

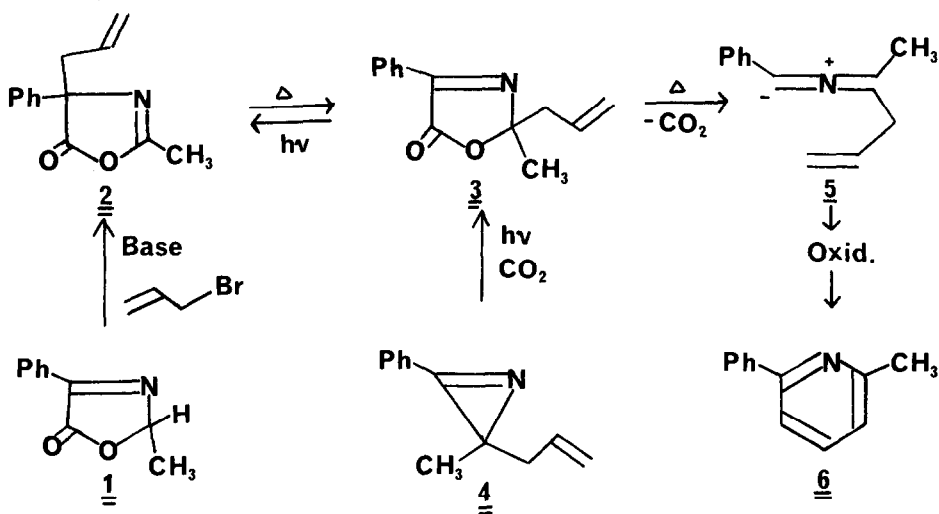
SIGMATROPIC REARRANGEMENTS IN THE ALLYL SUBSTITUTED  
OXAZOLINONE SYSTEM

Albert Padwa\*, Mitsuo Akiba, Leslie A. Cohen and J. Gavin MacDonald  
Department of Chemistry  
Emory University  
Atlanta, Georgia 30322

**Abstract:** Thermolysis and photolysis of several allyl substituted oxazolin-5-ones results in a sigmatropic rearrangement in accord with orbital symmetry predictions.

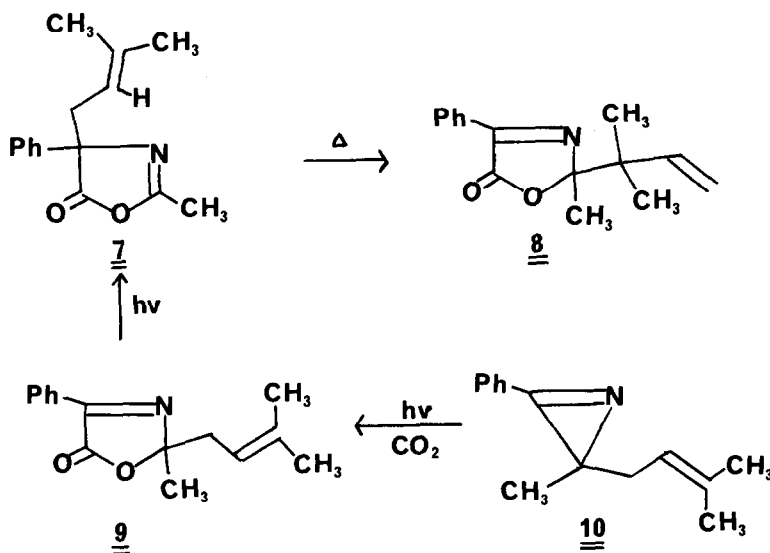
Nitrile ylides are a well known and thoroughly investigated class of 1,3-dipoles.<sup>1,2</sup> Access to this group of dipoles can be realized by (a) treatment of imidoyl chlorides with base,<sup>3</sup> (b) elimination of phosphoric acid ester from 2,3-dihydro-1,4- $\Delta^5$ -oxazaphospholes,<sup>4</sup> (c) photolysis of 2H-azirines<sup>1,2</sup> and (d) thermal elimination of carbon dioxide from oxazolinones.<sup>5</sup> 1,3-Dipolar cycloaddition of this class of 1,3-dipoles has led to the synthesis of a variety of interesting heterocyclic compounds.<sup>6,7</sup> Recently, it has been shown that 1,1-intramolecular cycloaddition of nitrile ylides can compete with the normal 1,3-addition when certain geometric constraints are imposed.<sup>8,9</sup> In these cases, the reactions can be formulated in terms of the carbene form of the dipole.<sup>10</sup> Because of the theoretical<sup>11</sup> and experimental challenge of nitrile ylide cycloaddition, we have studied the thermal and photochemical behavior of several allyl substituted oxazolinones in the hope of obtaining additional examples of 1,1-cycloaddition. We have found that these allyl substituted oxazolinones undergo a facile sigmatropic rearrangement prior to carbon dioxide extrusion. This communication summarizes some of our observations in this area.

