Studies on the Photoextrusion of Carbon Dioxide from the Δ^3-Oxazolin-5-one System[1]

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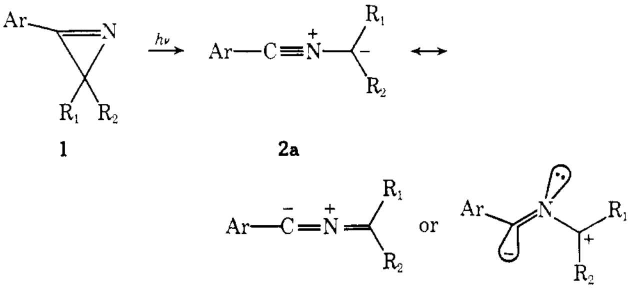
Abstract: Irradiation of dimethylphenylazirine (**7**) in a pentane solution saturated with carbon dioxide afforded 2,2-dimethyl-4-phenyl-Δ^3-oxazolin-5-one (**8**) in excellent yield. Similar results were obtained with methylphenylazirine. The Δ^3-oxazolinones undergo photoextrusion of carbon dioxide to produce nitrile ylides. These 1,3 dipoles are trapped with a variety of dipolarophiles to produce Δ^1-pyrrolines. A kinetic investigation, involving Stern–Volmer plots and relative reactivity studies, shows that the nitrile ylide generated from the photolysis of the Δ^3-oxazolinone system is identical with that generated from the corresponding azirine molecule. Evidence was obtained which indicates that the photochemically generated nitrile ylide does not thermally collapse back to the azirine ring. The chemical behavior of Δ^3-oxazolinones was also compared to the previously reported Δ^2-oxazolinone system.

In order to rationalize the intriguing photochemical cycloadditions that arylazirines (**1**) undergo with electron-deficient olefins, we proposed the intervention of a nitrile ylide (**2**) intermediate.[4,5] As a 1,3 dipole, this species can be intercepted with a variety of dipolarophiles to form five-membered rings.[6-10]

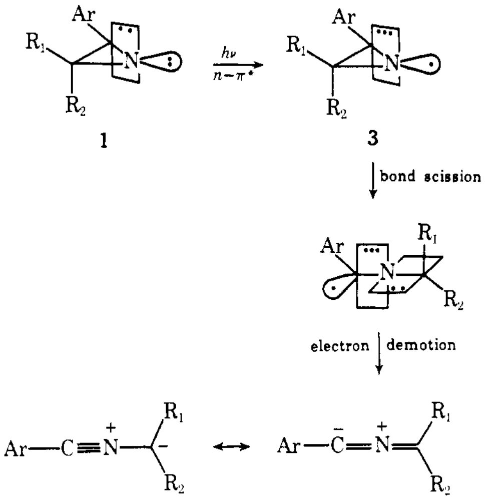


1 **2a**

2b **2c**

The cleavage of the C–C bond of the azirine ring proceeds from the n–π* singlet state[5] and was rationalized[5,11,12] in terms of an electrocyclic transformation by analogy with the cyclopropyl → allyl cation rearrangement.[13] One may envisage the n–π* excitation process as leading to a species resembling structure **3**, where the nonbonding orbital on nitrogen contains only one electron. The electron that was promoted to the antibonding π* orbital will partially reside on the carbon atom and consequently the nitrogen atom will become somewhat electrophilic and begin to resemble an aziridinyl cation (see Chart I). The remaining nonbonding electron on nitrogen, which is in the plane of the σ bonds of the ring, will overlap with the back lobe of the C–C bond of the saturated carbon and facilitate bond scission. Electron demotion would then result in the formation of nitrile ylide **2**. It should be noted that a similar nonbonding orbital overlap with an adjacent σ bond was postulated to account for the facile α cleavage (*i.e.*, Norrish Type I) encountered with carbonyl compounds.[14]

Chart I



1 **3**

2a **2b**

Salem has recently carried out some *ab initio* computations on the ground and excited state energy surfaces of the 2*H*-azirine molecule.[15a] His calculations indicate that the ring-opened intermediate should be capable of dual reactivity when it is intercepted by an added dipolarophile. The behavior of the system was predicted to be dependent on the geometry of the

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(1) Photochemical Transformations of Small Ring Heterocyclic Systems. LVI; for part LV, see A. Padwa and G. Lee, *J. Amer. Chem. Soc.*, **96**, 1634 (1974).

(2) Alfred P. Sloan Foundation Fellow, 1968–1972; National Institutes of Health Special Postdoctoral Fellow, 1972–1973.

(3) Virginia Military Institute Faculty Fellow, 1971–1973.

(4) A. Padwa and J. Smolanoff, *J. Amer. Chem. Soc.*, **93**, 548 (1971).

(5) A. Padwa, S. Clough, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Amer. Chem. Soc.*, **94**, 1395 (1972); *ibid.*, **95**, 1945, 1954 (1973).

(6) A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Lett.*, 4087 (1972).

(7) A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *J. Org. Chem.*, **38**, 1333 (1973).

(8) N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972).

(9) H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 745 (1972).

(10) B. Jackson, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 919 (1972).

(11) E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).

(12) B. Singh, A. Zweig, and J. B. Gallivan, *J. Amer. Chem. Soc.*, **94**, 1199 (1972).

(13) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(14) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

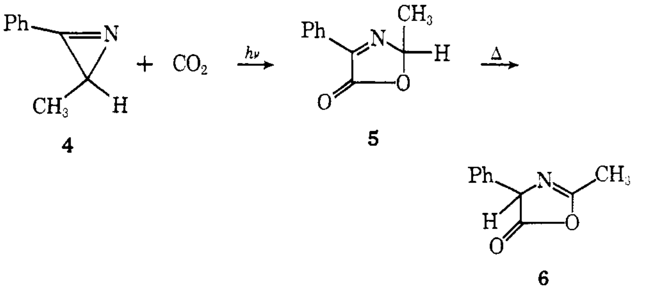
(15) (a) L. Salem, private communication; (b) A. Padwa and J. Smolanoff, *Chem. Commun.*, 342 (1973).

transient intermediate generated from the photolysis of the azirine ring. If the ring is opened to give a species with bent geometry (*i.e.*, **2c**), a diradical state with partial dipolar character will be obtained. On the other hand, opening of the azirine ring to an intermediate with linear geometry (*i.e.*, **2a** ↔ **2b**) will result in the formation of a species having closed-shell zwitterionic character. Salem's calculations also indicate that the reactive dipolar intermediate with linear geometry is best reached by internal conversion from an $n-\pi^*$ singlet state at a C–N–C angle of 100°. We had previously reported that arylazirines are converted to methoxyimines upon irradiation in methanol.[15b] This observation is more compatible with the linear nitrile ylide structure (**2a** ↔ **2b**) than with the bent structure (**2c**) for the ring-opened intermediate.

