of these aryl vinyl ether systems appears to be general when the heterodipolarophile is an aldehyde. The resulting product is typically a single stereoisomer (or in some cases the major isomer) in which the resulting alcohol is positioned toward the aromatic system. These results have been confirmed by single crystal X-ray analysis for **83**, **84** and **85**.

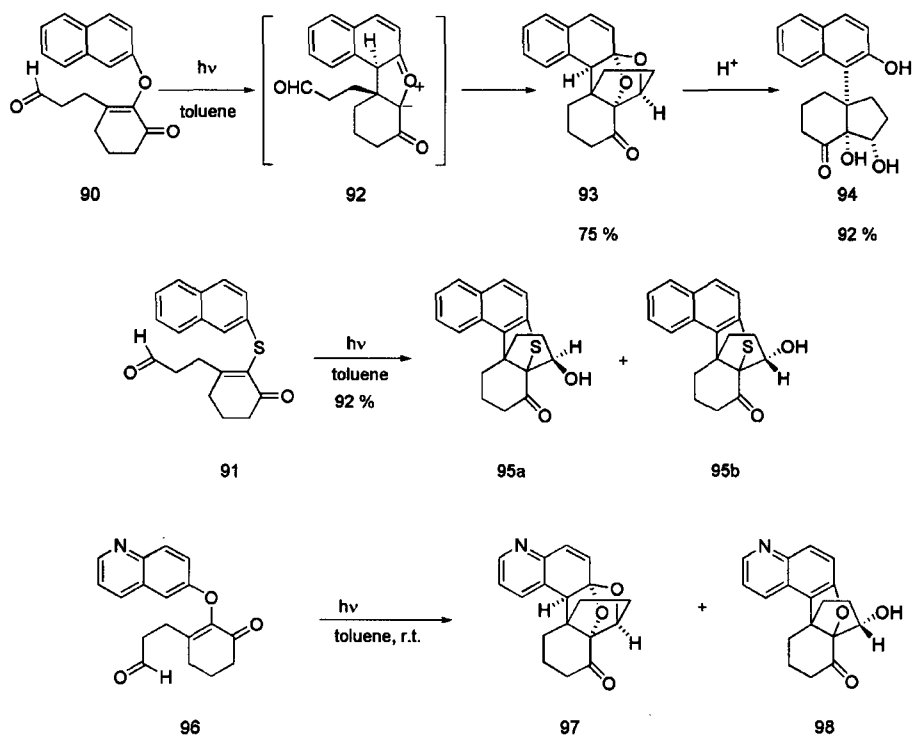
In a similar fashion aryl vinyl ether **86** provided product **87** in which the major isomer **87a** was confirmed by single crystal X-ray and had the stereochemistry shown. Notably the yield for **87a,b** was lower than is typical for these reactions (35%) and has not been optimized. Our experience with aryl vinyl amine systems shows a similar stereochemical preference. Thus **88** provided exclusively **89** in 81% yield as confirmed by X-ray analysis.

The photolyses of naphthyl vinyl sulfides and naphthyl vinyl ethers provide an interesting contrast in behavior. Thus photolysis of naphthyl vinyl ether **90** provides the novel ketal **93** in 75% yield. The formation of **93** is consistent with a photo-induced

