

2+2 PHOTOCYCLOADDITION TO A CARBON NITROGEN DOUBLE BOND II.

2-PHENYL-2-OXAZOLIN-4-ONE

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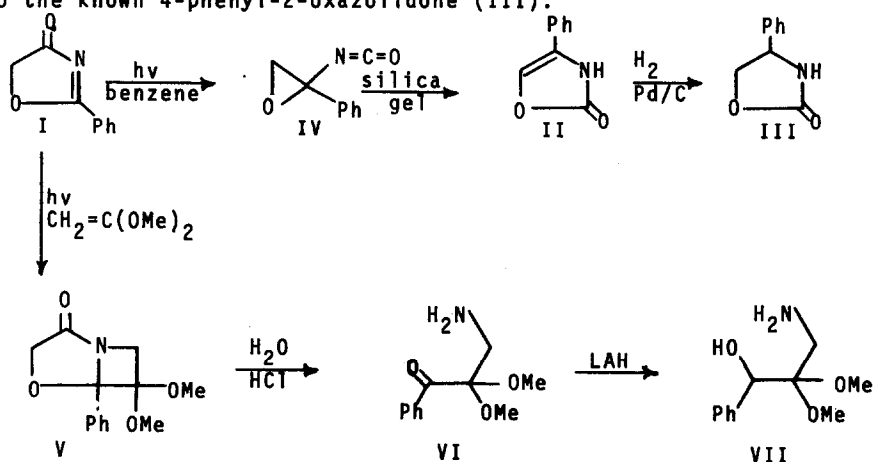
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In the previous paper¹ we reported the unique 2+2 photocycloaddition of olefins to the carbon nitrogen double bond of 3-ethoxyisoindolone, a molecule for which competitive α -cleavage² is unfavorable. We report here the photochemical 2+2 cycloaddition of 2-phenyl-2-oxazolin-4-one (I) to 1,1-dimethoxyethylene in competition with α -cleavage.³

Irradiation of a benzene solution of 0.5 g of I⁴ with a Corex filtered, 450 watt, mercury lamp for 8 hrs followed by chromatography on silica gel resulted in the isolation of a white crystalline product (m.p. 157-157.5°, 40% yield). The photoproduct was identified as 4-phenyl-4-oxazolin-2-one (II) by spectroscopic⁵ and chemical techniques. The structure was unambiguously established by the catalytic hydrogenation of the carbon carbon double bond with palladium on charcoal to the known 4-phenyl-2-oxazolidone (III).⁶



The extensive skeletal rearrangement of I was suggestive of a photochemical intermediate. A benzene solution of 2-phenyl-2-oxazolin-4-one in an ir solution cell was irradiated at room temperature with CS-053 filtered light from a Bausch and Lomb, super pressure, mercury light source, for 2 min. Subsequent scanning of the ir spectrum showed a decrease in the intensity of the 5.64 μ carbonyl stretching band of I and formation of a strong isocyanate stretching band at 4.43 μ . Continued irradiation with ir analysis indicated that II was not formed in the photochemical reaction. The only photoproduct observable in the infrared was the isocyanate assigned structure IV, 2-phenyl-2-oxiryl isocyanate. Treatment of IV with either silica gel or with a catalytic amount of a dilute sodium hydroxide solution in the dark resulted in rearrangement to II. Without chromatographic workup of the irradiation solution, the isocyanate can be isolated and has spectroscopic properties consistent with the assigned structure.⁷

The mechanism of the photochemical step is most likely homolytic cleavage of I, α to the carbonyl, followed by rearrangement to a 1,3-diradical and ring closure. The subsequent hydroxide catalyzed reaction is proposed to occur by nucleophilic addition of hydroxide to the isocyanate functional group followed by intramolecular nucleophilic attack on the oxirane and elimination of water.

The photochemical rearrangement of 2-phenyl-2-oxazolin-4-one is analogous to that of two other keto imines.^{2,8} For structurally related α,β -unsaturated ketones (except for those appropriately substituted in the α -position⁹) photodimerization¹⁰ or 2+2 photocycloaddition to olefins¹¹ is competitive with α -cleavage.