The present research began as an attempt to understand one intriguing aspect of the photochemistry of the azirine ring. We were particularly interested in knowing whether the photochemically generated nitrile ylide could thermally cyclize and regenerate the starting azirine. An upper limit of 20% would have to be imposed on this process in the diphenylazirine system, since the cycloaddition reaction proceeds with 80% quantum efficiency.[5] Of course, it is possible that the less than unity quantum yield obtained here can be attributed to other sources of inefficiency such as radiationless decay of the excited azirine ring. The approach selected to answer this question was to study the photochemistry of a related system, one which would also generate a nitrile ylide, and determine whether the azirine ring was formed. From preliminary studies in our laboratory, there was some indication that the Δ^3-oxazolin-5-one system could function in this capacity. In this paper we report on the generation of nitrile ylides by photochemical extrusion of carbon dioxide from several substituted Δ^3-oxazolin-5-ones. The results provide further insight into the chemical behavior of these reactive 1,3-dipolar intermediates.

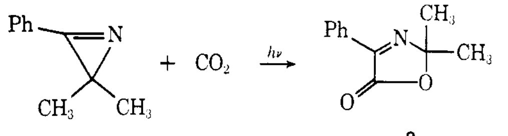
Results and Discussion

Photochemical Cycloaddition of Arylazirines with Carbon Dioxide. We have found that arylazirines undergo smooth photocycloaddition to carbon dioxide in an inert solvent. Irradiation of 3-methyl-2-phenylazirine (**4**) in a benzene solution saturated with carbon dioxide with an internal water-cooled mercury arc lamp affords 2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**5**) in 88% yield as the only identifiable product. The structure of **5** is based on analytical, infrared, ultraviolet, nmr, and mass spectral data (see Experimental Section). Heating azlactone **5** for 3 hr at 130° in xylene resulted in its partial conversion (20%) to the Δ^2-oxazolin-5-one system (**6**). Continued heating of the xylene solution for an additional 4 hr produced a dimeric material, mp 233–235°, whose structure was not investigated. The two azlactones could be readily distinguished on the basis of their characteristic infrared spectra. The carbonyl stretching frequency of azlactone **5** was located at 5.61 μ while that associated with **6** was found at 5.46 μ.



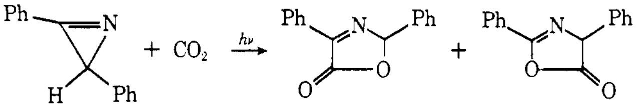
4 5 6

An analogous photochemical result was obtained using 3,3-dimethyl-2-phenylazirine (**7**) as the substrate. The adduct isolated (**8**) in high yield (94%) was a low-melting solid, mp 36–37°, whose nmr spectrum showed a methyl signal at τ 8.34. This material was stable on thermolysis.



7 8

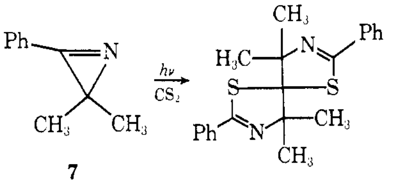
Irradiation of 2,3-diphenylazirine (**9**) in the presence of carbon dioxide produced equivalent quantities of azlactones **10** and **11**. The mixture of isomers could not be readily separated and consequently we did not pursue further investigations with this system.



9 10 11

The above photochemical reactions can readily be rationalized by 1,3-dipolar cycloaddition of an initially generated nitrile ylide to carbon dioxide. As far as we can tell, this represents the first case where carbon dioxide has been used as a dipolarophile in the 1,3-dipolar cycloaddition of nitrile ylides.[16,17]

It is interesting to note that when dimethylphenylazirine **7** was irradiated in the presence of carbon disulfide, a crystalline diadduct, mp 125–126°, was obtained in good yield. This material is assigned the structure of 5,5-spirobi(4,4-dimethyl-2-phenyl-Δ^2-thiazoline) (**12**) on the basis of its physical data. Although high concentrations of carbon disulfide and short reaction times were used, no 1:1 adduct could be isolated or detected in the reaction mixture. The formation of a 2:1 adduct finds precedent in some of Huisgen's work on the cycloaddition of nitrile imines with carbon disulfide.[18] In order to account for the formation of a diadduct, Huisgen suggested that the C–S double bond present in the initially formed 1:1 adduct reacted much faster than the C–S double bond of carbon disulfide.



7 12

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(16) The photochemical rearrangement of 3-phenylsydnone to 4-phenyl-Δ^2-1,3,4-oxadiazolin-5-one was postulated to involve a 1,3-dipolar cycloaddition of a nitrile imine with carbon dioxide; see C. H. Krauch, J. Kuhls, and H. J. Piek, *Tetrahedron Lett.*, 4043 (1966).

(17) Schmid and coworkers have independently reported similar observations.[9]

(18) R. Huisgen, H. Stangl, H. Sturm, R. Raab, and K. Bunge, *Chem. Ber.*, **105**, 1258 (1972).

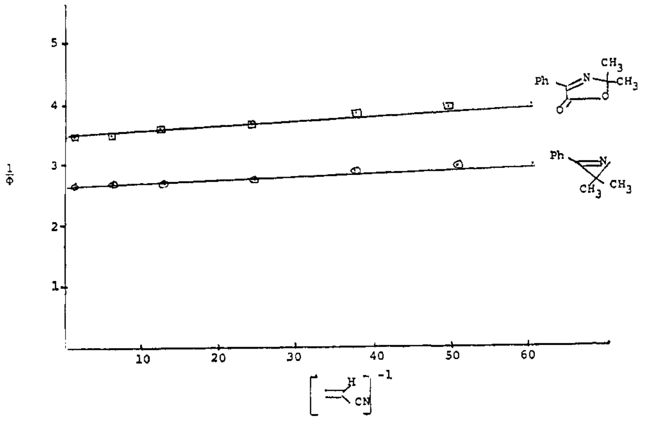


Figure 1. Plot of [quantum yield of cycloaddition]$^{-1}$ against [acrylonitrile]$^{-1}$.