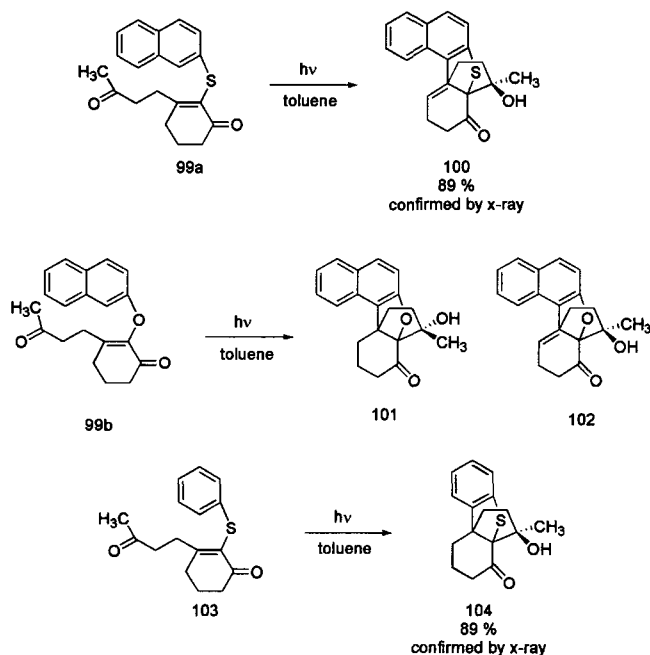


six electron conrotatory cyclization to give a trans-fused ylide intermediate **92** that undergoes subsequent intramolecular [3+2] dipolar cycloaddition to the side chain aldehyde. Acid catalyzed hydrolysis of **93** provides the diol **94**. In contrast, photolysis of aryl vinyl sulfide **91** provides **95a,b** as a 1:1 mixture of isomers. In summary, the addition reactions of pendant aldehydes on naphthyl vinyl sulfide and naphthyl vinyl ether systems parallels that of the corresponding alkene substituted systems in which naphthyl vinyl sulfides provide ene-like products and naphthyl vinyl ethers provide [3+2] adducts. Interestingly compound **96** also provided products which have spectral data consistent with the structures **97** and **98**.

Finally we examined the intramolecular addition reactions of systems bearing a methyl ketone in the side chain. Surprisingly aryl vinyl sulfide **99a** provided a single product **100** while aryl vinyl ether **99b** gave rise to two products **101** and **102** in nearly a 1:1 ratio. The stereoselectivity observed with the



naphthyl vinyl sulfide system is noteworthy and has also been observed with the corresponding phenyl vinyl sulfide **103** which provides two products. The major product **104** has the specific geometry shown as confirmed by X-ray while the second is of undetermined geometry.



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

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 which are involved in these transformations. Laser flash photolysis techniques were employed to characterize the ylides and to probe the reactivities of excited state intermediates.

Four systems were selected for study. Aryl vinyl sulfide **105a** and aryl vinyl ether **105b** incorporate simple chromophores, and previous studies have shown that they efficiently provide products **107** and **108**, respectively, upon photolysis. Aryl vinyl sulfide **17** and aryl vinyl ether **29** 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 had been reported previously for **105b** [2a,3b]. However, until this study there had been no reports on transients derived from **105a**, **17**, or **29** [2b].

#### *One Laser Flash Photolysis of Aryl Vinyl Sulfides*

Laser flash photolysis of the sulfur-containing compound **105a** 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  $\lambda_{\max}$  450 nm (Figure 1, Table 1). These absorptions are assigned to a thiocarbonyl ylide produced