4-Allyl substituted 2-methyl-4-phenyl- $\Delta^2$ -oxazolin-5-ones were prepared by treating oxazolinone 1 with an allylic halide in the presence of Hunig's base according to the general procedure of Steglich.<sup>12</sup> Heating a sample of  $\Delta^2$ -oxazolin-5-one 2 in benzene at 135°C resulted in the formation of the rearranged  $\Delta^3$ -oxazolin-5-one 3 (98% yield). This material was identified by comparison with an independently synthesized sample prepared from the irradiation of azirine 4 in the presence of carbon dioxide.<sup>13,14</sup> On further heating, oxazolinone 3 was converted to 2-methyl-6-phenylpyridine (6).<sup>15</sup> The formation of 6 can be postulated to arise by an initial extrusion of carbon dioxide to give nitrile ylide 5



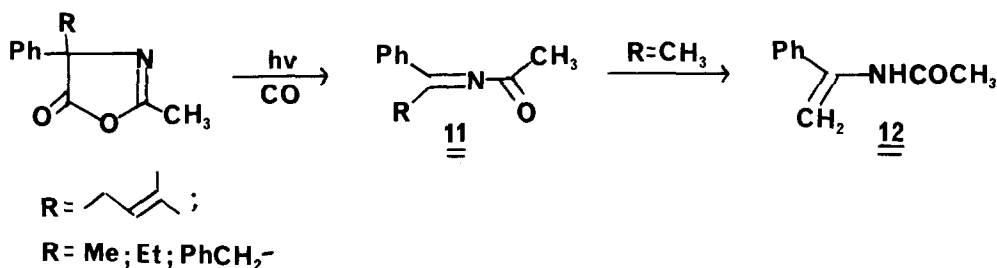
which undergoes internal cycloaddition followed by a subsequent oxidation. In contrast to the thermal results, the photolysis of 3 produced  $\Delta^2$ -oxazolinone 2 in quantitative yield. The conversion of 3 to 2 is probably related to the fact that 3 possesses a much larger extinction coefficient and is optically pumped to 2 with Pyrex filtered light.

In order to determine whether the sigmatropic rearrangement of oxazolinones 2 and 3 was of 1,3- or 3,3-character, the allyl moiety was replaced by a 3-methyl-2-butenyl group. Thermolysis of  $\Delta^2$ -oxazolin-5-one 7 in benzene at  $162^\circ\text{C}$  gave  $\Delta^3$ -oxazolin-5-one 8.<sup>17,18</sup> The



formation of the 1,1-dimethyl-2-propenyl substituted oxazolinone is only compatible with the 3,3-sigmatropic rearrangement route. In contrast, the direct irradiation of  $\Delta^3$ -oxazolin-5-one 9 gave exclusively the 4-(3-methyl-2-butenyl)-substituted  $\Delta^2$ -oxazolin-5-one 7.<sup>19</sup> Oxazolinone 9 was prepared by trapping the nitrile ylide derived from azirine 10 with carbon dioxide. The structure of 7 was unambiguously established by comparison with an independently synthesized sample. The above results indicate that the photoinduced rearrangement of the  $\Delta^3$ -oxazolinone system proceeds via a 1,3-sigmatropic shift of the allyl moiety. Thus, the sigmatropic nature of the rearrangement is perfectly consistent with orbital symmetry predictions.