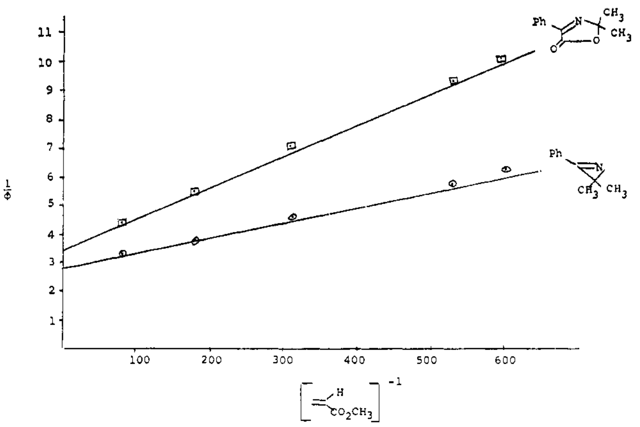
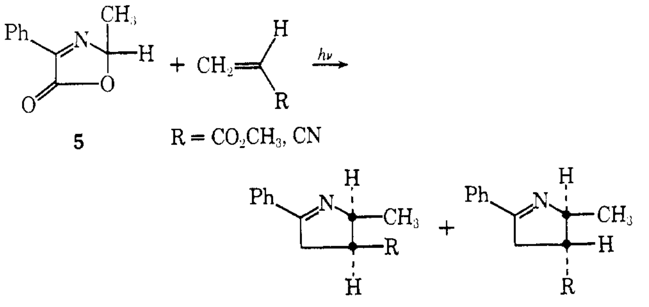


Figure 2. Plot of [quantum yield of cycloaddition]$^{-1}$ against [methyl acrylate]$^{-1}$.

Presumably, the same situation occurs with the azirine system.

Photochemical Extrusion of Carbon Dioxide from the Δ^3-Oxazolinone System. Irradiation of a pentane solution of methyl acrylate and 2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**5**) produced a mixture of *cis-* and *trans-*2-phenyl-4-carbomethoxy-5-methyl-Δ^1-pyrrolines (**13** (67%) and **14** (33%)). Photoaddition of **5** with acrylonitrile followed the same pattern and gave rise to a mixture of Δ^1-pyrrolines **15** and **16** in good yield (see Experimental Section).

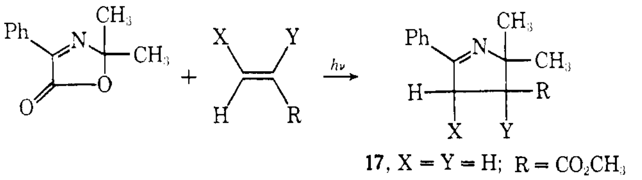


5 R = CO_2CH_3, CN

13, R = CO_2CH_3 **14**, R = CO_2CH_3

15, R = CN **16**, R = CN

Additional cases of the photocycloaddition reaction are provided by the photolysis of 2,2-dimethyl-4-phenyl-Δ^3-oxazolin-5-one (**8**) with methyl acrylate, acrylonitrile, methylacrylonitrile, and dimethyl fumarate. The configurations of the adducts obtained (**17–20**) were readily established by examination of their characteristic nmr spectra (see Experimental Section) and by comparison with authentic samples.[5]



17, X = Y = H; R = CO_2CH_3

18, X = Y = H; R = CN

19, X = H; Y = CH_3; R = CN

20, X = R = CO_2CH_3; Y = H

The fact that the regiospecificity and isomeric distribution (*i.e.*, ratio **13**/**14** and **15**/**16**) observed in these reactions are identical with that obtained from the irradiation of the corresponding azirine suggests that similar intermediates are involved in these two reactions. A nitrile ylide would be the most logical candidate. These observations, however, do not distinguish whether the nitrile ylide is formed directly from the azlactone or whether an azirine molecule is first formed which subsequently undergoes ring opening on further irradiation.

In order to derive additional mechanistic information concerning the photoextrusion process, a more quantitative investigation of these cycloaddition reactions was undertaken. To establish the multiplicity of the oxazolinone cycloaddition reaction, quenching and sensitization experiments were carried out. Identical Δ^3-oxazolinone-dipolarophile solutions containing 1,3-cyclohexadiene or piperylene were irradiated. Neither the rate of oxazolinone disappearance nor that of adduct formation was affected by the quenchers, each of which was present in concentrations known to diminish markedly the rates of established triplet processes.[19,20] Attempts to sensitize the photoextrusion reaction were also carried out using xanthone as a triplet sensitizer. The concentrations were adjusted so that xanthone absorbed more than 98% of the light. Also, the concentration of the Δ^3-oxazolinone was kept sufficiently low to ensure unimolecular destruction of xanthone excited singlet molecules prior to collision with ground state oxazolinone yet sufficiently high to guarantee collision of xanthone triplets with oxazolinone at a rate faster than xanthone decay. Under these conditions, no photocycloaddition was detected. The quenching and sensitization experiments suggest that the overall transformations of the Δ^3-oxazolinone system occur from the excited singlet manifold.[21] No fluorescence emission from **5** or **8** was observed.

Quantum yields for adduct formation were determined using cyclopentanone as the chemical actiometer.[22] Degassed and sealed Quartz tubes containing solutions of the Δ^3-oxazolinone and the dipolarophile were irradiated along with actinometer tubes in a rotating photochemical assembly equipped with a low-pressure mercury lamp. Similar measurements were performed with azirines **4** and **7**. Reactions were car-

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(19) A. J. Fry, R. S. H. Lin, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4781 (1966).

(20) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, **27**, 4111 (1962).

(21) Or possibly from a very short-lived triplet state.

(22) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

ried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by glpc using internal standards. The results of the quantum yield measurements in degassed pentane solutions are given in Figures 1 and 2. The quantum yield for adduct formation as a function of the concentration of acrylonitrile in a pentane solution saturated with carbon dioxide was also studied. The data are presented graphically in Figure 3 for the case of 2,2-dimethyl-4-phenyl-Δ^3-oxazolin-5-one (**8**).

Several features become apparent upon examination of the data shown in Figures 1–3. Although a good linear relationship is found between the inverse of the quantum yield for adduct formation and the inverse of concentration of dipolarophile, the slope of the line depends on both the structure of the dipolarophile and the substrate used to generate the nitrile ylide. At infinite dipolarophile concentration, the quantum yield for cycloaddition is 0.36 for azirine **7** and 0.30 for oxazolinone **8**. The magnitude of the intercept indicates that the oxazolinone cycloaddition is slightly less efficient than the azirine cycloaddition. These experiments also demonstrate that a significant path from the electronically excited singlet states of **7** and **8** involves bond rupture and formation of a nitrile ylide.