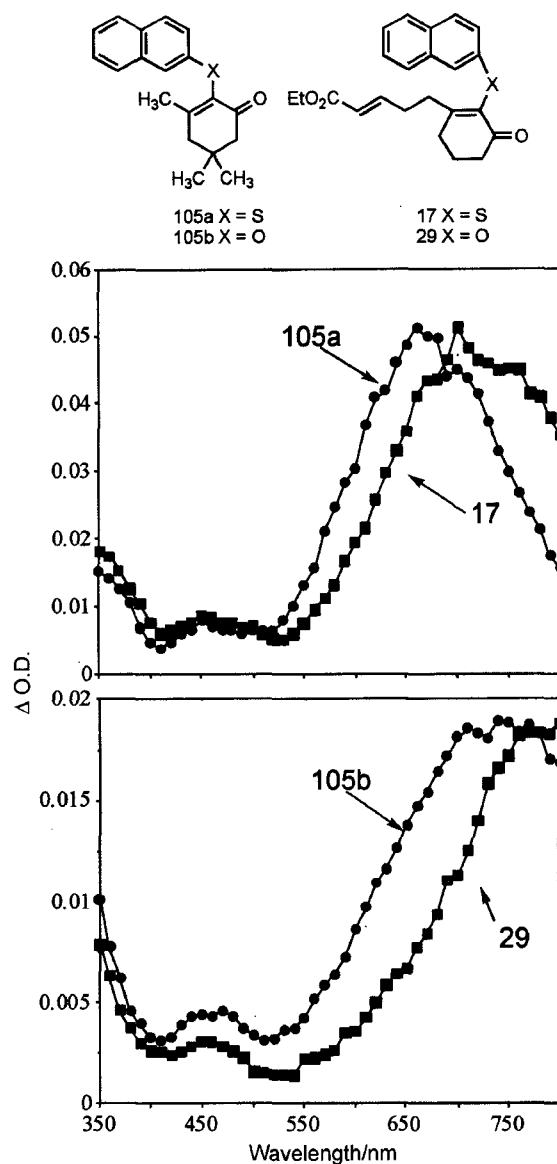
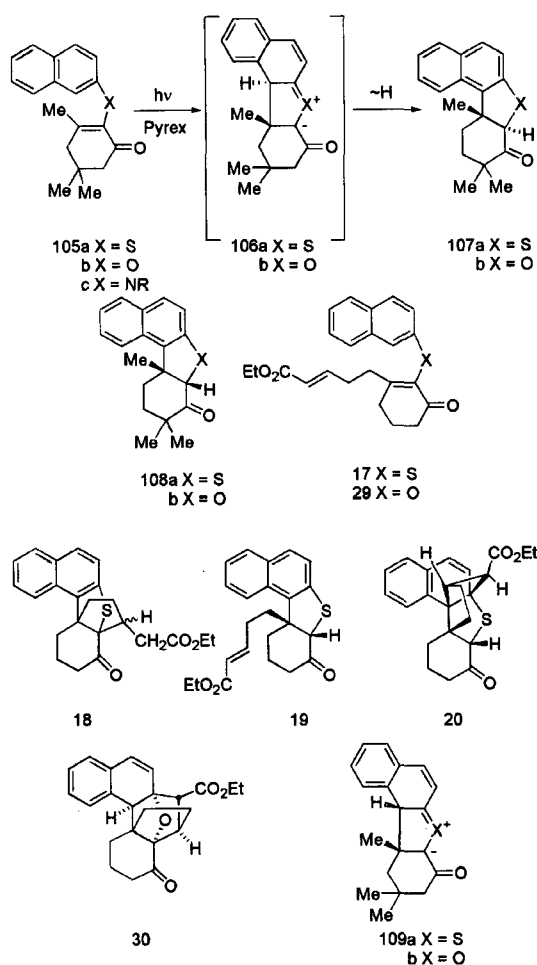


Figure 1. Transient absorption spectra of ylides derived from **5a** and **9a** (top) and **5b** and **9b** (bottom) following 308 nm photolysis in nitrogen-saturated benzene. Spectra were obtained 1  $\mu$ s after the laser pulse.

by cyclization of the naphthalene and vinyl moieties. A *trans* ring-fusion as shown in **106a** is inferred from an expected conrotatory cyclization [19] and has been demonstrated for related dipole systems via ylide trapping experiments [4,12]. However, the possibility of *cis*-fused system **109a** has not been ruled out.

Several spectroscopic and kinetic characteristics lead to the identification of the transient as a thiocarbonyl ylide: (i) the

Table 1. Lifetimes ( $\mu$ s) of Carbonyl and Thiocarbonyl Ylides

Solvent	Compound 105a		Compound 105b	
	750 nm	600 nm	830 nm	630 nm
C <sub>6</sub> H <sub>6</sub>	60	260	52	64
CH <sub>3</sub> OH	1.6	1.6	<0.1	<0.1
Solvent	Compound 17		Compound 29	
	750 nm	600 nm	830 nm	630 nm
C <sub>6</sub> H <sub>6</sub>	52	280	10	8.3
CH <sub>3</sub> OH	0.46	0.63	<0.1	<0.1

Lifetimes ( $\mu$ s) of carbonyl and thiocarbonyl ylides produced on photolysis of the indicated starting materials in benzene and methanol. Lifetimes were measured at two different absorption wavelengths within the ylide absorption band.

absorption spectrum closely resembles that of the corresponding carbonyl ylide reported by Wolff [3b], several structurally related thiocarbonyl ylides described by Herkstroeter and Schultz [2a], and a variety of carbene-derived sulfur and oxygen ylides [20]; (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).

