(14) The small upward shift of the rate constants in the range of concentrations of II up to nearly 0.2 M can be explained by the favorable[9] replacement of sodium by potassium ions. Such a cation effect may be noticeable under these experimental conditions because the presence of *tert*-butyl alcohol interferes with the otherwise excellent solvation of either Na^+ or K^+ by Me_2SO. This conclusion is consistent with the fact that the above mentioned upward shift is more pronounced at the higher level of *tert*-butyl alcohol.
(15) The formation of a 2:1 complex would be expected to give two plateaus as the concentration of Me_2SO is increased. Calculations based on the assumption of a 2:1 complex gave very inconsistent values for the association constants. On the assumption that the formation of a 1:1 complex is indeed the limit of hydrogen bonding between a diaryl hydrazone and Me_2SO, one is tempted to speculate that the preferred planar conformation of the hydrazone impedes sterically the association of Me_2SO with one of the N–H bonds (the "endo" N–H).
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Intramolecular Dipolar Cycloaddition Reactions of Unsaturated 2*H*-Azirines[1]

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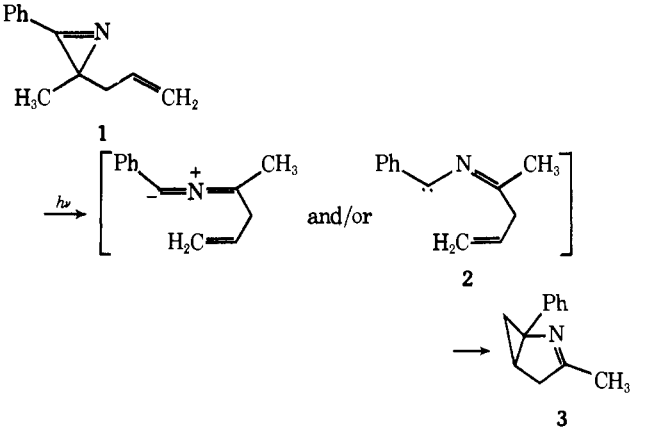
Abstract: The intramolecular dipolar cycloaddition reaction of 2-(4-pentenyl)-2*H*-azirines has been examined in mechanistic detail. Upon irradiation with ultraviolet light, this system undergoes rearrangement to cyclopenta[*b*]pyrroles via a transient nitrile ylide. This reactive 1,3-dipole can be intercepted with added dipolarophiles to give Δ^1-pyrroline derivatives. Although frontier molecular orbital theory correctly rationalizes the regioselectivity of all known bimolecular nitrile ylide cycloadditions, it fails completely when applied to these intramolecular cycloadditions. The inversion of regiospecificity can be attributed to steric factors which destabilize the transition states for formation of the expected regioisomers. A kinetic investigation, involving Stern–Volmer plots and relative reactivity studies, shows that there is a marked leveling of the rate profile associated with these internal cycloadditions. The photochemistry and thermal chemistry of the homologous 2-(3-butenyl)-2*H*-azirine system was also studied. Evidence was obtained which indicates that the spatial relationship of the nitrile ylide and dipolarophile π orbitals plays an extremely important role in controlling the mode of intramolecular cycloaddition. The thermolysis of but-3-enyl substituted 2*H*-azirines was found to give substituted pyridines and biphenyl derivatives via a novel 1,4-hydrogen transfer from the methylene group of an initially formed vinylnitrene intermediate.

1,3-Dipolar cycloadditions have been shown to be an astonishingly fruitful synthetic method for the preparation of five-ring heterocycles.[2-6] Numerous possibilities for variation are available by changing the structure of both the dipolarophile and dipole. In spite of the copious literature dealing with bimolecular cycloaddition reactions, intramolecular examples have received only a minimum of attention.[7] 1,3-Dipoles bearing a functional group able to behave as a dipolarophile are extremely interesting substrates. In fact, the intramolecular cycloaddition of a properly functionalized 1,3-dipole represents a general scheme for the synthesis of novel fused ring heterocycles. Intramolecular dipolar cycloadditions have been carried out with nitrones,[8-14] diazoalkanes,[15-19] azides,[20-24] azomethine imines,[25,26] carbonyl oxides,[27] and nitrile imines.[28,29]

Our research group has recently investigated the intramolecular cycloaddition reactions of nitrile ylides[30,31] generated by photolysis of 2*H*-azirines.[32] Nitrile ylides may be classified as nitrilium betaines, a class of 1,3-dipoles containing a central nitrogen atom and a π bond orthogonal to the 4π-allyl system. Among the possible forms of a nitrile ylide, a carbene structure (i.e., **2**) can be envisaged which makes conceivable a 1,1-cycloaddition of this 1,3-dipole.[33] We uncovered the first example of such a process during a investigation of the photochemistry of 3-phenyl-2-methyl-2-allyl-2*H*-azirine (**1**).[30] The formation of a 1,1-cycloadduct (i.e., **3**) from the photolysis of **1** clearly indicates that the spatial relationship of the dipole and dipolarophile plays an important role in controlling the intramolecular dipolar cycloaddition reactions of nitrile ylides. The primary spatial requirement for intramolecular 1,3-dipolar cycloaddition is that the distance between the two reacting centers should be sufficiently short so that effective three-



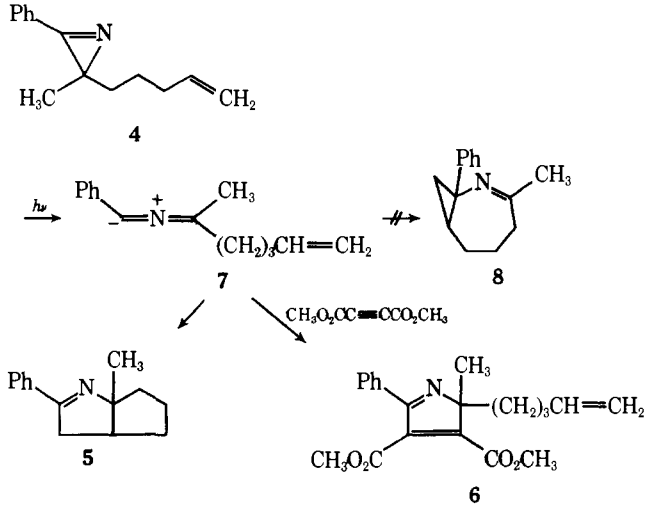
center overlap of the 1,3-dipole with the dipolarophile occurs. For concerted 1,3-dipolar cycloaddition to take place, the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the nitrile ylide.[2] Inspection of molecular models of the allyl-substituted nitrile ylides indicates that the normal "two-plane" orientation approach of the ylide and allyl π system is impossible as a result of the geometric restrictions imposed on the system. Consequently, the normal mode of 1,3-dipolar addition does not occur here. With this system, attack by the double bond is constrained to occur perpendicular to the plane of the nitrile ylide. The second LUMO of the dipole, which is perpendicular to the ylide plane, is low lying and presents a large vacancy at C-1 for attack by the more nucleophilic terminus of the neighboring double bond, without the possibility of simultaneous bonding at the C-3 carbon. In

view of the stringent spatial requirements associated with the intramolecular cycloaddition of nitrile ylides, we thought it worthwhile to consider what effect a variation in the spatial proximity between the dipole and dipolarophile would have on the course of the intramolecular cycloaddition reaction. In this paper, the synthesis and chemistry of olefinic 2*H*-azirines containing unsaturation three and four bonds away from the azirine ring are described.