The results obtained using 3,3-dimethyl-2-phenylazirine (**7**) as the nitrile ylide precursor are consistent with the mechanism outlined below (see Scheme I).

Scheme I

$$A_0 \xrightarrow{h\nu} A^{*1}$$

$$A^{*1} \xrightarrow{k_1} A_0$$

$$A^{*1} \xrightarrow{k_2} NY$$

$$NY + O \xrightarrow{k_3} \text{adduct}$$

$$NY + A_0 \xrightarrow{k_3} \text{dimer}$$

In this scheme, A_0 = 3,3-dimethyl-2-phenylazirine, NY = nitrile ylide, and O = dipolarophile. By making the usual steady state assumption, we can write

$$\frac{1}{\Phi} = \frac{1}{\tau k_2}\left[1 + \frac{k_4[A_0]}{k_3[O]}\right]$$

where τ is the excited single lifetime and Φ is the quantum yield of adduct formation. According to this mechanistic scheme, the slope of the plot should be dependent on both the initial concentration of the azirine as well as the magnitude of k_3 and k_4. Quantitatively, if $k_3 \gg k_4[A_0]$, then little variation in slope is to be expected as the concentration of the azirine is increased. This is the case when olefins of high dipolarophilic acitivy, such as acrylonitrile or methyl acrylate, are used.

In order to adequately explain the results encountered with the oxazolinone system (**8**), it becomes necessary to modify Scheme I. With the azirine system, the reaction which effectively competes with Δ^1-pyrroline formation is the 1,3-dipolar cycloaddition reaction of the nitrile ylide with a ground state azirine molecule.[7] Since no azirine could be detected in any of the oxazolinone photolyses, the process which best accounts for the diminution of the quantum yield of cycloaddition as the dipolarophile concentration is decreased is the 1,3-dipolar addition of the photogenerated nitrile ylide to carbon dioxide. This will lead to the regeneration of the Δ^3-oxazolinone and consequently diminish the overall cycloaddition efficiency. Reaction Scheme II

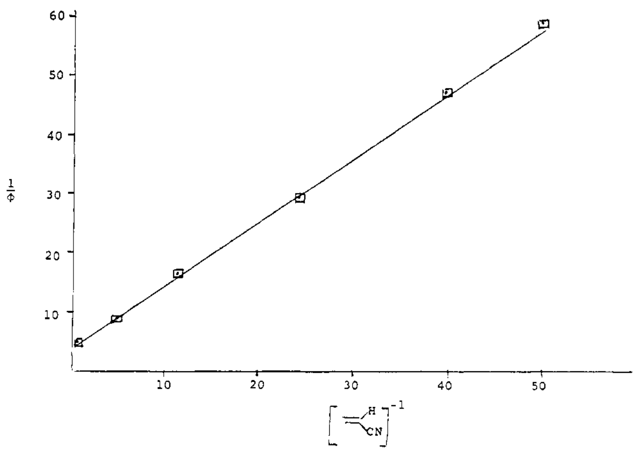


Figure 3. Plot of [quantum yield of cycloaddition]$^{-1}$ against [acrylonitrile]$^{-1}$ for 2,2-dimethyl-4-phenyl-Δ^3-oxazolin-5-one in pentane saturated with carbon dioxide.

Scheme II

$$OX_0 \xrightarrow{h\nu} OX^{*1}$$

$$OX^{*1} \xrightarrow{k_5} OX_0$$

$$OX^{*1} \xrightarrow{k_6} NY + CO_2$$

$$NY + O \xrightarrow{k_3} \text{adduct}$$

$$NY + CO_2 \xrightarrow{k_7} OX_0$$

adequately describes this situation. In this scheme, OX_0 = Δ^3-oxazolinone **8**, NY = nitrile ylide, and O = dipolarophile. By making the usual steady state approximation, we can write

$$\frac{1}{\Phi} = \frac{1}{\tau k_6}\left[1 + \frac{k_7[CO_2]}{k_3[O]}\right]$$

According to this mechanistic scheme, the slope of the plot should depend on both the concentration of carbon dioxide as well as the magnitude of k_3 and k_7. The fact that the quantum yield for cycloaddition varied when the irradiation of **8** was carried out to low but significant conversion (*ca.* 6%) indicates the existence of a small but "effective" concentration of carbon dioxide which is capable of reacting with the nitrile ylide. The "effective" concentration is related to the average quantity of carbon dioxide generated during the course of the reaction. In the above experiments, the concentration of oxazolinone used was 8.3×10^{-3} *M*. As a rough approximation, we can assume that the "effective" concentration of carbon dioxide is *ca.* 2.5×10^{-4} *M* (*i.e.*, 3% of 8.3×10^{-3} *M*). The fact that the slopes of these plots are relatively small can be attributed to the low "effective" carbon dioxide concentration as well as to the extremely reactive nature of the dipolarophiles used in this study.

In order to verify the quantum yield dependence of these plots on carbon dioxide concentration, the Stern–Volmer experiments were repeated using acrylonitrile solutions saturated with carbon dioxide. Jolley and Hildebrand have previously determined that the con-

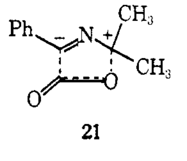
Table I. Kinetic Data from the Stern–Volmer Analysis of the Photocycloaddition of the Nitrile Ylide Precursors with Methyl Acrylate and Acrylonitrile[a]

Ylide precursor[b]	Dipolarophile	$[CO_2]$, M	Slope[e]	Intercept	k_7/k_3	k_4/k_3	k_1/k_2	k_5/k_6
Δ^3-Oxazolinone **8**	Methyl acrylate	2.5×10^{-4} [c]	1.1×10^{-2}	3.35	13.2			2.35
	Acrylonitrile	2.5×10^{-4} [c]	9.96×10^{-3}	3.35	11.9			2.35
	Acrylonitrile	0.11[d]	1.09	3.40	2.90			2.40
Azirine **7**	Methyl acrylate		5.4×10^{-3}	2.75		0.24	1.75	
	Acrylonitrile		3.9×10^{-3}	2.75		0.17	1.75	

[a] See Figures 1–3. [b] Precursor concentration = 8.3×10^{-3} M. [c] Due to the photogeneration of CO_2 from Δ^3-oxazolinone **8**. [d] Prepared by saturation of a pentane solution with CO_2. [e] Calculated by use of a nonlinear least-squares program (KINET); see J. L. Dye and V. Nicely, *J. Chem. Educ.*, **48,** 443 (1971).

centration of such solutions is about 0.11 M.[23] These saturated solutions provide us with a significant and reasonably constant value of carbon dioxide which can be used in the kinetic expression. The results of these measurements are summarized in Figure 3. From this figure it can be seen (compare with Figure 1) that the slope of the plot is significantly enhanced while the value of the intercept remains unchanged. The formation of the cycloadduct is severely retarded by the presence of added carbon dioxide even though an extremely reactive dipolarophile was employed as the trapping agent. This observation strongly supports the mechanism outlined in Scheme II.

