

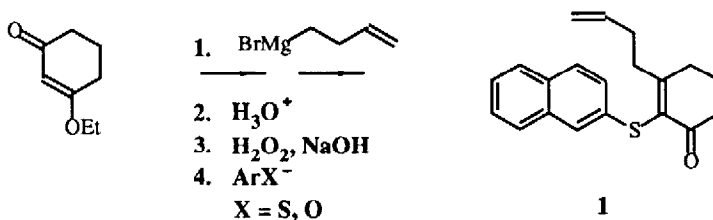
INTRAMOLECULAR ADDITION REACTIONS
DURING HETEROATOM DIRECTED PHOTOARYLATION

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Abstract: The intramolecular addition reactions of phototransient species generated upon heteroatom directed photoarylation were investigated. Novel temperature effects were observed for both the photocyclization and intramolecular addition reactions. Moreover, the addition products observed differ considerably from the (3 + 2) cycloadducts which were obtained upon intermolecular addition to the phototransient species.

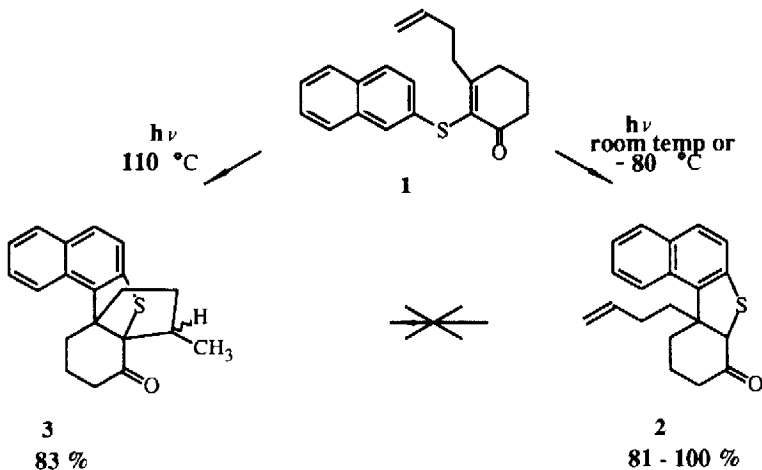
The six-electron heteroatom directed photoarylation reaction reportedly proceeds via dipolar intermediates. Thus, on photolysis, aryl vinyl sulfides, aryl vinyl ethers and aryl vinyl amines give rise to the corresponding thiocarbonyl ylides, carbonyl ylides and azomethine ylides.¹ Many of these species have been characterized spectroscopically.² However, only limited work has been done involving the addition reactions of the phototransient species.³ These studies have only been conducted with aryl vinyl sulfides and the reported products are (3 + 2) cycloadducts which arise from dipolar cycloaddition to the presumed thiocarbonyl ylide intermediates. We report here our preliminary results concerning the intramolecular addition reactions of intermediates generated upon photolysis of aryl vinyl sulfides and aryl vinyl ethers. In contrast to the previous work, the intramolecular addition reactions yield ene-like products.⁴

The preparation of 1, which is shown below, illustrates the general method which was used for the preparation of the aryl vinyl sulfides and aryl vinyl ethers employed in this study.



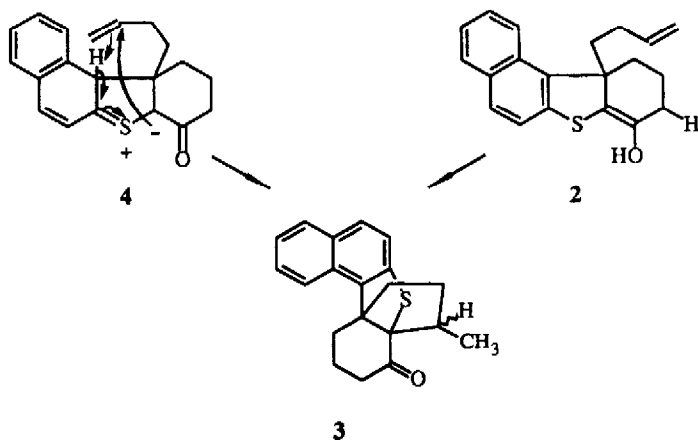
Irradiation of a solution of 1 in benzene (2×10^{-3} M) for 10 h at 25 °C provided the photocyclized product 2 in 81% isolated yield (no trapping observed). Interestingly, low temperature irradiation of a solution of 1 in toluene (3×10^{-3} M, -78 °C) provided 2 in quantitative yield after only 25 minutes. In contrast to these experiments, high temperature photolysis of a solution of 1 in toluene (3×10^{-3} M, 110 °C) for 3.5 h resulted in formation of the addition product 3, which was obtained as a mixture of diastereoisomers (79% isolated yield). Control experiments demonstrated that both light and heat were required to effect formation of 3. Thus, heating a solution of 1 in toluene at reflux temperature for 6 hours in the dark results in recovery of starting material. Likewise, 2 was shown to be stable in both refluxing toluene and under the reaction conditions (heat and light) used for formation of 3. These data suggest that a transient species generated from 1 via a photochemical