Results and Discussion

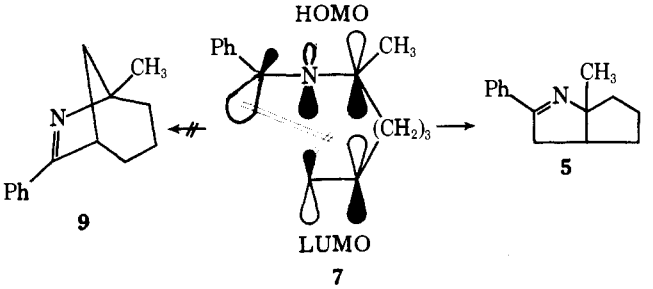
Reversal of Regioselectivity in the Intramolecular Dipolar Cycloadditions of 2-(4-Pentenyl)-2*H*-azirines. As our first model we chose to investigate the photochemistry of 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**). The synthesis of **4** was straightforward and involved a modified Neber reaction in which 2-methyl-1-phenyl-6-hepten-1-one was first treated with dimethylhydrazine. Reaction of the resulting dimethylhydrazone with methyl iodide followed by treatment with base gave azirine **4** in high yield. When a thoroughly deaerated solution of **4** was irradiated with light of wavelength >280 nm, an extremely rapid and clean conversion to a single photoproduct occurred. Assignment of this product as 3,3a,4,5,6,6a-hexahydro-6a-methyl-2-phenylcyclopenta[*b*]-pyrrole (**5**) was made on the basis of its straightforward spectral properties: UV (cyclohexane) 241 nm (ε 16 100); NMR (100 MHz) τ 8.57 (3 H, s), 7.5-8.5 (m, 7 H) 7.32 (dd, 1 H, *J* = 18.0 and 3.0 Hz), 6.69 (dd, 1 H, *J* = 18.0 and 9.0 Hz), 2.1-2.7 (m, 5 H). The formation of **5** could be completely suppressed when the irradiation of **4** was carried out in the presence of excess dimethyl acetylenedicarboxylate. The only product formed under these conditions was 2*H*-pyrrole **6**. Similar results were obtained when methyl acrylate was used as the trapping reagent. Clearly, nitrile ylide **7** is an intermediate in these reactions and **5** arises by intramolecular 1,3-dipolar cycloaddition of the transient ylide with the neighboring double bond (Scheme I). No detectable quantities of

Scheme I

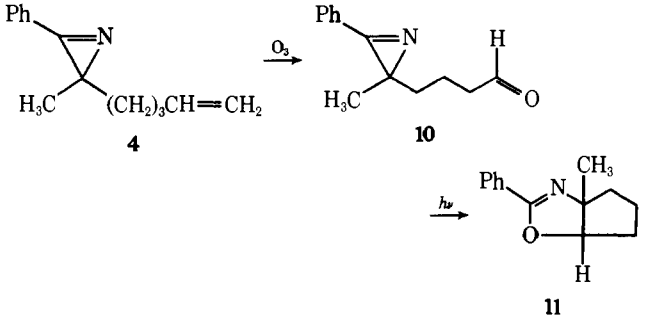


a 1,1-cycloadduct (i.e., **8**) could be observed in the crude reaction mixture. In this case, it appears as though the methylene chain is sufficiently long enough to allow the dipole and olefinic portions to approach each other in parallel planes.

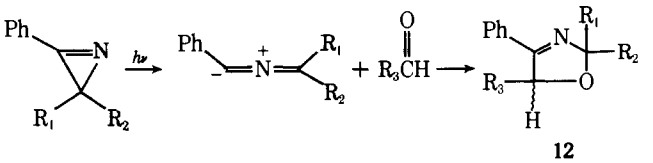
The exclusive orientation observed in this reaction is unusual and can not be adequately accounted for on the basis of frontier orbital theory. According to the frontier orbital treatment of 1,3-dipolar cycloadditions,[34-38] the relative reactivity of a given 1,3-dipole toward a series of dipolarophiles will be determined primarily by the extent of stabilization afforded the transition state by interaction of the frontier orbitals of the two reactants. When nitrile ylides are used as 1,3-dipoles, the dipole highest occupied (HO) and dipolarophile lowest unoccupied (LU) interactions will be of greatest importance in stabilizing the transition state. Regioselectivity will be controlled by union of the atoms with the largest coefficients in the dipole HO and dipolarophile LU. Earlier results from our laboratory have established that the electron density is highest on the disubstituted carbon atom (C-1) of the nitrile ylide.[39,40] Recent calculations by Houk and Caramella[38] support our experimental observations. These workers find (a) that the bent nitrile ylide geometry is favored over the planar form by 11.1 kcal/mol and (b) that the disubstituted carbon atom (C-1) is the nucleophilic terminus of nitrile ylides. Electron releasing groups attached to an ethylenic double bond are known to lower the coefficient at the point of attachment in the HO and raise that coefficient in the LU.[35] Thus, alkyl substituted olefins have the largest coefficient on the substituted carbon in the LU orbital. The preferred regioisomeric transition state should be that in which the larger coefficients of the interacting orbitals are united. Using these generalizations, the regioselectivity prediction for the HOMO controlled intramolecular cycloaddition of nitrile ylide **7** proves to be incorrect, since the internal cycloaddition of **7** should have given azabicyclo-[3.2.1]octene **9** rather than structure **5**.



A similar inconsistency also was found upon irradiation of 2-methyl-3-phenyl-2*H*-azirine-2-butyraldehyde (**10**). This compound was readily prepared by ozonolysis of azirine **4**. Irradiation of **10** in benzene gave 3a,5,6,6a-tetrahydro-3a-methyl-2-phenyl-4*H*-cyclopentoxazole (**11**) as the exclusive photoproduct.

