

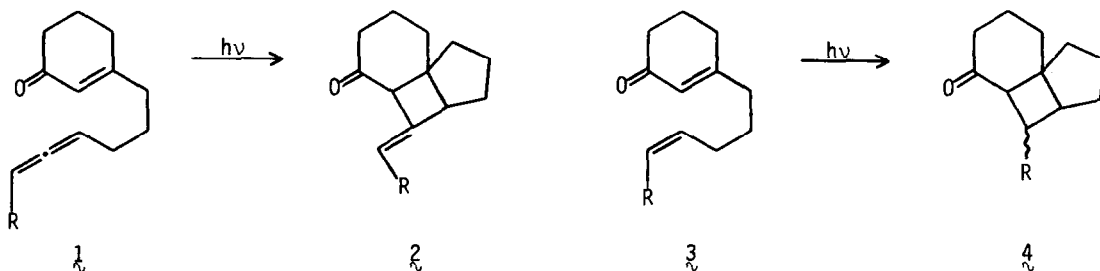
STEREOCHEMISTRY OF INTRAMOLECULAR [2+2] PHOTOCYCLOADDITIONS  
OF 4-(4,5-HEXADIENYL)-2-CYCLOHEXEN-1-ONES

William G. Dauben\* and Gideon Shapiro

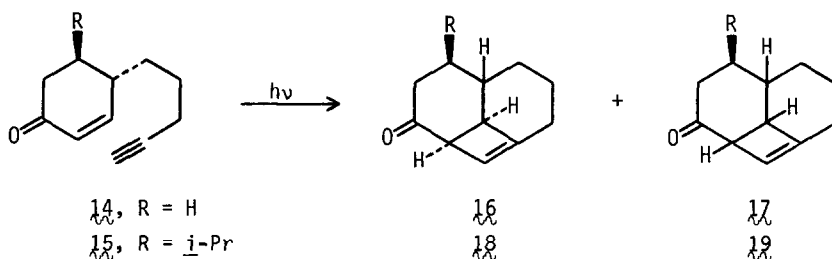
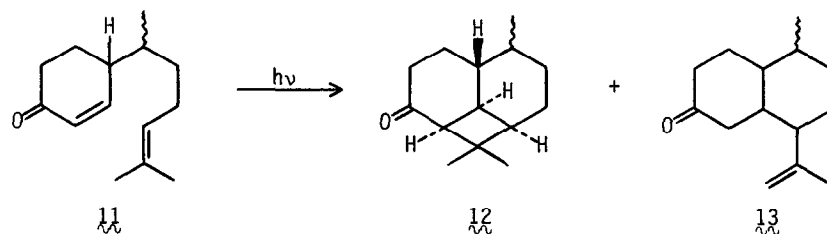
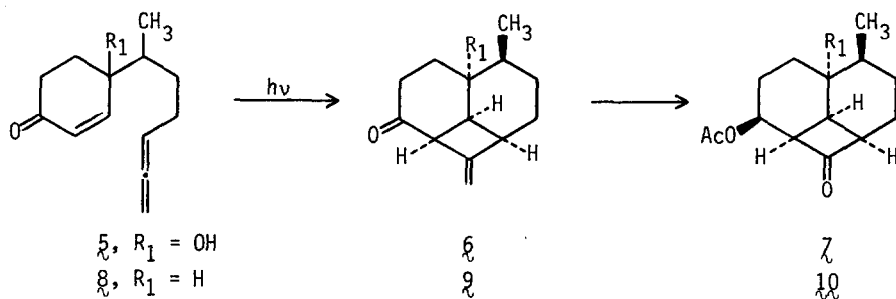
Department of Chemistry, University of California, Berkeley, California 94720

**Abstract.** Intramolecular [2+2] photocycloaddition of 4-(allenic-substituted)-2-cyclohexen-1-ones has been shown to be sensitive to change in substitution pattern and the nature of the reacting unsaturates. Initial bonding at C-2 of the enone is indicated.

It has recently been shown that the intramolecular photocycloaddition of 3-substituted 1,6-unsaturated-cyclohexenones<sup>1</sup> proceeds with initial bond formation at C-3 of the enone both for allenes and olefins (i.e.,  $\lambda$  to  $\zeta$  and  $\xi$  to  $\delta$ ).<sup>2</sup> We would like to present results which indicate



that initial bonding at C-2 is an important process in the intramolecular photocycloaddition of 4-(allenic-substituted) cyclohexenones. Recently, we have reported<sup>3</sup> that the irradiation of compound 5, as a 60:40 mixture of anti to syn diastereomers at -70 °C, resulted in quantitative cycloaddition of the anti diastereomer to yield 6.<sup>4</sup> The structure of 6 was determined by conversion to 7 whose structure was determined by X-ray crystallography. Compound 7 was, subsequently, transformed to 8 resulting in a formal synthesis of trihydroxydeciadiene. The stereospecific formation of a cis-decalin ring fusion in 6 was quite surprising in light of the previously reported irradiation of olefin 9 which afforded a 1:1 mixture of trans-fused cycloadducts 10 and "ene" products 11.<sup>5</sup> In addition, irradiation of acetylenes 12 and 13 affords mixtures of cycloadducts in which the trans-fused isomers 14 and 15 predominated.<sup>6</sup>