process undergoes a thermally induced addition reaction to give 3.

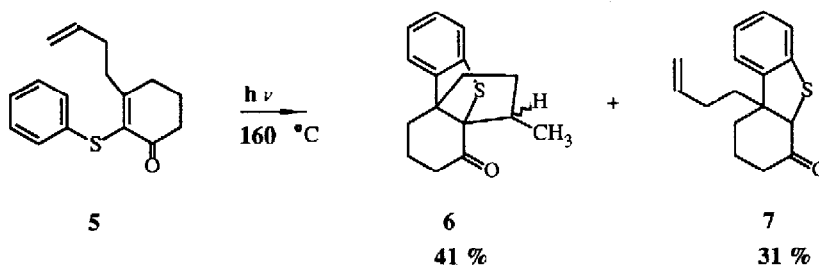


Separation of the mixture of diastereoisomers 3 was achieved by HPLC (SiO_2 , 16:1 Hexane: Ethyl acetate). Structural assignment for each isomer is based on IR, mass spectral, ^1H NMR and ^{13}C NMR analyses.⁵ We have conducted extensive ^{13}C and 2-dimensional NMR experiments to confirm the structural assignment. We note that ring closure in the naphthyl vinyl sulfide 1 occurs only toward the 1-position of the naphthalene system. This result is consistent with previous experiments.¹

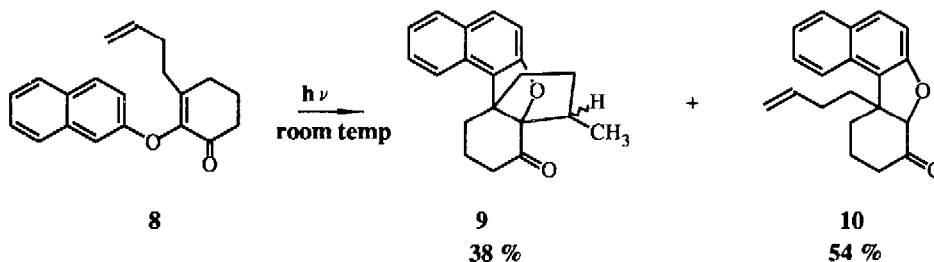
A possible mechanism for formation of 3, involves a radical addition pathway occurring from the thiocarbonyl ylide 4. Hydrogen abstraction either intramolecularly or from the solvent would provide the 5-membered ring product. Conversely an ene-like process as shown for 4 may be operative. This pathway, however, requires a cis orientation of the hydrogen and butenyl side chain. Since the product which is expected from a photochemically allowed conrotatory cyclization places these substituents in a trans orientation, the latter process is less likely.⁶ An ene reaction occurring from the enol tautomer of 2 is also ruled out on the basis of control experiments.



Phenyl vinyl sulfide 5 provided similar results as 1, however higher reaction temperatures were required to produce the photocyclized addition product. Thus, irradiation of a solution of 5 in mesitylene (4×10^{-3} M) at reflux temperature for 3 hours resulted in formation of aryl ketone 6 (41% isolated yield). The product, which was obtained and characterized as a mixture of diastereoisomers, was accompanied by 31% of the photocyclized material 7 and 11% recovered starting material 5. Structural assignment for 6 was based on comparison with data obtained for 3. As before, control experiments demonstrated that both heat and light were required to effect the transformation of 5 to 6.