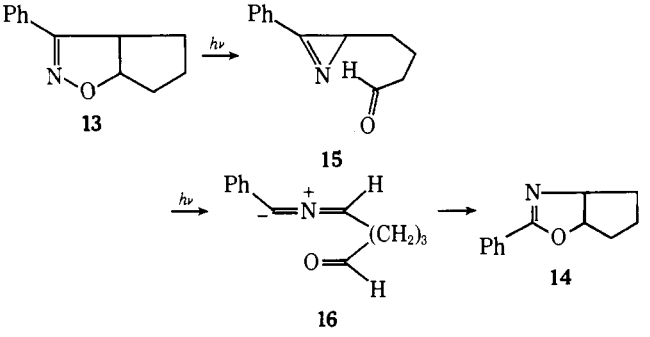


Arylazirines are known to undergo photochemical cycloaddition with aldehydes to give Δ^3-oxazolines (**12**).[41-44] The



aldehyde group also shows the same mode of addition with nitrile ylides which are generated from the treatment of benzimidoyl chlorides with triethylamine.[45] It is important to note that the orientation of the intramolecular cycloaddition reaction of aldehyde **10** proceeds in an alternate sense from that observed with related intermolecular nitrile ylide-aldehyde cycloadditions. In a somewhat related case, Schmid and co-

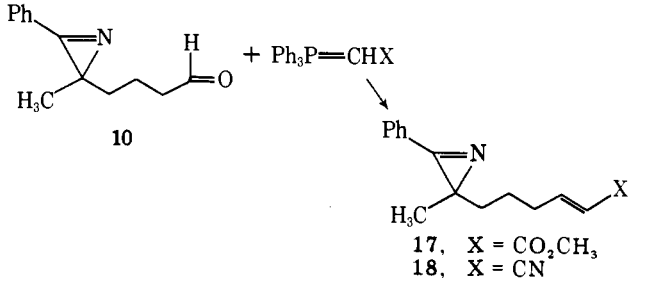
workers reported on the photoisomerization of dihydroisoxazole **13** to dihydrooxazole **14**.[46] The reaction was proposed to proceed via a transient azirine (i.e., **15**). This intermediate was not isolated, but was suggested to undergo rapid ring opening to nitrile ylide **16** which cyclized to the observed photoproduct via an internal 1,3-dipolar cycloaddition reaction.



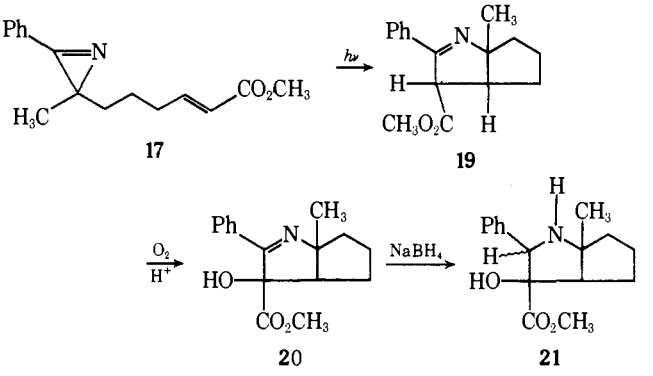
The intramolecular cycloaddition reactions of azirines **4** and **10** clearly indicate that geometrical factors can force the reaction to occur in a manner opposite to that normally encountered. The inversion of regiospecificity must be related to steric effects which destabilize the transition states for formation of the alternate bridged structures. Similar "orientation-inversions" have been reported with a number of other 1,3-dipoles which undergo intramolecular dipolar cycloadditions.[28,47,48]

The intramolecular cyclization of azirine **4** is a particularly interesting case in that it involves cycloaddition of a nitrile ylide with an unactivated olefin, a substrate which is generally unreactive toward nitrile ylides. Conjugated and electron-deficient olefins are known to react readily with nitrile ylides,[49,50] since such a pair of addends possesses a narrow dipole-HOMO dipolarophile-LUMO gap.[36] Bimolecular reactions of nitrile ylides with electron-rich olefins, however, have never been observed, thereby indicating that the dipole LU-dipolarophile HO interaction is never large. Because of their high nucleophilicities, nitrile ylides generally undergo reactions with their precursors, dimerize, or isomerize faster than they undergo reactions with electron-rich alkenes.[51-53] Since the intramolecular cyclization of azirine **4** involves an electron-rich double bond, one might inquire why the reaction occurs at all. Undoubtedly, the rate of internal cycloaddition reflects an extremely favorable entropy factor which offsets the unfavorable electronic factor.

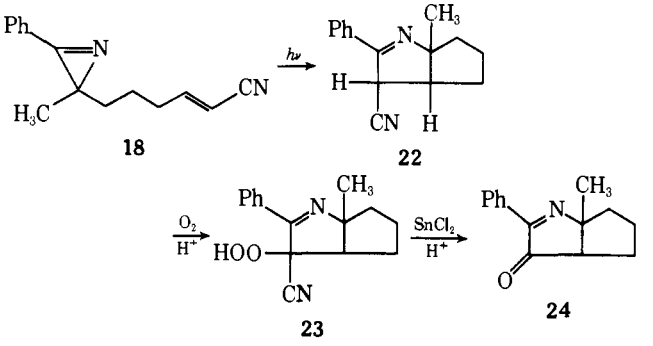
In order to assess the importance of the entropy term, we decided to compare the rate of internal cycloaddition of **4** with that of a related system which possesses an electron-withdrawing substituent on the double bond. To this end we synthesized methyl (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate (**17**) and (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenenitrile (**18**). These compounds were readily prepared by treating the aldehyde **10** with carbomethoxy- and cyanomethylenetriphenylphosphorane.



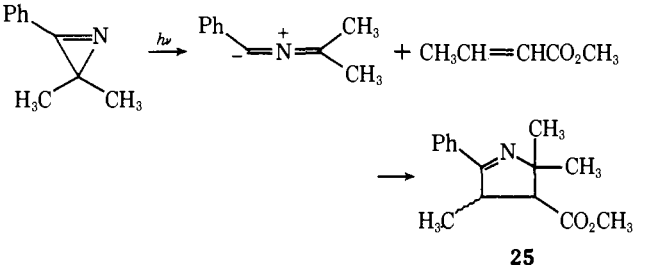
Irradiation of **17** in benzene using a 450-W Hanovia immersion apparatus equipped with a Corex filter sleeve led to the complete consumption of reactant in 40 min. The only product obtained was methyl 3,4,5,6,6a-pentahydro-6a-methyl-2-phenylcyclopenta[*b*]pyrrole-3-carboxylate (**19**) [NMR (100 mHz) τ 7.4–8.8 (m, 10 H), 6.40 (s, 3 H), 6.18 (d, 1 H, J = 3.0 Hz), and 2.2–2.8 (m, 5 H)]. On standing in an aerated solution at 25 °C (or on thick-layer chromatography), **19** undergoes smooth conversion to alcohol **20**, mp 132–133 °C. This structure was supported by reduction with sodium borohydride to methyl octahydro-3-hydroxy-6a-methyl-2-phenylcyclopenta[*b*]pyrrole-3-carboxylate (**21**), mp 136–137 °C [NMR (100 MHz) τ 8.2–8.6 (m, 9 H), 7.2–7.9 (m, 2 H), 6.8–7.0 (1 H, broad s), 6.30 (3 H, s), 5.40 (1 H, s), 2.4–2.8 (m, 5 H)]. The oxidation of enamines and certain Schiff bases with molecular oxygen has been reported in the literature[54-57] and provides good chemical analogy for the conversion of **19** into **20**.