By knowing the magnitude of the slope and intercept, it becomes possible to determine the ratio of the rate constants involved in these cycloaddition reactions. The values are summarized in Table I. The relative fate of the photochemically generated nitrile ylide is indicated by the magnitude of k_7/k_3 or k_4/k_3. The results indicate that carbon dioxide is a much better dipolarophile for the nitrile ylide than is dimethylphenylazirine 7. This conclusion was reached by comparing the value of k_7/k_3 in the oxazolinone system (*i.e.*, 2.9) to the corresponding ratio in the azirine system (*i.e.*, k_4/k_3 = 0.17). In these cases, carbon dioxide and azirine 7 are competing with the added dipolarophile for the same photogenerated nitrile ylide. The apparent discrepancy between the ratios of k_7/k_3 (*i.e.*, 2.9 *vs.* 11.9) found in the photocycloaddition of oxazolinone **8** with acrylonitrile in the presence and absence of added carbon dioxide deserves some comment. The high value found for this ratio when carbon dioxide was initially absent seemingly implies that our estimate of the "effective" carbon dioxide concentration, generated during the course of the reaction, is somewhat low. This initial underestimation on our part can now be understood by considering the details of the photoexpulsion of carbon dioxide from the oxazolinone system. If the carbon dioxide released from the oxazolinone is not just randomly expelled into the solution, but rather is maintained in an associative or "cage-like" state (*i.e.*, **21**) with the nitrile ylide, then an artificially high concentration of carbon dioxide would be generated near the nitrile ylide. When the Stern–Volmer plots are carried out with solutions that have been saturated with carbon dioxide, this "artificial" concentration of carbon dioxide is no longer significant when compared to the initial concentration of carbon dioxide. Or stated in other terms, return from the "cage-like" structure (**21**) to Δ^3-oxazolinone **8** is less important than return from a free nitrile ylide. This explanation would suggest that the value of k_7/k_3 = 2.90 is the more reliable number for this ratio.



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Another point meriting attention is the identical chemical reactivity of the nitrile ylides generated from both precursors. Generation of the nitrile ylide by irradiating either precursor in the presence of a mixture of dipolarophiles creates a competitive system from which the ratio of relative rates may be obtained by standard treatment of the kinetic data. The required data for the calculation of k_{rel} are the initial concentration of each of the competing dipolarophiles and the concentration of each at a subsequent stage in the reaction. In principle, these data may be determined either directly by measuring the amount of dipolarophile remaining or indirectly from a knowledge of the concentration of the reaction products.

$$k_{\text{rel}} = \frac{k_{\text{olefin B}}}{k_{\text{olefin A}}} = \frac{\log([O_B]_i/[O_B]_f)}{\log([O_A]_i/[O_A]_f)}$$

The near identity of the relative rate data (see Table II) coupled with the isomeric "fingerprint" (*i.e.*, products **13–16**) strongly implicates the intermediacy of a common intermediate in these photolyses.

Table II. Relative Reactivities of Dipolarophiles toward the Nitrile Ylides Generated from Dimethylphenylazirine (**7**) and Dimethylphenyl-Δ^3-oxazolinone (**8**)

	Relative rate	
Dipolarophile	Azirine **7**	Oxazolinone **8**
	Slow set	
Methyl methacrylate	1	1
Methyl acrylonitrile	1.3	1.4
	Fast set	
Methyl acrylate	1	1
Acrylonitrile	2.1	2.1

Turning now to the matter of whether azirine **7** is an initial intermediate in the photolysis of oxazolinone **8**, we note that no azirine could be detected when the irradiation of **8** was carried out in the absence of a dipolarophile. Furthermore, spectral and chromatographic analysis of the reaction mixture showed that of the many products formed, none were identical with those obtained from the photolysis of the azirine itself.[7] This result implies that oxazolinone **8** loses carbon

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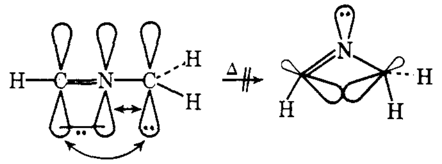
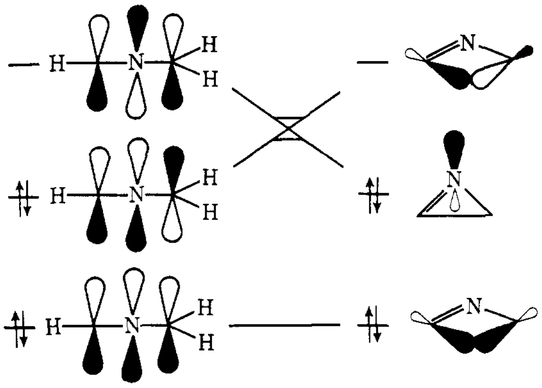
(23) J. E. Jolley and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **80**, 1050 (1958).

dioxide directly to generate the nitrile ylide and that this species does not recyclize to generate the azirine ring. The absence of azirine dimers supports this contention. If azirine **7** were formed, it should be present in sufficient concentration to intercept the ylide and produce photodimers. This is not the case.

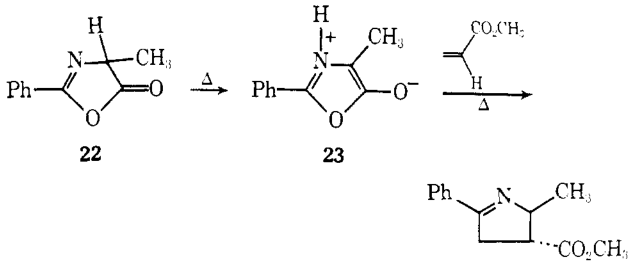
Schmid has recently published results which support these conclusions.[24] He found that the irradiation of a number of substituted arylazirines in a rigid matrix at −185° gave rise to a new maximum in the ultraviolet spectrum (*ca.* 350 nm) which he attributed to a nitrile ylide. His results also demonstrated that the dipole undergoes photochemical but not thermal reversion to starting azirine. It should also be pointed out that thermolysis of the azirine ring does not generate a nitrile ylide[25] but instead gives rise to a vinyl nitrene.[26,27] Consequently, it would appear as though a high energy barrier exists for the thermal interconversion of azirines and nitrile ylides. This may be related to the fact that a "least-motion" cyclization would be expected to be a $[\pi_{s}{}^{2} + \omega_{s}{}^{2}]$ forbidden process. Another way of looking at this is to correlate the "allyl" orbitals of the nitrile ylide with those of the azirine ring. This is described in Scheme III. By simultaneous bending and rotation, the unfavorable correlation might be overcome, but attainment of the sterically easy transition state appears to be a high-energy forbidden process.