The intramolecular addition reaction is not limited to aryl vinyl sulfides. In fact, we have observed similar behavior for aryl vinyl ethers. Thus, photolysis of a solution of 8 in toluene (3×10^{-3} M) for 1 h at room temperature afforded, after chromatography, the adduct 9 (38%) as a mixture of diastereoisomers and photocyclized product 10 (54%). Notably the addition reaction involving the aryl vinyl ether occurs at much lower temperature than the corresponding aryl vinyl sulfide.



In summary, the sequential photocyclization-dipole addition procedure promises to be a valuable method for preparation of several potentially useful and synthetically valuable ring systems. We are currently investigating the scope and limitations of this method and are engaged in a study of the novel temperature effects which we have observed for these reactions. A report of our findings will soon follow.

Acknowledgement is made to the WPI-RDC and to NIH (GM 37939-01) for support of this research.

References and Notes

1. For reviews see:

Schultz, A.G., *Acc. Chem. Res.* 1983, **16**, 210; Schultz, A.G.; Motyka, L. in "Organic Photochemistry", A. Padwa, Ed. Marcel Dekker, New York, 1983, Vol. 6, p. 1.

2. Herkstroeter, W.G.; Schultz, A.G. *J. Am. Chem. Soc.* 1984, **106**, 5553. See also Wolff, T.J. *J. Am. Chem. Soc.* 1978, **100**, 6157; Wolff, T. *J. Org. Chem.* 1981 **46** 978-983.

3. Schultz, A.G.; Detar, M.B. J. Am. Chem. Soc. 1976, 98, 3564.
4. Photochemical experiments were conducted using a 450-watt 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. For high and low temperature runs a vacuum-jacketed quartz immersion well was employed with a pyrex sleeve filter. The immersion well was placed in a large scale (~ 200 mL) reactor. Heating was carried out with a silicon oil bath and cooling was achieved with a Neslab ULT-80DD low-temperature circulating bath.
5. All products gave spectral data (^1H NMR, IR) which were consistent with the assigned structures. Satisfactory combustion analyses were obtained for all new products. Spectral data obtained for the isomers of 3 is as follows.

Major isomer: ^1H NMR (300 MHz, CDCl_3): δ 8.01 (d, J = 8.54 Hz, 1H), 7.86 (d, J = 8 Hz, 1H), 7.73 (d, J = 8.55 Hz, 1H), 7.51 (t, J = 8.45 Hz, 1H), 7.41 (t, J = 8 Hz, 1H), 7.28 (d, J = 8.57 Hz, 1H), 3.12-2.99 (m, 1H), 2.87-2.71 (m, 3H), 2.46-2.31 (m, 1H), 2.18-2.04 (m, 1H), 1.87-1.59 (m, 4H), 1.58-1.42 (m, 1, H), 1.25 (d, J = 6.66 Hz, 3H); ^{13}C NMR (50.3 MHz, CDCl_3): δ 208.99, 138.13, 137.34, 132.70, 129.58, 129.44, 129.40, 126.42, 124.04, 122.41, 119.91, 76.37, 68.90, 40.95, 40.70, 36.52, 36.00, 32.28, 19.68, 16.31; IR (Nujol): 3020, 2940, 2860, 1700, 1620, 1590, 1500, 1450, 1370, 1230, 1140 cm^{-1} ; GC/MS (70 eV): m/e 308 (M^+).

Minor isomer: ^1H NMR (300 MHz, CDCl_3): δ 7.96 (d, J = 8.49 Hz, 1H), 7.87 (d, J = 7.92 Hz, 1H), 7.72 (d, J = 8.56 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.56 Hz, 1H), 2.86-2.56 (m, 3H), 2.53-2.27 (m, 3H), 2.25-2.14 (m, 1H), 2.04-1.80 (m, 3H), 1.63-1.46 (m, 1H), 1.30 (d, J = 7 Hz, 3H); ^{13}C NMR (50.3 MHz, CDCl_3): 209.48, 139.17, 135.6, 132.73, 129.55, 129.54, 129.106, 126.35, 124.00, 123.02, 120.46, 76.33, 65.89, 48.12, 39.45, 38.73, 34.78, 32.50, 18.79, 15.23; IR (Nujol): 2920, 1700, 1620, 1590, 1500, 1450, 1370, 1220, 1150, cm^{-1} ; GC/MS (70 eV): m/e 308 (M^+).

6. Woodward, R.B.; Hoffman, R. "The Conservation of Orbital Symmetry" Academic Press, New York, 1970. For a detailed discussion of the reaction mechanism see references 1 and 3.

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