Attention was next turned to the photochemical behavior of azirinyl nitrile **18**. Photolysis of **18** in benzene afforded cycloadduct **22** as the only identifiable product in 93% yield [NMR (100 MHz) τ 8.0–8.8 (m, 9 H), 6.80 (t, 1 H, J = 3.5 Hz), 6.10 (d, 1 H, J = 3.5 Hz), 2.1–2.9 (m, 5 H)]. This compound was readily oxidized to 4,5,6,6a-tetrahydro-3-cyano-3-hydroperoxy-6a-methyl-2-phenylcyclopenta[*b*]pyrrole (**23**), mp 138–139 °C, on thick-layer chromatography. The structure of **23** was further confirmed by its conversion to **24** on treatment with an acidic stannous chloride solution according to the general procedure of Watt and Selikson.[58]



The regioselectivities encountered in the above cycloadditions are in complete variance with frontier molecular orbital theory. For example, the ylide derived from the photolysis of dimethylphenylazirine reacts with methyl crotonate to give **25**



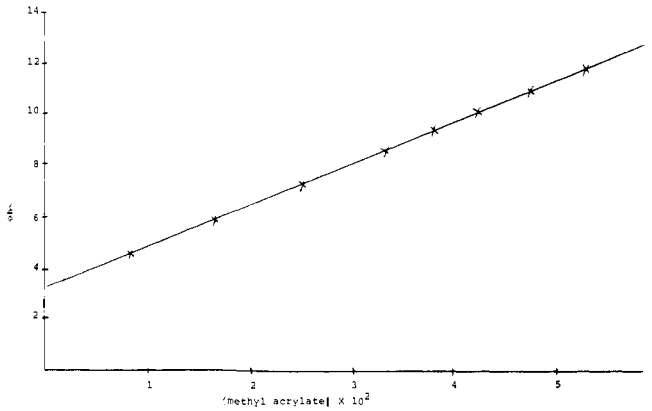


Figure 1. Plot of [quantum yield of cyclization]$^{-1}$ against (methyl acrylate) for 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**).

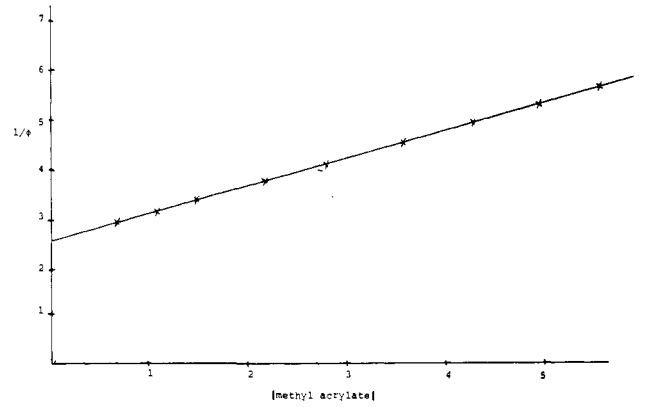


Figure 2. Plot of [quantum yield of cyclization]$^{-1}$ against [methyl acrylate] for methyl (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate (**17**).

as the exclusive cycloadduct.[59] As was pointed out earlier, the dipole HO-dipolarophile LU orbitals control regioselectivity with nitrile ylides. The formation of **25** is perfectly consistent with the principles of frontier MO theory. Although the frontier MO model correctly rationalizes the orientation of all known bimolecular nitrile ylide cycloadditions, it fails completely when applied to intramolecular examples. Clearly, the frontier orbital method needs to be modified and steric factors must be taken into consideration when attempting to rationalize the regiochemistry of intramolecular dipolar cycloadditions.

Rate Studies. In order to derive additional mechanistic information concerning the intramolecular dipolar cycloaddition reaction, a more quantitative investigation of these cycloadditions was undertaken. Quantum yields for product formation were determined using cyclopentanone as the chemical actinometer.[60] Degassed and sealed Quartz tubes containing solutions of azirines **4** and **17** were irradiated along with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by GLC using internal standards. The quantum yield for product formation as a function of the concentration of added methyl acrylate was also studied. The data are presented graphically in Figures 1 and 2 for the 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**) and methyl (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate (**17**) systems.

Several features become apparent upon examination of the data shown in Figures 1 and 2. Good linear relationships are observed between the inverse of the quantum yield for product formation and the concentration of added methyl acrylate. The slopes and intercepts of the plots depend on the structure of the azirine used. At zero dipolarophile concentration, the quantum yield for cyclization is 0.32 for azirine **4** and 0.41 for azirine **17**. The magnitude of the intercept indicates that cyclization of azirine **4** is ca. 20% less efficient than cyclization of **17**. The high quantum efficiencies observed with these systems demonstrate that a significant path from the electronically excited state of the unsaturated azirine involves bond rupture and formation of a nitrile ylide intermediate.

The results obtained using these unsaturated azirines as nitrile ylide precursors are consistent with the mechanism outlined in Scheme II. In this scheme, Ao = unsaturated azirine (**4** or **17**), NY = nitrile ylide, P = product, and O = dipolarophile (i.e., methyl acrylate).

Scheme II

$$\mathrm{Ao} \xrightarrow{h\nu} \mathrm{A}^*$$

$$\mathrm{A}^* \xrightarrow{k_d} \mathrm{Ao}$$

$$\mathrm{A}^* \xrightarrow{k_r} \mathrm{NY}$$

$$\mathrm{NY} \xrightarrow{k_1} \mathrm{P}$$

$$\mathrm{NY} + \mathrm{O} \xrightarrow{k_2} \text{adduct}$$

By making the usual steady-state assumption, we can write

$$1/\Phi_p = [(k_d + k_r)/k_r][1 + (k_2[\mathrm{O}]/k_1)]$$

where k_d represents the nonradiative decay of excited azirine, k_r is the rate of C-C bond cleavage of the excited azirine ring, and Φ_p is the quantum yield of product formation.