Scheme III



It is interesting at this point to compare the chemical behavior of the Δ^3-oxazolinone ring with that of the previously reported Δ^2-oxazolinone system.[28] As noted by Huisgen, Δ^2-oxazolinones which contain a hydrogen atom in the 4 position (*i.e.*, **22**) of the ring undergo smooth thermal cycloaddition with electron-deficient olefins.[29] The reaction was suggested to proceed by tautomerization of **22** to a mesoionic oxazolium 5-oxide (**23**) which then combines with the dipolarophile.[30]



22 **23**

14

When the 4 position of the Δ^2-oxazolinone ring was blocked with alkyl groups, the cycloaddition reaction did not proceed. All of our attempts to effect a thermal cycloaddition of the corresponding Δ^3-oxazolinone system (*i.e.*, **5**) with a variety of dipolarophiles failed. Even when the thermolysis was carried out under more forcing conditions than those employed by Huisgen, the reaction afforded only starting material. The difference in thermal behavior of these two systems can be attributed to the reluctance of the Δ^3-oxazolinone to form a mesoionic intermediate.

One additional point which is noteworthy is the fact that the Δ^2-azlactone does not undergo photocycloaddition with electron-deficient olefins. This is not totally unexpected since this system contains a markedly different chromophore unit from that present in the Δ^3-oxazolinone system. At any rate, the photoextrusion of carbon dioxide and 1,3-dipolar cycloaddition of the resulting dipole from the Δ^3-azlactone provides a useful synthetic variation to the known thermal cycloaddition reactions of Δ^2-oxazolinones.

Experimental Section[31]

Preparation of 2-Methyl-4-phenyl-Δ^3-oxazolin-5-one (5). A solution containing 1.0 g of 3-methyl-2-phenylazirine (**4**)[32] in 300 ml of benzene was saturated with carbon dioxide. The solution was irradiated for 1.5 hr using a 450-W Hanovia lamp equipped with a Corex filter sleeve. During the irradiation, carbon dioxide was continually bubbled through the solution. At the end of the irradiation, the solvent was removed under reduced pressure and the residue was chromatographed through a 3 × 20 cm column containing 30 g of silica gel with benzene as the eluent. The benzene fractions were combined and the solvent was removed under reduced pressure to give 1.04 g (88%) of a light yellow oil. Distillation of this residue at 80–85° (0.06 mm) gave a colorless oil which was assigned as 2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**5**) on the basis of the following data: ir (neat) 3.35, 5.62, 6.18, 7.68, 8.70, 9.38, 10.78, 12.37, 13.39, and 14.58 μ; nmr τ 8.40 (3 H, d, J = 6.5 Hz), 3.78 (1 H, q, J = 6.5 Hz), 2.2–2.5 (3 H, m), and 1.3–1.5 (2 H, m); *m/e* 175 (M$^+$), 131 (base), 104, and 77.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.52; H, 5.32; N, 7.80.

2-Methyl-4-phenyl-Δ^3-oxazolin-5-one was observed to undergo thermal dimerization. A solution of 350 mg of **5** in 10 ml of xylene was heated at 130°. After 3 hr, the reaction mixture consisted of unchanged starting material (80%) as well as a new compound (20%), whose nmr spectrum showed signals at τ 7.70 (3 H,

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(31) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz using a Jeol-MH-100 spectrometer.

(32) A. Hassner and F. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).

d, J = 2.0 Hz) and 4.60 (1 H, m). On the basis of the nmr spectrum, this new compound is assigned the structure of 2-methyl-4-phenyl-Δ^2-oxazolin-5-one (**6**). Continued heating of the above solution at 140° for an additional 2 hr resulted in the disappearance of these signals and the appearance of singlets at τ 7.26 and 8.0 in the nmr. Removal of the solvent under reduced pressure left a yellow residue which was recrystallized from chloroform–hexane to give 89 mg (24%) of a crystalline dimer, mp 233–235°: nmr ($CDCl_3$) τ 8.0 (3 H, s), 7.26 (3 H, s), 4.2 (1 H, s), 3.46 (1 H, broad s), and 2.3–3.0 (10 H, m); m/e 350 (M^+), 308, 249, 237, 222, 176, 175, 167, 148, 132, 104 (base), and 77. The structure of the dimer was not investigated further.

Preparation of 2,2-Dimethyl-4-phenyl-Δ^3-oxazolin-5-one (8). A solution containing 0.5 g of 3,3-dimethyl-2-phenylazirine (**7**)[33] in 250 ml of benzene was saturated with carbon dioxide. The solution was photolyzed using a Corex filter sleeve during which time carbon dioxide was continually bubbled through the solution. After 1.5 hr, the solvent was removed under reduced pressure and the residue was distilled at 100–105° (0.02 mm) to give 0.61 g (94%) of a clear oil which solidified on standing. The solid obtained was recrystallized from hexane to give an analytical sample of 2,2-dimethyl-4-phenyl-Δ^3-oxazolin-5-one (**8**), mp 36–37°: ir (neat) 3.37, 5.63, 6.17, 6.91, 8.10, 11.03, 12.31, 13.25, and 14.50 μ; nmr ($CDCl_3$) τ 8.34 (6 H, s), 2.3–2.5 (3 H, m), and 1.4–1.6 (2 H, m); uv (pentane) 263 nm (ϵ 13,800) and 224 (7200); m/e 189 (M^+), 145, 104 (base), and 77.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.75; H, 5.98; N, 7.46.

Photoaddition of 3,3-Dimethyl-2-phenylazirine with Carbon Disulfide. A solution containing 0.4 g of 3,3-dimethyl-2-phenylazirine (**7**) and 2.52 g of carbon disulfide in 60 ml of pentane was irradiated under a nitrogen atmosphere for 1.5 hr using a 2537-Å lamp. The solvent was removed under reduced pressure and the residue was subjected to thick layer chromatography. The major band was extracted with chloroform and concentrated under reduced pressure to a yellow oil which was distilled at 145–150° (0.03 mm). Repeated recrystallization of this material from hexane gave a crystalline solid, mp 125–126°, whose structure was assigned as 5,5-spirobi-4,4-dimethyl-2-phenyl-Δ^2-thiazoline (**12**) on the basis of the following data: ir (KBr) 3.45, 6.24, 8.37, 8.87, 11.64, and 13.24 μ; uv (95% ethanol) 246 and 316 nm (ϵ 20,700 and 900); nmr ($CDCl_3$) τ 8.31 (6 H, s), 8.23 (6 H, s), and 2.2–2.9 (10 H, m); m/e 366 (M^+), 319, 264, 263 (base), 190, 189, 145, 104, 103, and 77.