One final point of interest is that on prolonged irradiation, the  $\Delta^2$ -oxazolinones were found to undergo decarbonylation to give acetimides 11 which were easily hydrolysed to the corresponding ketones. Additional examples of this type of photodecarbonylation were pro-



vided by the photolysis of a series of  $\Delta^2$ -oxazolin-5-ones (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, PhCH<sub>2</sub>). In all of these cases, the acetimides 11 were formed which on hydrolysis gave the expected ketones. As additional evidence, the acetimide derived from the 4-methyl-oxazolinone was found to undergo base induced tautomerization to yield enamide 12. This material was independently prepared from the reaction of benzonitrile, methylmagnesium bromide and acetyl chloride.

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### References

- (1) A. Padwa, Acc. Chem. Res., 9, 371 (1976).
- (2) P. Gilgen, H. Heimgartner, H. Schmid and H. J. Hansen, Heterocycles, 6, 143 (1977).
- (3) R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, Angew. Chem., 74, 31 (1962).
- (4) K. Burger and J. Fehn, Chem. Ber., 105, 3814 (1972).
- (5) J. Fischer and W. Steglich, Angew. Chem. Int. Ed. Engl., 18, 167 (1979).
- (6) R. Huisgen, Angew. Chem. Int. Ed. Engl., 2, 565, 633 (1963).
- (7) A. Padwa, Angew. Chem. Int. Ed. Engl., 15, 123 (1976).
- (8) A. Padwa and N. Kamigata, J. Am. Chem. Soc., 99, 1871 (1977).
- (9) A. Padwa, P. H. J. Carlsen, A. Ku, J. Am. Chem. Soc., 99, 2798 (1977).
- (10) A. Padwa and P. H. J. Carlsen, J. Am. Chem. Soc., 98, 2006 (1976); 99, 1514 (1977).
- (11) P. Caramella and K. N. Houk, J. Am. Chem. Soc., 98, 6397 (1976); P. Caramella, R. Gandour, J. A. Hall, C. G. Deville and K. N. Houk, J. Am. Chem. Soc., 99, 385 (1977).
- (12) S. Gotze and W. Steglich, Chem. Ber., 109, 2327 (1976).
- (13) A. Padwa and S. I. Wetmore, Jr., J. Am. Chem. Soc., 96, 2414 (1976).
- (14) H. Giezendanner, M. Marky, H. J. Hansen and H. Schmid, Helv. Chim. Acta., 55, 745 (1972).
- (15) The identity of 2-methyl-6-phenylpyridine (6) was established by comparison with an independently synthesized sample.<sup>16</sup>
- (16) J. M. Bonnier, J. Court and T. Fay, Bull. Soc. Chim. Fr., 1204 (1967).
- (17) All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given in our full paper.
- (18) Oxazolinone 8; NMR ( $C_6D_6$ , 90 MHz)  $\delta$  1.26 (s, 6H), 1.60 (s, 3H), 4.77 (d, 1H, J=10.0 Hz), 4.80 (d, 1H, J=18.0 Hz), 5.63 (dd, 1H, J=18.0 and 10.0 Hz); ir (neat) 1770 and 1620  $cm^{-1}$ .
- (19) Oxazolinone 7; NMR ( $CDCl_3$ , 90 MHz)  $\delta$  1.55 (s, 3H), 1.64 (s, 3H), 2.20 (s, 3H), 2.73 (d, 2H, J=7.5 Hz), 4.98 (t, 1H, J=7.5 Hz), 7.2-7.6 (m, 5H); ir (neat) 1810 and 1680  $cm^{-1}$ .

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