From the slope and intercept of the Stern-Volmer analysis for product formation with a given dipolarophile, we find that the slope/intercept = k_2/k_1. For the case of azirine **4**, $k_2/k_1 = 50$ while, with azirine **17**, $k_2/k_1 = 0.23$. These values indicate that the nitrile ylide intermediate obtained from azirine **4** is much more easily trapped with an added dipolarophile than the 1,3-dipole derived from the carbomethoxy substituted olefin **17**. If we assume that the rate of cycloaddition (i.e., k_2) of both nitrile ylides with methyl acrylate is the same,[61] we can obtain the relative rate difference for internal cycloaddition of these two azirines:

$$[k_2/k_1(\text{azirine } \mathbf{4})/k_2/k_1(\text{azirine } \mathbf{17})] = k_{17}/k_4 = k_{rel} = 217$$

The observation that the cyclization of the nitrile ylide derived from azirine **17** proceeds at a faster rate (217 times) than that of ylide **7** is unexceptional. This is to be expected since nitrile ylide cycloadditions are HO controlled,[37] reacting readily with electron-deficient olefins and not at all with electron-rich ones. What is surprising, however, is that the rate difference is so small. The rate constants associated with bimolecular cycloadditions usually range over many powers of 10. For example, fumaronitrile undergoes cycloaddition at a rate which is 189 000 times faster than methyl crotonate.[50] Ordinary olefins react so sluggishly that their bimolecular rate constants cannot be measured. Clearly, there has been a marked leveling of the rate profile associated with the above intramolecular cycloadditions.

One interesting possibility to account for this leveling effect is that the transition state for the intramolecular cycloaddition of a nitrile ylide with a dipolarophile involves appreciable interaction of both the in plane and out of plane π-unoccupied orbitals of the dipole with the filled orbitals of the dipolarophile. For this to occur, a slight contortion away from the strictly parallel planes approach of the dipole and dipolarophile

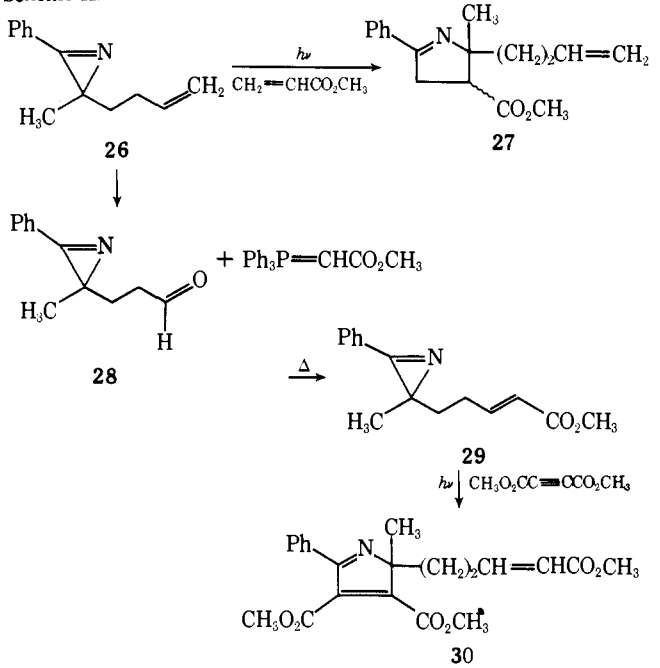
would be necessary. The interaction of the LU orbital(s) of a bent nitrile ylide with the HO orbital of the olefin could lead to a stabilizing "secondary orbital interaction" which could significantly enhance the rate of internal cycloaddition with an unactivated olefin.

Another factor which undoubtedly plays an important role in the intramolecular cycloaddition process is the high degree of order already present in the transition state. Bimolecular cycloadditions exhibit large negative entropies of activation[3] since the reactants must be precisely aligned with respect to each other. The interplay of entropy and enthalpy will control the rate-determining activation process. The larger entropy term associated with the intramolecular cycloaddition will tend to compress the rate scale. Perhaps this is the key to understanding the "leveling-effect", since the smaller the steric requirements of the transition state, the less sensitive the system is toward disturbance.

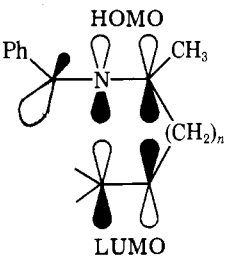
Photochemistry of 2-(But-3-enyl)-2*H*-azirines. As part of our continuing program of exploration of the mechanistic nuances and synthetic scope of intramolecular 1,3-dipolar cycloadditions of unsaturated 2*H*-azirines, we decided to investigate the photochemistry of the next lower homologous series. The several new azirines employed in these studies were synthesized from known starting materials using synthetic sequences similar to those outlined above. Whereas azirine **4** was smoothly converted to cyclopenta[*b*]pyrrole **5** on irradiation, photolysis of the homologous azirine **26** resulted in the formation of polymeric material. When the irradiation of **26** was carried out in the presence of methyl acrylate, however, a mixture of isomeric Δ^1-pyrrolines (**27**) was obtained in good yield. The initially generated nitrile ylide could also be trapped when dimethyl acetylenedicarboxylate was used as an added dipolarophile. All attempts to detect an intramolecular cycloadduct from the photochemically generated nitrile ylide failed.

In order to determine whether an electron-withdrawing substituent on the double bond would facilitate intramolecular cyclization, we examined the photochemistry of methyl (*E*)-5-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate (**29**). This material was formed in high yield by ozonization of azirine **26** to aldehyde **28** followed by reaction with carbomethoxymethylenetriphenylphosphorane in benzene at 25 °C (Scheme III). Unfortunately, the irradiation of **29** led to a

Scheme III

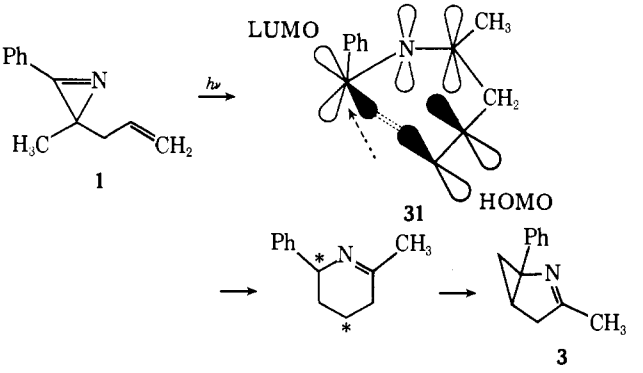


complex mixture of products which resisted all attempts at purification. The crude NMR spectrum of the photolysate showed that the vinyl protons were still present. When the irradiation of **29** was carried out in the presence of dimethyl acetylenedicarboxylate, 2*H*-pyrrole **30** was obtained in 93% yield. The isolation of this cycloadduct indicates that the expected nitrile ylide is formed, but that intramolecular cycloaddition does not occur. Examination of molecular models suggests a simple explanation for this result. With the ylide derived from azirine **29** (or **26**), the methylene chain is not of sufficient length to allow the dipole and dipolarophile to approach each other in parallel planes. Consequently, intramolecular 1,3-dipolar cycloaddition does not occur. The situation is very different with the homologous unsaturated nitrile ylide **7**. With this system, the transition state for cycloaddition allows easy attainment of the "parallel-plane approach".