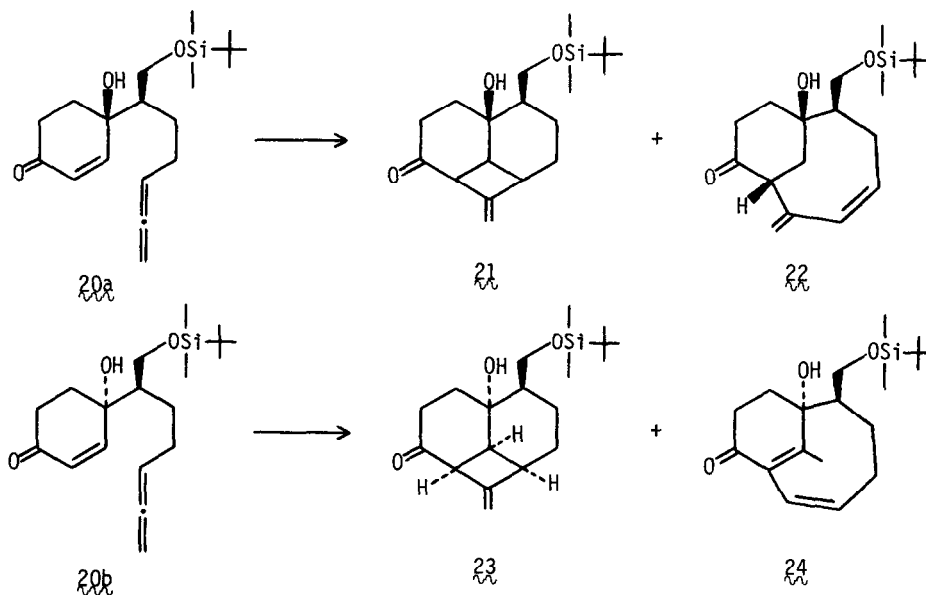


It is possible that the different stereoselectivity observed with  $5$ , a 4-substituted cyclohexenone, as compared to  $11$ ,  $14$  and  $15$  is due to a fundamental mechanistic difference between the cycloaddition of allenes and the other types of unsaturation in this series. However, the possibility that the hydroxyl group in  $5$  influences the stereochemical course of reaction cannot be completely ruled out. To establish the effect of the allene function and the hydroxyl group on the stereochemical course of cycloaddition, compound  $8$  was prepared by acid catalyzed equilibration of its known  $\beta,\gamma$ -unsaturated isomer.<sup>3</sup> Room temperature irradiation of an equal diastereomeric mixture of  $8$  (5.3 mM in ether)<sup>3</sup> gave six products (capillary GC analysis, elution order) in 23, 14, 26, 9, 14 and 14% yields.<sup>7</sup> However, irradiation at  $-70^\circ\text{C}$  gave five of the six previous products in 38, 13, 19, 0, 19 and 11% yields, the fourth eluted product not being found. The major product of the low temperature irradiation was shown to be anti-cycloadduct  $9$  by conversion to relay compound  $10$ .

This result shows, conclusively, that the allene function confers the stereoselectivity on this system. There are examples in the literature where photocycloadditions of olefins are stereoselective while those of allenes are not, both in the intermolecular and intramolecular reaction with cyclohexenones and that the specificity is dependent upon the structure of the

enone.<sup>8</sup> The complete stereospecificity of *anti*-**5** and the stereoselectivity of **8** contrast with these results. The opposite stereoselectivities observed for the different types of unsaturation in 4-substituted-cyclohexenones can be accounted for by the site of initial bond formation. It is clear from the formation of **13** that initial C-3 bond formation is most likely occurring with **11**. One cannot be certain that the diradical obtained from initial C-3 closure leads to cycloadduct **12**. However, the stereoselectivity observed is consistent with a decalin intermediate in which one would anticipate preferential formation of a *trans* ring fusion. If initial C-2 bond formation occurs, a bicyclo[5.3.1] diradical is produced which should show a marked preference for a *cis* orientation of the bridgehead substituents (H, OH). This species prefers a closure to an all *cis* cyclobutane, on thermodynamic grounds, which leads to a *cis*-decalin fusion, as is observed for allenes **5** and **8**.