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  $\mu$ s versus 60  $\mu$ s at 750 nm. Schultz also found two first-order decays within the long wavelength absorption envelope of several similar thiocarbonyl ylides [2a]. In those systems the lifetimes differed by as much as 2 orders of magnitude depending on the absorption wavelength monitored. Similar spectroscopic and kinetic behavior was observed for **17**.

#### One Laser Flash Photolysis of Aryl Vinyl Ethers

Intermediates derived from aryl vinyl ethers **105b** and **29** exhibited behavior different from those produced from the aryl vinyl thioethers. Photolysis of **105b** yielded two major transient absorption bands ( $\lambda_{\text{max}}$  750, 440 nm) exhibiting dramatically different lifetimes and a third minor absorption band ( $\lambda_{\text{max}}$  460 nm) that decays at roughly the same rate as the long-lived major band at 750 nm (see Figures 1 and 2). The

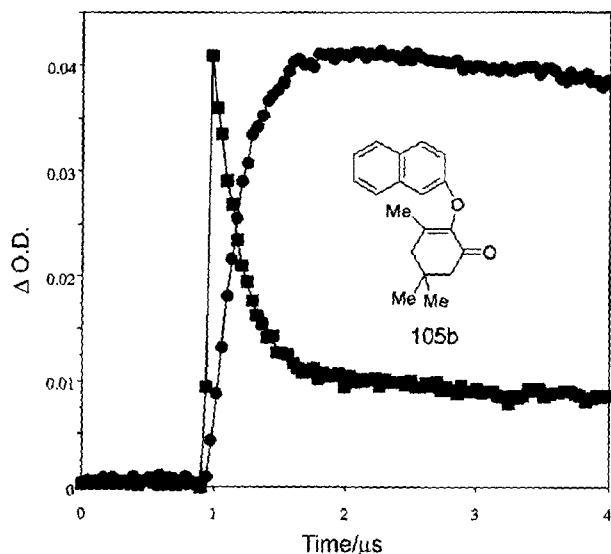


Figure 2. Transient decay obtained at 440 nm (square symbols) and 750 nm (round symbols) following 308 nm photolysis of compound **105b** in nitrogen-saturated benzene.

long-lived species absorbing at 750 nm was identified as the ylide and correlates well with data reported by Wolff. [3b] The second band ( $\lambda_{\text{max}}$  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) [3b]. 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 **105b** versus 60.9 kcal/mol for naphthalene) [21]. 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  $\mu$ s after the laser pulse) exhibits a peak at  $\lambda_{\text{max}}$  750 nm and a minor absorption band at  $\lambda_{\text{max}}$  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 **105b** points to two ylide bands within the same long wavelength absorption envelope. However, there is a much smaller difference in their lifetimes (52  $\mu$ s at 830 nm versus 64  $\mu$ s at 630 nm) than in the corresponding thioether systems (60  $\mu$ s at 750 nm versus 260  $\mu$ s at 600 nm). Similar behavior was noted for aryl vinyl ether **29**. Decay rates measured for each of the aryl vinyl ether-derived ylides were faster than for the corresponding thioethers. Thus, the ylides produced from **105b** decayed faster than those from **105a** and **29** faster than **17**. Reaction with added MeOH was also more efficient for the ether-derived ylides. While the lifetimes of the sulfur ylides for **105a** and **17** decreased to 1.6  $\mu$ s in neat MeOH, the ylide lifetimes for the oxygen systems **105b** and **29** 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 **105b** 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 **29** 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 **105a** and **17** 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 [2a,4].

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 **105a** and **17** 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 **105** versus those derived from **17** and **29**. Ylides derived from either **105a** or **105b** are expected to exhibit decay kinetics which reflect the efficiency of the intramolecular hydrogen shift whereas ylides derived from **17** and **29** can decay by either intramolecular hydrogen shift or an intramolecular ylide-alkene addition process. Indeed, ylide lifetimes for **29** are considerably shorter than for **105b**. Compound **29** provides exclusively compound **30**. The structure of **30** is consistent with intramolecular six-electron conrotatory cyclization occurring from **29** to provide ylide **45a** 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 **17** provides three products, **18-20**. Both **19** and **20** occur as products of intramolecular hydrogen shift. Compound **19**, which is formed initially, is converted to **20** by a secondary photoprocess involving intramolecular [2+2] cycloaddition. The mechanism for formation of compound **18** is not certain. However, other work indicates that it may involve an intramolecular ylide olefin addition process. Furthermore, neither **19** nor **20** is involved in the formation of **18** [13].