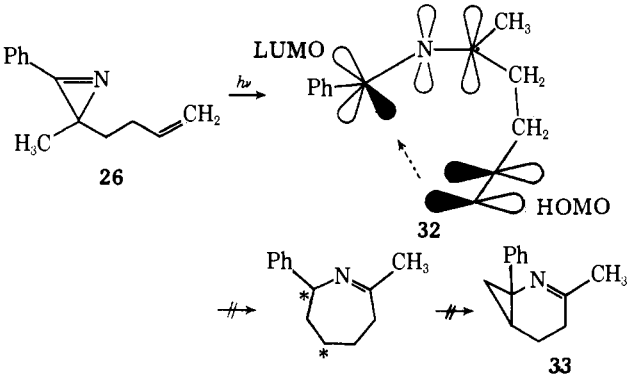


"parallel-plane approach"

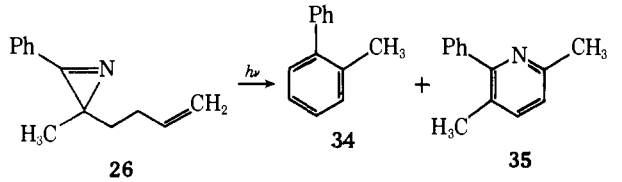
While this analysis satisfactorily explains the absence of intramolecular 1,3-dipolar cycloaddition with azirines **26** and **29**, it does not account for the absence of a 1,1-cycloaddition reaction. As was pointed out elsewhere,[1] the 1,1-cycloaddition of allyl substituted 2*H*-azirines occurs because the p orbitals of the olefin are constrained to attack perpendicular to the bent nitrile ylide plane. The geometry of the transition state involved in this process is significantly different from that required for concerted 1,3-dipolar cycloaddition. The 1,1-cycloaddition reaction is initiated by interaction of the terminal carbon of the olefin with the second LUMO of the nitrile ylide. With allyl substituted 2*H*-azirines, attack by the alkene group produces a six-membered ring zwitterion and involves orbital overlap as illustrated by formula **31**. With this system, there is no particular constraint in locating the p orbital of the terminal olefin carbon in the proper position for maximum overlap with the second LUMO of the nitrile ylide. The situation is very different when an additional carbon atom is added to the azirine side chain. In such a case, the positioning of the p orbital along the dotted line representing collinear approach requires considerable bond distortion, as shown in formula **32**. Consequently, 1,1-cycloaddition does not take place and alternate reactions, such as dimerization of the ylide, occurs.[50] Clearly, the spatial relationship of the nitrile ylide and dipolarophile p orbitals plays an extremely important role in controlling the mode of intramolecular cycloaddition.



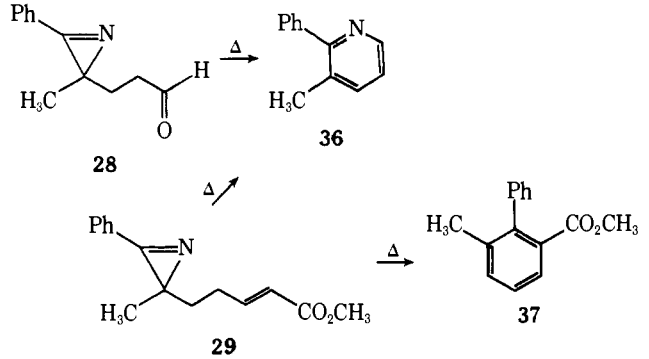
Thermal Chemistry of 2-(But-3-enyl)-2*H*-azirines. In contrast to the complex behavior encountered on irradiation of the



2-(but-3-enyl)-2*H*-azirine system, the thermal chemistry of this system is remarkably clean and novel. When a solution of **26** in toluene was heated at 195 °C for several days, two products were isolated in good overall yield. The major product (49%) was identified as 2-methylbiphenyl (**34**) while the minor product (15%) was assigned as 2,5-dimethyl-6-phenylpyridine (**35**), in each case the material isolated was compared with an authentic sample.[62]



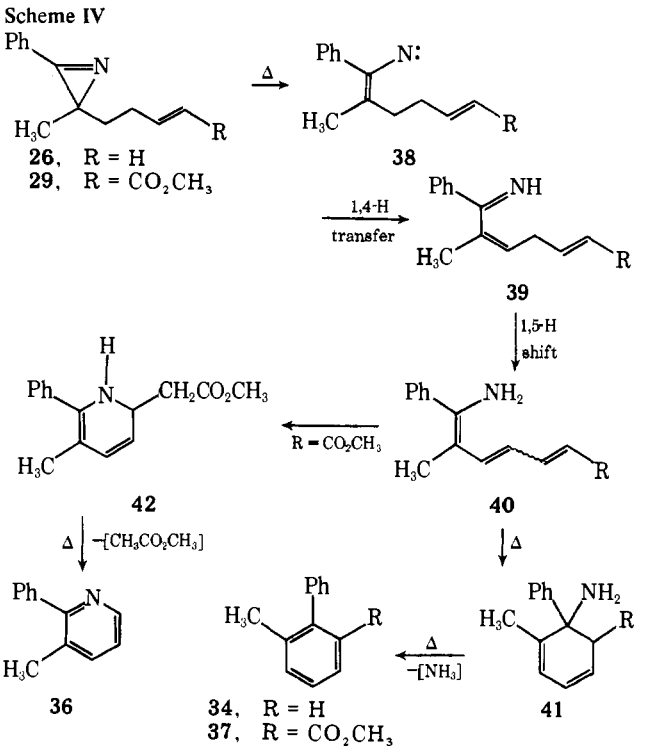
Attention was next turned to the thermal behavior of the related azirines **28** and **29.** The only product obtained from the thermolysis of **28** was 2-phenyl-3-methylpyridine (**36**). This material was identified by comparison with an authentic sample.[63] When azirine **29** was heated for several days in a toluene solution at 195 °C, 2-phenyl-3-methylpyridine (**36**) (59%) as well as methyl 6-methylbiphenyl-2-carboxylate (**37**)



