

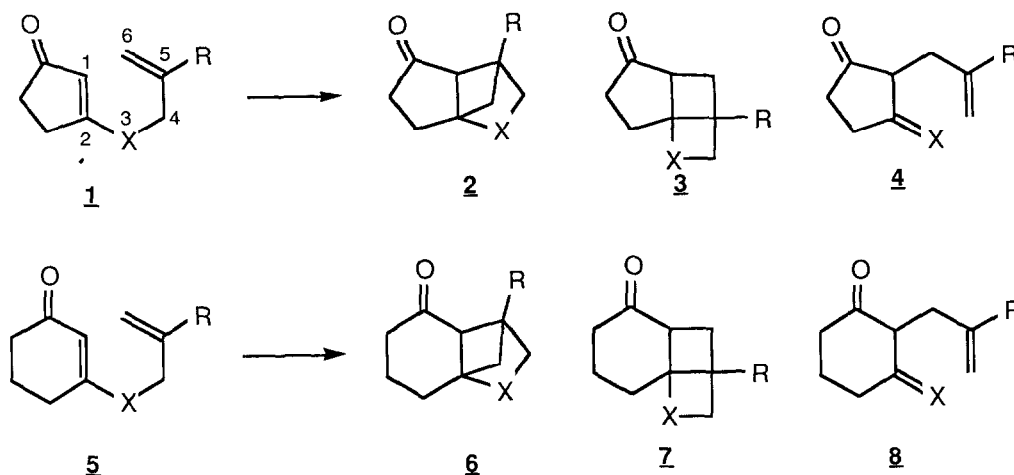
## INTRAMOLECULAR PHOTOCYCLOADDITION REACTIONS OF 1-ACYL-3-OXA-1,5-HEXADIENES

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**Abstract:** The regioselectivity of the intramolecular [2 + 2] photocycloadditions of 1-Acyl-3-oxa-1,5-hexadienes appears, in general, to follow "rule of five" closure and give annelated 2-oxa-bicyclo[2.1.1]hexanes.

In an effort to expand the scope and utility of intramolecular [2 + 2] photocycloadditions, we have been exploring the effects of oxa-substitution on the regioselectivity of the reactions of 1,5-hexadienes.<sup>1</sup> In the preceding communication, we showed that 4-oxa substitution in 2-acyl-1,5-hexadienes gave rise to the first example of 1,6 closure in a 2-acyl system.<sup>2</sup> Here we wish to present our results with 3-oxa substituted 1-acyl-1,5-hexadienes **1ab** and **5ab**.

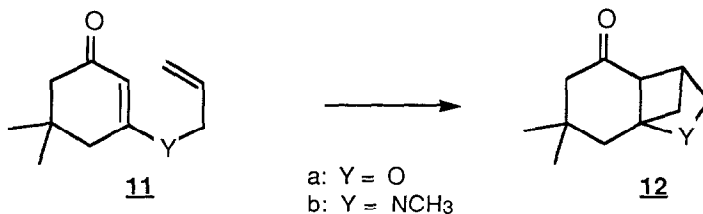


- a: X = O, R = H
- b: X = O, R = CH<sub>3</sub>
- c: X = CH<sub>2</sub>, R = H
- d: X = CH<sub>2</sub>, R = CH<sub>3</sub>

Wolff and Agosta have shown that the mode of photocycloaddition in 1-acyl and 3-keto-1,5-hexadienes ("crossed" **2** vs. "straight", **3**) can be controlled by the proper choice of substitution and annelation along the diene system.<sup>3</sup> Examination of the putative biradical intermediates **9** (1,5 closure, crossed) and **10** (1,6 closure, straight) suggested that 3-oxa substitution should have little effect on the relative stabilities of the two biradicals and that one might expect similar product distributions for  $X = O$  and  $X = CH_2$ .



Dienones **1ab** and **5ab** were synthesized in yields ranging from 40-70% by condensing 1,3-cyclopentadione or 1,3-cyclohexadione with either allyl alcohol or methallyl alcohol (TsOH, benzene, 16h).<sup>4</sup> The dienones were dissolved in either benzene or hexane (~0.01M) and photolyzed in a pyrex vessel ( $\lambda \geq 280$  nm). Results of the photolyses are presented in Table 1 along with data from other 1-acyl systems. The yields of the photochemical reactions for dienones **1ab** and **5a** are highly dependent on the extent of conversion. At high conversions, secondary Type I cleavage reactions consume the initial photoproduct.