Considering the additional pathways that are available to **17** it is surprising that the lifetimes for the ylides derived from **105a** and **17** 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 **105a** in benzene provided exclusively *cis*-fused product **108a** at concentrations ranging from  $10^{-3}$  to  $10^{-4}$  M. Interestingly, analysis of mixtures produced by 308 nm laser irradiation of **105a** showed evidence of both *cis*- and *trans*-fused products **108a** and **107a**. The ratio of **108a** to **107a** 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 **105b** provided mixtures of *cis* and *trans* products in both the laser and lamp studies. Pyrex-filtered Hg lamp irradiation of **105b** in benzene provided a mixture of *cis*-fused and *trans*-fused products that varied with the concentration. Thus, photolysis of **105b** at  $3.5 \times 10^{-4}$  M gave a mixture of **108b** to **107b** in a ratio of 3.6:1. Photolysis of **105b** at  $9 \times 10^{-3}$  M, however, provided **108b** and **107b** in a ratio of 6.4:1. Finally, photolysis of **105b** in methanol provided exclusively *cis*-fused product **108b**.

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 **105a** supports a mechanism involving photoenolization of the initial cycloadducts. In order to confirm this, the following experiment was carried out. A sample of **105a** was irradiated in benzene with 1500 pulses from the 308 nm laser source. Product analysis by NMR showed the presence of both **107a** and **108a**. 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 **108a**. 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 [22].

#### Two Laser Photolysis

Theoretical studies predict that carbonyl ylides may undergo fragmentation following photoexcitation [23,24], and numerous experimental examples exist that support this prediction [25]. Direct time-resolved evidence for ylide photochemistry was obtained by two-laser flash photolysis of the carbonyl ylide formed by addition of fluorenylidene with acetone [26]. 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

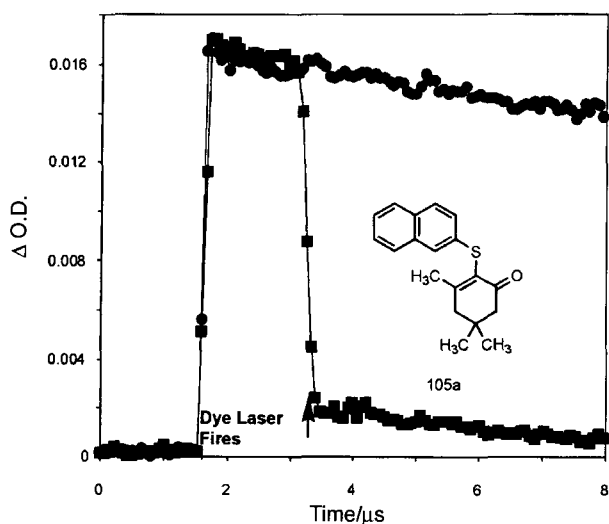


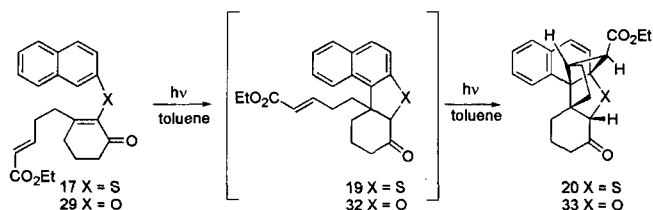
Figure 3. Transient decay obtained at 600 nm following one-laser (308 nm; round symbols) and two-laser (308+640 nm; square symbols) photolysis of compound **105a** in nitrogen-saturated benzene.

accelerated the thermal decay process, i.e., ring closure to form the oxirane. Given the reported photoreactivity 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 **105a**. 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 observation [2a] 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 **105a** were subjected to several hundred pairs of laser pulses. The samples were concentrated and analyzed by NMR. However, 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 **105a** may also occur photochemically.