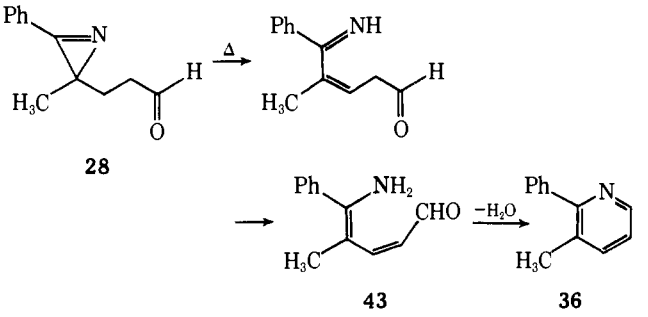
(12%) are formed. The structure of this ester was verified by hydrolysis to the known 6-methylbiphenyl-2-carboxylic acid.[64]

Photochemical and thermal bond cleavage preferences in 2*H*-azirines appear to be quite distinct. Products formed during photochemical isomerizations invariably appear to involve carbon–carbon bond cleavage[32] while thermal isomerization products arise from initial carbon–nitrogen bond cleavage.[65-75] The formation of the substituted biphenyl derivatives (**34** and **37**) can be explained by the sequence shown in Scheme IV. Thermal equilibration of the 2*H*-azirine with a transient vinyl nitrene (**38**)[76] followed by a 1,4-hydrogen transfer from the methylene group generates azatriene **39.** This reactive intermediate undergoes a thermally allowed 1,5-sigmatropic shift to give triene **40.** Electrocyclic closure of **40** to cyclohexadiene **41** followed by loss of ammonia readily accounts for the formation of the substituted biphenyl derivatives. The isolation of 2-phenyl-3-methylpyridine (**36**) from azirine **29** can also be readily accounted for and involves an internal Michael addition of **40** to give **42,** followed by loss of methyl

Scheme IV



acetate. The key feature of the mechanism outlined in Scheme IV is the 1,4-hydrogen transfer. Related hydrogen transfers have been observed in reactions of vinyl carbenes[77-82] and more recently with iminocarbenes[83] which provide reasonable chemical analogies. The proposed 1,4-hydrogen transfer was further substantiated by the thermal conversion of **28** to **36.** In this case, a series of 1,4- and 1,5-hydrogen transfers gives **43** which may reasonably cyclize to 2-phenyl-3-methylpyridine (**36**).



The formation of small quantities of 2,5-dimethyl-6-phenylpyridine (**35**) from the thermolysis of **26** is also of interest and merits some comment. A reasonable postulate to account for the formation of **35** would involve a competitive intramolecular addition of the vinyl nitrene onto the adjacent π bond to give a bicycloaziridine[84] which is converted to the observed product by ring opening, followed by an oxidation step. Additional work is required before this scheme can be established with certainty.

Experimental Section[85]

Preparation of 2-Methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (4). A mixture of 160 g of 5-bromo-1-pentene and 450 g of sodium iodide in 1500 ml of acetone was heated at reflux for 6 h. The solvent was removed under reduced pressure, and the resulting residue was taken up in 1 l. of water and extracted with ether. The ethereal solution was dried over magnesium sulfate and concentrated under reduced pressure to give 176 g of 5-iodo-1-pentene: IR (neat) 3.47, 6.15, 7.02, 7.07, 8.20, 8.57, 10.09, 10.97, 12.73, and 13.32 μ; NMR ($CDCl_3$) τ 7.6–8.4 (4 H, m), 6.83 (2 H, t, J = 6.5 Hz), 4.8–5.1 (2 H, m), 3.9–4.6 (1 H, m).

To a solution containing 120 g of propiophenone in 1 l. of dimethyl sulfoxide was added 24 g of sodium hydride. After the evolution of hydrogen gas had ceased, 176 g of 5-iodo-1-pentene was added to the mixture over a 1-h period at 30 °C. The reaction mixture was allowed to stir at room temperature for an additional 12 h and was then poured into 1 l. of water. The aqueous solution was neutralized with hydrochloric acid and extracted with ether. The ether solution was subsequently washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residual oil was distilled at 94–96 °C (0.04 mm) to give 153 g (86%) of 2-methyl-1-phenylhept-6-en-1-one as a clear oil: IR (neat) 3.31, 3.45, 5.94, 6.10, 6.28, 6.87, 6.93, 7.29, 8.16, 8.50; NMR ($CDCl_3$) τ 8.81 (3 H, d, J = 7.0 Hz), 7.8–8.7 (6 H, m), 6.53 (1 H, sextet, J = 7.0 Hz), 4.9–5.3 (2 H, m), 3.9–4.5 (1 H, m), and 2.0–2.8 (5 H, m); *m/e* 202, 134, 105 (base), and 77.

A mixture containing 20.2 g of 2-methyl-1-phenylhept-6-en-1-one, 20 g of dimethylhydrazine, 0.1 g of acetic acid, 10.0 g of sodium acetate, and 10.0 g of magnesium sulfate was heated at 120 °C for 3 days in a Carius tube. The mixture was taken up in ether, and the inorganic salts were filtered. Removal of the solvent under reduced pressure left a yellow oil which was distilled at 95–97 °C (0.4 mm) to give 22.5 g (92%) of 2-methyl-1-phenylhept-6-en-1-one-*N*,*N*-dimethylhydrazone: IR (neat) 3.41, 6.10, and 6.84 μ; NMR ($CDCl_3$) τ 8.94 (3 H, d, J = 7.0 Hz), 7.9–8.8 (6 H, m), 7.68 (5 H, s), 7.50 (1 H, s), 6.33 (1 H, sextet, J = 7.0 Hz), 4.9–5.4 (2 H, m), 3.9–4.6 (1 H, m), and 2.1–3.0 (5 H, m); *m/e* 244, 132 (base), 105, and 77.