Anal. Calcd for $C_{21}H_{22}N_2S_2$: C, 68.83; H, 6.05; N, 7.65. Found: C, 68.83; H, 6.19; N, 7.53.

Photoaddition of 2,3-Diphenylazirine with Carbon Dioxide. A solution containing 0.75 g of diphenylazirine in 250 ml of benzene was saturated with carbon dioxide. The solution was irradiated for 1 hr using a 450-W Hanovia lamp equipped with a Corex filter sleeve. Carbon dioxide was continually bubbled through the solution during the course of the photolysis. Removal of the solvent under reduced pressure gave a colorless oil whose nmr spectrum revealed it to be a 1:1 mixture of 2,4-diphenyl-Δ^3-oxazolin-5-one (**10**) (nmr τ 4.47 (1 H, s), 2.3–2.6 (8 H, m), and 1.3–1.5 (2 H, m)) and 2,4-diphenyl-Δ^2-oxazolin-5-one (**11**) (nmr τ 2.97 (1 H, s), 2.3–2.6 (8 H, m), and 1.7–1.9 (2 H, m)). The mixture of isomers could not be readily separated and consequently further investigation on this system was terminated.

Photoaddition of 2-Methyl-4-phenyl-Δ^3-oxazolin-5-one with Methyl Acrylate. A solution containing 50 mg of **5**, 0.5 ml of methyl acrylate, and 10 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a low-pressure mercury arc. The mixture of compounds obtained on removal of the solvent could not be separated into its component parts. Characterization was accomplished by nmr spectroscopy ($CDCl_3$, 100 MHz). The major adduct (62%) showed a doublet at τ 8.80 (3 H, J = 7.0 Hz), a multiplet at 6.9 (3 H), a singlet at 6.28 (3 H), a multiplet at 5.30 (1 H), and a multiplet from 2.1 to 2.9 (5 H). The minor adduct (30%) showed a doublet at τ 8.53 (3 H, J = 7.0 Hz), a multiplet at 6.90 (3 H), a singlet at 6.31 (3 H), a multiplet at 5.63 (1 H), and a multiplet from 2.1 and 2.9 (5 H). The structure of this 2:1 epimeric mixture of *cis*- and *trans*-4-carbomethoxy-5-methyl-2-phenyl-Δ^1-pyrroline (**13** and **14**) was established by comparison with authentic samples.[5] The isomer distribution was virtually identical with that obtained from the irradiation of the corresponding azirine (**4**) with methyl acrylate.[5]

Photoaddition of 2-Methyl-4-phenyl-Δ^3-oxazolin-5-one with Acrylonitrile. A solution containing 150 mg of azlactone **5**, 5 ml of acrylonitrile, and 200 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a 450-W Hanovia lamp equipped with a Corex filter sleeve. The mixture of compounds obtained on removal of the solvent was characterized by nmr spectroscopy. The major adduct (50%) showed signals at τ 8.50 (3 H, d, J = 6.5 Hz), 7.40 (1 H, ddd, J = 9.5, 8.0, and 7.0 Hz), 6.80 (2 H, m), and 5.59 (1 H, t, J = 7.0 and 6.5 Hz). The minor adduct (20%) showed signals at τ 8.53 (3 H, d, J = 6 and 5 Hz), 6.73 (3 H, m), 5.53 (1 H, m), and 2.2–2.9 (5 H, m). The structure of this 5:2 epimeric mixture of *cis*- and *trans*-2-phenyl-4-cyano-5-methyl-Δ^1-pyrroline (**15** and **16**) was established by comparison with authentic samples.[5] The isomer distribution was identical with that obtained from the irradiation of the corresponding azirine with acrylonitrile.[5]

Photoaddition of 2,2-Dimethyl-4-phenyl-Δ^3-oxazolin-5-one with Methyl Acrylate. A solution containing 50 mg of azlactone **8**, 0.5 ml of methyl acrylate, and 10 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a low-pressure mercury arc. Removal of the solvent under reduced pressure gave 2-phenyl-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**17**) (43%) as a crystalline solid, mp 55–56°: ir (KBr) 5.80 and 6.20 μ; uv (cyclohexane) 243 nm (ϵ 17,700); nmr ($CDCl_3$) τ 8.85 (3 H, s), 8.45 (3 H, s), 6.72 (3 H, m), 6.26 (3 H, s), 2.1–2.8 (5 H, m); m/e 231, 200, 172, 145 (base), 115, and 104. This material was identical in every respect with an authentic sample prepared from the irradiation of 2-phenyl-3,3-dimethylazirine (**7**) with methyl acrylate.

Photoaddition of 2,2-Dimethyl-4-phenyl-Δ^3-oxazolin-5-one with Acrylonitrile. A solution containing 50 mg of azlactone **8**, 0.5 ml of acrylonitrile, and 10 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a low-pressure mercury arc. Removal of the solvent under reduced pressure afforded 2-phenyl-4-cyano-5,5-dimethyl-Δ^1-pyrroline (**18**, 66%) as a crystalline solid, mp 65–66°: ir (KBr) 4.50 and 6.19 μ; uv (cyclohexane) 224 nm (ϵ 17,100); nmr ($CDCl_3$) τ 8.56 (3 H, s), 8.50 (3 H, s), 7.09 (1 H, dd, J = 10.0 and 8.0 Hz), 6.76 (1 H, dd, J = 17.0 and 8.0 Hz), 6.58 (1 H, dd, J = 17.0 and 10.0 Hz), 2.2–2.8 (5 H, m); m/e 198, 145 (base), 104, and 77. This material was identical in every respect with an authentic sample prepared from the irradiation of 2-phenyl-3,3-dimethylazirine (**7**) with acrylonitrile.