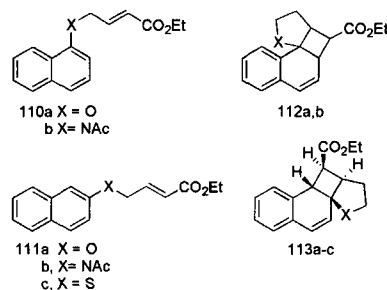
Analogous two-laser behavior has been reported for the carbonyl ylide formed by the reaction of acetone and fluorenylidene. While the long wavelength absorption of this ylide was efficiently depleted by a second laser pulse, no new product formation was observed [26].

#### Further Development of the Photoinitiated Intramolecular Ylide Alkene Cycloaddition Reaction

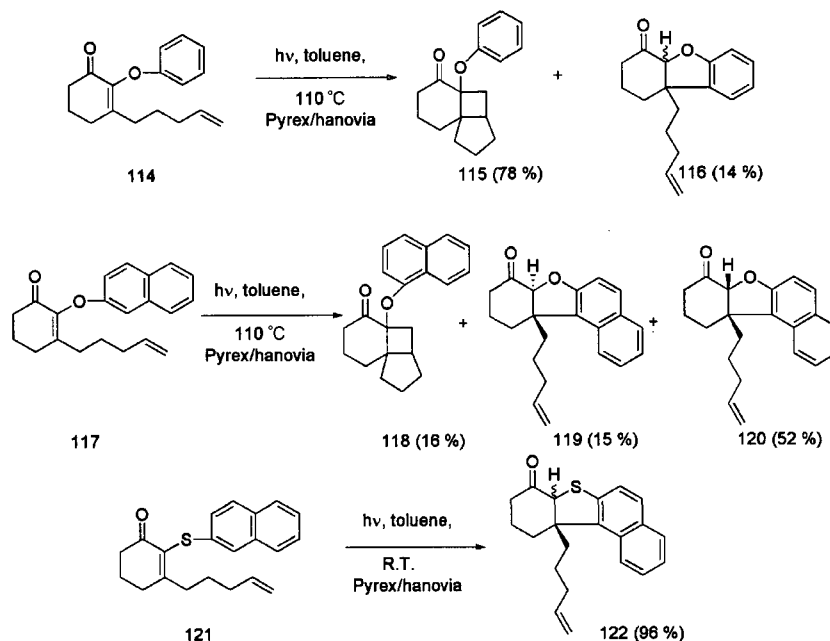
In an effort to explore the scope of this method for application to natural products synthesis we have initiated studies in a number of areas and report some of our results here. An early concern had been the opportunity for competing photoprocesses. Indeed we have already observed secondary [2+2] photoreactions which occur on photolysis of **17** and **29**.



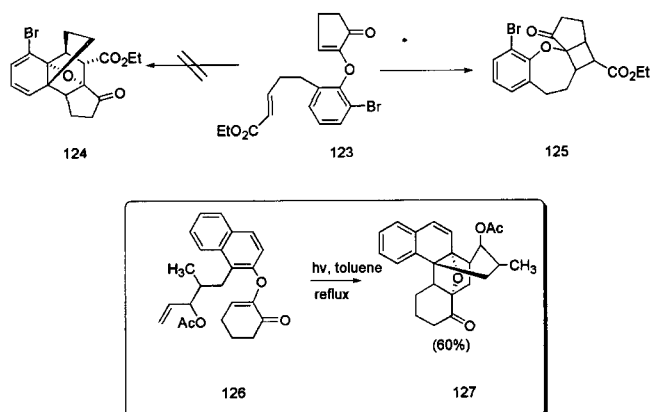
The ease of formation of [2+2] adducts in the forgoing reactions led us to explore the chemistry of naphthalene systems **110-111** which are readily available from the corresponding naphthol, naphthalenethiol or aminonaphthalene. Direct irradiation through Pyrex provided products which had spectral data consistent with formation of [2+2] adducts [15-16]. Although a full discussion of the results is beyond the scope of this article we report here that structure **113b** has been confirmed by X-ray analysis.



An area of concern for us was the impact of lengthening the pendant dipolarophile which then provides an opportunity for an intramolecular [2+2] cycloaddition rather than the photoarylation leading to ylide products. Accordingly, the following systems were evaluated to assess the viability of using five atom dipolarophilic side chains in the Photoinitiated Intramolecular Ylide-Alkene Cycloaddition Reaction. As shown, the [2+2] cycloaddition effectively competes with photoarylation in the photolysis of phenyl vinyl ether system **114**. However, this can be shifted to favor products of photoarylation by changing the aryl substituent to a naphthalene as in **117**. In fact the [2+2] reaction can be completely suppressed as in the case with aryl vinyl sulfide **121**.