Inspection of the data in Table 1 reveals that, in general, oxa- substitution at position 3 alters the regioselectivity of the photocyclization and produces crossed closure products. These results are in accord with Tamura's observations that oxa or aza- substituted **11ab** furnish crossed closure products **12ab**.<sup>5,9</sup> The propensity for dienes to undergo crossed closure has long been noted as the "rule of five".<sup>6</sup> This empirically based rule has been attributed to a combination of ring strain and entropic factors effecting the formation of cyclic biradical intermediates. Recent studies by Wolff and Agosta have shown that photolysis of 1-acyl-1,5-hexadienes give freely reverting biradical intermediates (eg. **9** and **10**,  $X = CH_2$ ).<sup>7</sup> The change in the regioselectivity seen with 3-heteroatom substitution may be due to kinetic selectivity in the initial bond closure, giving biradicals **9ab**, which preferentially close to **2ab** rather than fragment to starting dienones **1ab**.

The notable exception to the "rule of five" in this work is dienone **1b**, which produces straight closure product **3b**. The regioselectivity exhibited by **1b** is the same as that seen with the alkenyl analog **1d**. The behavior of **1b** is consistent with the argument that alkyl substitution at C-5 sterically inhibits 1,5 closure and promotes 1,6 closure by stabilizing the radical center at C-5. It is puzzling that **5b** does not give any volatile photoproducts upon direct or sensitized irradiation.<sup>9</sup> Methyl substitution in this case completely inhibits 1,5 closure without any apparent enhancement in straight closure.

Table 1. Photolysis of 1-Acyl-1,5-Hexadienes.

Dienone	Photoproducts (yield. %)	1,5 : 1,6 closure	ref
1a	2a (95) <sup>a,e</sup>	> 50 : 1	
1b	3b (20) <sup>b,e</sup>	1 : >50	
1c	2c (7), 3c (56) <sup>c</sup>	10 : 90	10
1d	3d (84) <sup>c</sup>	1,6 only	10
5a	6a (54) <sup>d,e</sup>	> 50 : 1	
5b	no volatile products <sup>e</sup>	---	
5c	6c (69), 7c (22) <sup>c</sup>	74 : 26	3
5d	6d (11), 7d (76) <sup>c</sup>	13 : 87	3
11a	12a (72) <sup>e</sup>	1,5 only	5
11b	12b (55) <sup>e</sup>	1,5 only	5

a) Yield at 30% conversion. b) Yield at 50% conversion. c) Irradiated at  $\lambda \geq 340$  nm. d) Yield at 100% conversion. The yield rises to 77% at 75% conversion. e) Irradiated at  $\lambda \geq 280$  nm.

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Notes and References

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2. For related studies on oxa-substituted 1,6-heptadienes and 1,7-octadienes see: a) Martin, S.F.; White, J.B. Tetrahedron Lett. **1982**, 23, 23. b) Tamura, Y.; Ishibashi, H.; Kita, Y.; Ikeda, M. J. Chem. Soc. Chem. Commun. **1973**, 101. c) Umehara, T.; Inouye, Y.; Kaskisawa, H. Bull. Chem. Soc. Jpn. **1981**, 54, 3492. d) Ikeda, M.; Takahashi, M.; Uchino, T.; Ohno, K.; Tamura, Y.; Kido, M. J. Org. Chem. **1983**, 48, 4241. e) Ikeda, M.; Takahashi, M.; Uchino, T.; Tamura, Y. Chem. Pharm. Bull. **1984**, 32, 538.
3. Wolff, S.; Agosta, W.C. J. Am. Chem. Soc. **1983**, 105, 1292.
4. All new compounds have been characterized by <sup>13</sup>C and <sup>1</sup>H NMR, IR, and MS.
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7. Schroder, C.; Wolff, S.; Agosta, W.C. J. Am. Chem. Soc. **1987**, 109, in press.
8. The bicyclo[2.2.0] system in **3b** survives preparative GC at 120 C, but suffers retro-cycloaddition to give **1b** and **4b** at higher temperatures (190 C, 3h, benzene, sealed tube). Bicyclo[2.2.0] systems are known to undergo ring opening reactions at lower temperatures than the isomeric [2.1.1] systems. Wolff and Agosta have used this difference in thermal stability to aid in the characterization of photoproducts **2cd** and **3cd**. See reference 3.
9. A C-5, C-6 alkyl substituted 3-aza compound related to **11b** has been shown to give both straight and crossed photoproducts. Swindell, C.S.; deSolms, S.J.; Springer, J.P. Tetrahedron Lett. **1984**, 25, 3797.
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11. It is interesting to note that the related 3-oxa-5-methyl-5-hexenyl radical regioselectively cyclizes to give 1,5 products (tetrahydrofurans). Smith, T.W.; Butler, G.B.; J. Org. Chem. **1978**, 43, 6.

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