Photoaddition of 2,2-Dimethyl-4-phenyl-Δ^3-oxazolin-5-one with Methylacrylonitrile. A solution containing 50 mg of azlactone **8**, 0.5 ml of methylacrylonitrile, and 10 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a low-pressure mercury arc. Removal of the solvent left 2-phenyl-4-cyano-4,5,5-trimethyl-Δ^1-pyrroline (**19**) (38%) as a colorless oil: nmr ($CDCl_3$) τ 8.70 (3 H, s), 8.68 (3 H, s), 8.57 (3 H, s), 7.11 (1 H, d, J = 16.5 Hz), 6.60 (1 H, d, J = 16.5 Hz), 2.2–2.9 (5 H, m). This material was identical in every respect with an authentic sample prepared from the irradiation of 2-phenyl-3,3-dimethylazirine (**7**) with methylacrylonitrile.

Photoaddition of 2,2-Dimethyl-4-phenyl-Δ^3-oxazolin-5-one with Dimethyl Fumarate. A solution containing 50 mg of **8**, 0.5 ml of dimethyl fumarate, and 10 ml of pentane was irradiated under a nitrogen atmosphere for 1 hr using a 2537-Å source. Removal of the solvent under reduced pressure gave 2-phenyl-3,4-*trans*-dicarbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**20**) (78%) as a crystalline solid, mp 84–85°: ir (KBr) 3.40, 5.82, 7.00, 8.65, 12.78, 13.00, and 14.35 μ; uv (cyclohexane) 242 nm (ϵ 14,200); nmr ($CDCl_3$) τ 8.80 (3 H, s), 8.37 (3 H, s), 6.64 (1 H, d, J = 8.0 Hz), 6.38 (3 H, s), 6.25 (3 H, s), 5.21 (1 H, d, J = 8.0 Hz), 2.1–2.8 (5 H, m); m/e 289, 230, 170, 145 (base), 127, 104, and 77.

Competitive Reactivity Studies. Relative reactivity studies were carried out photochemically on mixtures of an arylazirine or Δ^3-oxazolin-5-one, an internal standard, and two different dipolarophiles in sealed, degassed tubes. The relative reactivities were determined by gas chromatography using the relation

$$k_{\mathrm{rel}} = (\log A/A_0)(\log B/B_0)$$

where A_0 and B_0 are the areas of the two dipolarophiles relative to the internal standard prior to the reaction, and A and B are the same quantities after reaction. Since cycloaddition rates varied considerably between systems, tubes were removed periodically and analyzed by glc until optimum conversion times for analysis had been determined. The final peak areas were determined by glc after *ca.* 40% of the dipolarophiles had been consumed.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly at room temperature using a Rayonet reactor equipped with 2537-Å lamps. Samples were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Cyclopentanone solutions were used as the chemical

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(33) N. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967).

actinometer for which a quantum yield of 0.38 was used[22] giving a reproducible lamp output of 2.01×10^{16} quanta sec^{-1}. After irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions were run to 10% or less. Octadecane and *p*-phenylbenzophenone were used as internal standards.

Quenching and Sensitization Studies. Solutions of the Δ^3-oxazolin-5-one (or arylazirine) and dipolarophile containing excess piperylene as a standard triplet quencher were irradiated under conditions where more than 98% of the light was absorbed by the Δ^3-oxazolinone (or azirine). The reaction was monitored by glpc and in no case was the amount of adduct formed affected by the piperylene. The quencher was present in concentrations sufficiently high to suppress established triplet process.[19,20]

Sensitization experiments utilized xanthone as a standard triplet sensitizer. The concentrations were adjusted so that xanthone absorbed greater than 98% of the light. The reaction was monitored by glpc and under the conditions employed; there was no significant cycloaddition detected from the Δ^3-oxazolinone (or azirine) system with methylacrylonitrile.

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Conformational Analysis. XIX. Silacyclohexanes[1,2]

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Abstract: The structure and steric energies of silacyclohexane and the various methylsilacyclohexanes have been calculated by force field methods. Silacyclohexane is predicted to exist in a modified chair conformation in which the ring is more flattened than cyclohexane in the region of silicon and is more puckered in the region of C_4. The 2-, 3-, and 4-methylsilacyclohexanes are calculated to be 1.87, 1.66, and 1.27 kcal/mol, respectively, more stable in the equatorial conformation than in the axial conformation. However, 1-methylsilacyclohexane is predicted to be more stable in the axial conformation by 0.20 kcal/mol. The preference of the 1-methyl group for the axial position is due to a larger negative nonbonded energy term for the axial conformation. Conformational homogeneity of silacyclohexane derivatives could be achieved by the presence of a *tert*-butyl group at the 3 or 4 position as the calculated steric energy differences between equatorial and axial conformations are 4.85 and 6.69 kcal/mol, respectively. 1-*tert*-Butylsilacyclohexane is more stable in the equatorial conformation by only 1.28 kcal/mol. Therefore, *cis*-4-methyl-1-*tert*-butylsilacyclohexane is predicted to be most stable in the conformation with the *tert*-butyl group axial and the methyl group equatorial. *cis*-3,5-Dimethylsilacyclohexane is predicted to be conformationally homogeneous in the diequatorial conformation. The steric energies of four transition states and two skew-boat conformations which may be involved in the ring inversion of 1,1-dimethylsilacyclohexane are calculated. The energies of three of the four possible transition states are consistent with the experimental activation energy obtained by other workers. The structure and steric energies of 3-silabicyclo[3.2.1]octane as well as the 3-methyl and 3,3-dimethyl derivatives are calculated.

Conformations of heterocyclic compounds are affected by many more molecular variables than those of carbocyclic compounds.[3] The differences in bond lengths and angles as well as the force constants for bond stretching and bond angle bending make any conformational analogy between heterocycles and carbocycles a tenuous one at best. The change in molecular geometry from that of carbocycles gives rise to subtle changes in van der Waals interactions. Furthermore, heterocycles containing nitrogen[4] and oxygen[5] have lone pairs of electrons which may affect conformation.

Heterocycles containing the third row elements phosphorus[6] and sulfur[7] have been discussed in the literature. The proton on phosphorus in phosphacyclohexane prefers the axial position[8] as does that in protonated thiacyclohexane.[9] These cases are complicated both by the presence of lone pairs of electrons and by serious deviation, around phosphorus and sulfur, from tetrahedral geometry. We therefore decided to investigate by force field calculation methods the case of a heterocycle containing a third row element not affected by these types of difficulties, namely silacyclohexane. Silacyclohexane should serve as a reference point for the discussion of the conformation properties of other heterocycles containing third row elements.

It has recently been established that force field calculations allow ready prediction of the conforma-

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(2) This research was supported by NSF Grant GP 33423. The authors acknowledge the computer time allotted for these calculations from The Ohio State University Computer Center.

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