Room temperature irradiation of compound **20a**<sup>9</sup> gave straight cycloadduct **21**,<sup>1</sup> the bicyclo[5.3.1] diene **22**<sup>10</sup> and two unidentified products in 41, 29, 16 and 14% yields, respectively.<sup>11</sup> The formation of **22** is more evidence for the importance of initial C-2 bonding in the intramolecular photocycloaddition of 4-substituted, 1-7-unsaturated, allenic cyclohexenones. However,



a mechanism for formation of **22** involving initial hydrogen abstraction by C-3 of the excited enone followed by radical combination cannot be ruled out.<sup>12</sup> In the irradiation of the *anti* diastereomer **20b**, cycloadduct **23**<sup>13</sup> and compound **24** are the only products received in 4:1 ratio at room temperature and 9:1 ratio at -70 °C. The postulated structure of **24** has been assigned on the basis of spectral data<sup>14</sup> and is in line that initial bonding at C-2 is occurring. We have not as yet, however, been able to formulate a satisfactory mechanism for its formation.

In conclusion, these results indicate that the intramolecular photocycloaddition of 4-substituted cyclohexenones is a very complex reaction which is very sensitive to changes in substitution pattern and the nature of the reacting unsaturation. With the allene derivative, initial attack at the C-2 position of the enone is indicated.

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### References and Notes

- The systems studied have either 1,6 or 1,7 unsaturation as defined by numbering from C alpha of the enone until the first unsaturated atom of the allene function is reached. Cycloaddition involving bonding of the termini of this chain is called straight cycloaddition while that involving the bonding of a terminal atom with an internal one corresponds to crossed cycloaddition.
- a) Becker, D.; Nagler, M.; Hirsh, S.; Ramun, J. *J.C.S. Chem. Comm.* 1983, 371. b) Becker, D.; Harle, Z.; Nagler, M.; Gillon, A. *J. Org. Chem.* 1982, 47, 3297.
- Dauben, W. G.; Shapiro, G. *J. Org. Chem.* 1984, 49, in press. Irradiation procedure is given in this report.
- The syn isomer yielded three products which were not characterized.
- Croft, K. D.; Ghisalberti, E. L.; Jefferies, P. R.; Stuart, A. D.; Raston, D. L.; White, A. H. *J. Chem. Soc. Perkin II* 1981, 1473.
- a) Koft, E. R.; Smith, A. B. III *J. Am. Chem. Soc.* 1982, 104, 5568. b) Koft, E. R.; Smith, A. B. III *J. Am. Chem. Soc.* 1984, 106, 2115.
- These yields are corrected for recovered starting material.
- a) Wiesner, K. *Tetrahedron* 1975, 31, 1655. b) Cargill, R. L.; Morton, G. H.; Bordner, J. *J. Org. Chem.* 1980, 45, 3930. c) Duc, D. K. M.; Fetizon, M.; Hanna, I.; Oleska, A. *J. Chem. Soc. Chem. Commun.* 1980, 1209. d) Baker, W. R.; Senter, P. D.; Coates, R. M. *J. Chem. Soc. Chem. Commun.* 1980, 1011. e) Pirrung, M. C. *J. Am. Chem. Soc.* 1981, 103, 82. f) Becker, D.; Harel, Z.; Nagler, M.; Gillon, A. *J. Org. Chem.* 1982, 47, 3297.
- Compounds 20a and 20b were prepared via the same sequence as compound 5 (see ref. 2) and were assigned their structures by analogy. The ratio of anti isomer 20b to syn isomer 20a was 60:40 as with 5; 20a and 20b were separable by MPLC.
- The structures of these compounds rest on <sup>1</sup>H NMR, <sup>13</sup>C NMR data. The stereochemistry of the decalin fusion in 21 is unknown.
- It is of interest that the irradiation of 20a at -70 °C gives a 28, 51, 8 and 9% yield of these products.
- This is a known process in the intramolecular photocycloaddition of 1,6-unsaturated olefinic cyclopentenones. Agosta, W. C.; Wolff, S. *Pure and Appl. Chem.* 1982, 54, 1579.
- The stereochemistry of the decalin fusion of 23 is unknown.
- The spectral data is as follows: IR 1695 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) 6.04 (d, 1, J = 10.5 Hz), 5.73 (dt, 1, J = 10.5, 8.2 Hz), 4.70-4.85 (s, 1), 3.50-3.59 (m, 2), 2.68-2.87 (m, 2), 2.16-2.29 (m, 2), 1.96 (s, 1), 1.55-1.85 (m, 4), 0.86 (s, 9), 0.07 (s, 6); <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 204.9 (s), 133.0 (d), 131.3 (s), 129.0 (d), 73.1 (s), 66.4 (t), 44.6 (d), 40.4 (t), 35.8 (overlap-t), 28.8 (t), 27.2 (s), 25.7 (q).

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