When a 0.5 g sample of I is irradiated for 8 hrs in benzene in the presence of 3.5 g of 1,1-dimethoxyethylene, photorearrangement is not observed and a new product, 6,6-dimethoxy-5-phenyl-4-ox-1-azabicyclo[3.2.0]heptan-2-one (V), is isolated in 65% yield (m.p. 50-1°). The structure is assigned on the basis of the spectroscopic evidence¹² and chemical degradation. Hydrolysis of the cycloadduct with 3N hydrochloric acid at room temperature gives α,α -dimethoxy- β -amino-propriophenone (VI, 94% yield). Reduction of the carbonyl of VI with lithium

aluminum hydride yields the expected alcohol VII (84% yield), establishing the regiochemistry of the cycloaddition reaction as assigned. The methylene protons of VII appear as an AB pattern at δ 2.53 and 2.92 ppm ($J=13$ Hz). The low field doublet is further split by the methine proton ($J=1.5$ Hz).¹³ For the corresponding degradation product of the cycloadduct with regiochemistry opposite to that of V, the methylene protons would have been strongly coupled to the methine proton.

Now that photocycloaddition can be competitive with photochemical α -cleavage, we are examining other molecules with the keto imino ether functional group to establish a structure reactivity relationship.

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Footnotes and References

- (1) T. H. Koch and K. A. Howard, Tetrahedron Let., (1972).
- (2) T. H. Koch and R. J. Sluski, Ibid., 2391 (1970).
- (3) Reported in part at the 163rd ACS National Meeting, Boston, Mass., April 1972, Abstract ORGN-26.
- (4) 2-Phenyl-2-oxazolin-4-one was prepared by an intramolecular displacement reaction of N-(chloroacetyl)benzamide. A. J. Gordon, 14th Annual Report on Research, Petroleum Research Fund, 185 (1969).
- (5) Oxazolinone (II) gives the following spectral absorptions: ir (CHCl_3), 2.90, 3.17, 5.65, and 5.71 μ ; nmr δ 7.12 (d, $J=1.5$ Hz, 1H), 7.42 (m, 5H), and 10.06 ppm (broad, 1H); mass spectrum m/e 161 (parent ion, base peak).
- (6) A. Hassner and C. Heathcock, J. Org. Chem., 32, 540 (1967).
- (7) In the nmr IV gives a 2H singlet at δ 4.50 and a 5H multiplet from δ 7.2-7.7 ppm.
- (8) T. Sasaki, S. Eguchi, and M. Ohno, J. Am. Chem. Soc., 92, 3192 (1970).
- (9) W. C. Agosta, A. B. Smith, III, A. S. Kende, R. G. Eilerman, and J. Benham, Tetrahedron Let., 4517 (1969); W. C. Agosta and A. B. Smith, III, J. Am. Chem. Soc., 93, 5514 (1971); D. L. Chapman and J. D. Lassila, Ibid., 90, 2449 (1968); O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, Ibid., 91, 6856 (1969); J. Griffiths and H. Hart, Ibid., 90,

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- (10) P. E. Eaton and W. S. Hurt, *Ibid.*, 88, 5671 (1966); J. L. Ruhlen and P. A. Leermakers, *Ibid.*, 89, 4944 (1967); E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *Ibid.*, 89, 3482 (1967); P. J. Wagner and D. J. Bucheck, *Ibid.*, 91, 5090 (1969).
- (11) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *Ibid.*, 86, 5570 (1964); P. de Mayo, J.-P. Pete, and M. Tehir, *Can. J. Chem.*, 46, 2533 (1968).
- (12) Cycloadduct V gives the following spectral absorptions: ir (KBr) 5.73 μ ; nmr δ 2.96 (s, 3H), 3.43 (s, 3H), 3.78 (d, J=10.2 Hz, 1H), 3.87 (d, J=10.2 Hz, 1H), 4.28 (s, 2H), 7.2-7.7 (m, 5H); mass spectrum m/e 249 (parent ion, 0.57%), 88 (base).
- (13) Preferential long range coupling of the methine proton to one of the methylene protons probably results from a favorable intramolecularly hydrogen bonded form of VII.