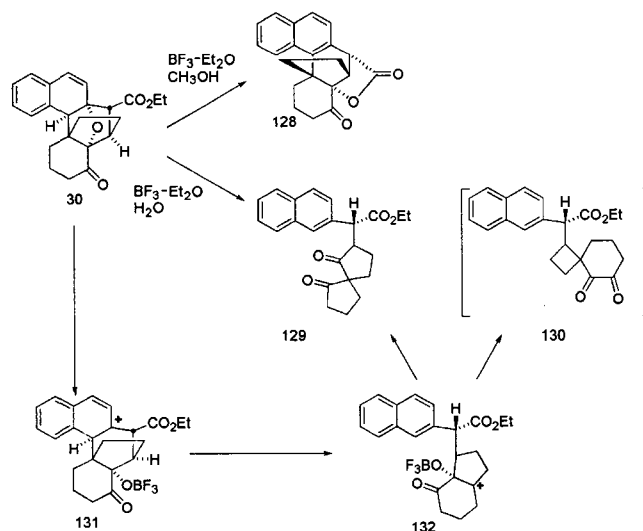


We also considered that relocation of the pendant dipolarophile may allow access to [3+2] products similar in structure to those previously studied without the complications of competing [2+2] cycloadditions (e.g. **123**→**124**). In this regard we have had some success. Thus although phenyl vinyl ether **123** gives rise to exclusively [2+2] product **125**, naphthyl vinyl ether **126** provides the product of photoarylation and subsequent intramolecular [3+2] cycloaddition **127**. These results are encouraging and suggest that the photophysical parameters of the photosubstrates can be adjusted to favor photoarylation over [2+2] cycloaddition.



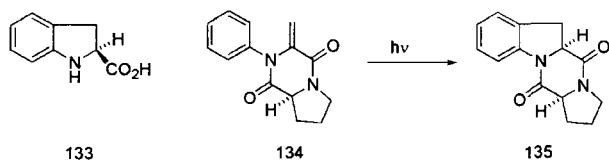
Recently we examined methods for the removal of oxygen from [3+2] products such as **30**. Treatment of **30** with 2.0 equivalents of  $\text{BF}_3\text{-Et}_2\text{O}$  in methanol provides lactone **128**. On the other hand, treatment with 1.2 equivalents of  $\text{BF}_3\text{-Et}_2\text{O}$  in water provides a rearrangement product which has spectral data consistent with product **129**. Thus far however, we

cannot rule out formation of **130**. Both can be rationalized as occurring from a common intermediate **132**.



With respect to an asymmetric variant of the photoarylation, we have only cursory data. Bellus however, has demonstrated the successful utilization of chiral auxiliaries in the photocyclization of aryl vinyl amines for enantioselective synthesis of *S*-(-)-indoline carboxylic acid **133** [27]. A chiral auxiliary was used to influence the stereochemical outcome of the C-C bond formation in **134** and thus dictate the stereochemistry of intramolecular hydrogen transfer which is known to proceed by a suprafacial migration. In an interesting twist of this reaction he was able to employ **133** as the chiral auxiliary and thus obviate the necessity for separation of auxiliary and product at

the end of the synthesis.



### Summary

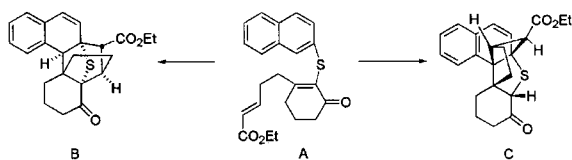
In closing the heteroatom directed photoarylation pioneered by Arthur G. Schultz has proven to be a rich area of study and promises to provide new and efficient methods for construction of exceedingly complex multicyclic systems in just a few experimental operations. Much has been learned in the course of this study. However, there is much more to be gained by a more thorough understanding of the photophysical and structural features that govern the mechanistic pathways involved in these reactions.

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