A solution containing 17.5 g of the above hydrazone, 32 g of methyl iodide, and 10 ml of absolute ethanol was heated at reflux for 8 h. Removal of the solvent left a dark-yellow oil which was taken up in 200 ml of 2-propanol. To this solution was added a sodium isopropoxide solution prepared from 1.63 g of sodium and 220 ml of 2-propanol. The reaction mixture was allowed to stir for 1 h at 30 °C, and the solvent was then removed under reduced pressure. The residue was extracted with cyclohexane and then concentrated to a yellow oil. Distillation of this material at 75 °C (0.01 mm) gave 13.0 g (91%) of 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**) as a clear liquid: IR (neat) 3.52, 5.88, 6.17, 6.98, 7.37, 7.78, 8.39, 8.64, 9.32, 9.70, 9.94, 11.01, 13.12, and 14.55 μ; UV (cyclohexane) 243 nm (ϵ 15 000); NMR ($CDCl_3$) τ 8.61 (3 H, s), 7.7–8.4 (6 H, m), 4.9–5.2 (2 H, m), 4.1–4.4 (1 H, m), and 2.1–2.6 (5 H, m); *m/e* 199, 104 (base), and 77.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.14; H, 8.67; N, 6.96.

Preparation of 2-Methyl-3-phenyl-2*H*-azirine-2-butyraldehyde. A solution containing 2.50 g of 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**) in 120 ml of methanol was ozonized at −78 °C. After the ozone stream was shut off, 3 ml of dimethyl sulfide was added and the solution was allowed to stir at −10 °C for 1 h and then at room temperature for an additional hour. The solvent was removed under reduced pressure, and the residue was extracted with ether. The ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left 2.36 g (95%) of 3-methyl-3-phenyl-2*H*-azirine-2-butyraldehyde (**10**) as a clear oil: IR (neat) 3.44, 5.78, 6.90, 7.28, 8.32, 8.94, 9.32, 13.02, and 14.47 μ; UV (cyclohexane) 243 nm (ϵ 10 400); NMR ($CDCl_3$) τ 8.52 (3 H, s), 8.1–8.5 (4 H, m), 7.5–7.7 (2 H, m), 2.2–2.6 (5 H, m), and 0.33 (1 H, t, J = 2.0 Hz); *m/e* 201, 200, 172, 85 (base), and 77.

Preparation of Methyl (*E*)-6-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate (17). A solution containing 2.30 g of the above azirinyl aldehyde (**10**) and 3.82 g of carbomethoxymethylenetriphenylphosphorane[86] in 60 ml of methylene chloride was stirred at room temperature for 12 h. Removal of the solvent under reduced pressure left an oil which was triturated with hexane. The precipitated triphenylphosphine oxide was filtered, and the filtrate was concentrated under reduced pressure. The crude oil was purified by dry column chromatography (silica gel) using a 1:4 ether–pentane mixture as the eluent. The major fraction (1.6 g) obtained was identified as methyl (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate (**17**) on the basis of the following data: IR (neat) 3.47, 5.85, 6.96, 7.14, 7.35, 7.92, 8.40, 9.65, 10.27, 13.08, and 14.51 μ; UV (cyclohexane) 242 nm (ϵ 13 600); NMR ($CDCl_3$) 8.74 (3 H, s), 7.7–8.5 (6 H, m), 6.34 (3 H, s), 4.1–4.4 (1 H, m), 2.9–3.4 (1 H, m), and 2.0–2.6 (5 H, m); *m/e* 257, 228, 198, 187, 170, 158, 130, 105 (base), 104, 103, and 77.

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.43; H, 7.42; N, 5.49.

Preparation of (*E*)-6-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenenitrile (18). A solution containing 1.50 g of 2-methyl-3-phenyl-2*H*-azirine-2-butyraldehyde (**10**) and 2.32 g of cyanomethylenetriphenylphosphorane[87] in 35 ml of methylene chloride was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residual oil was triturated with hexane in order to precipitate triphenylphosphine oxide. Concentration of the filtrate left a yellow oil which was purified by dry column chromatography (silica gel) using a 1:4 ether–cyclohexane mixture as the eluent. The major fraction obtained (1.45 g) was a light-yellow oil and was identified as (*E*)-6-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenenitrile (**18**) on the basis of the following data: IR (neat) 3.43, 4.52, 5.80, 6.14, 6.92, 7.28, 8.18, 8.32, 10.25, 13.03, and 14.48 μ; UV (cyclohexane) 243 nm (ϵ 13 400); NMR ($CDCl_3$) τ 8.63 (3 l(, s), 7.4–8.6 (6 H, m), 4.6–4.9 (1 H, m), 3.1–3.8 (1 H, m), and 2.1–2.6 (5 H, m); *m/e* 224, 221, 206, 186, 142, 134, 121, 115, 104 (base), and 77.

Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 79.97; H, 7.27; N, 13.00.

Photolysis of 2-Methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine. A solution containing 254 mg of 2-methyl-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**) in 450 ml of benzene was irradiated through a Corex filter sleeve for 30 min. Removal of the solvent under reduced pressure left a pale-yellow oil which was purified by thick-layer chromatography using a 1:4 ether–cyclohexane mixture as the eluent. The major component (206 mg) was a clear oil and was identified as 3,3a,**4**,5,6,6a-hexahydro-6a-methyl-2-phenylcyclopenta[*b*]pyrrole (**5**) on the basis of the following data: IR (neat) 3.33, 3.44, 3.55, 6.19, 6.36, 6.73, 6.93, 7.34, 7.51, 8.05, 8.41, 8.51, 8.66, 9.31, 9.69, 9.82, 10.86, 13.13, and 14.39 μ; UV (cyclohexane) 241 nm (ϵ 16 100); NMR ($CDCl_3$) τ 8.57 (3 H, s), 7.5–8.5 (m, 7 H), 7.32 (1 H, dd, J = 18.0 and 3.0 Hz), 6.69 (H, dd, J = 18.0 and 9.0 Hz), 2.1–2.7 (5 H, m); *m/e* 199, 170 (base), 158, 157, 156, 129, 104, 96, 81, and 77.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.01; H, 8.68; N, 6.86.

Photochemical Trapping of the Nitrile Ylide Derived from 2-Methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine. A solution containing 200 mg of 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine (**4**) and 10.0 g of methyl acrylate in 240 ml of benzene was irradiated for 20 min through a Corex filter sleeve. Removal of the solvent and excess methyl acrylate under reduced pressure left a yellow oil which was purified by thick-layer chromatography using a 1:4 ether–cyclohexane mixture as the eluent. The major fraction contained 243 mg (85%) of a light-yellow oil whose NMR spectrum showed it to be a 1:1 mixture of the cis and trans isomers of 4-carbomethyoxy-5-methyl-5-(4-pentenyl)-2-phenyl-Δ^1-pyrroline. All attempts to separate the mixture into its component parts failed, and consequently the mixture was analyzed without separation: NMR ($CDCl_3$) τ 8.84 and 8.44 (3 H, s), 7.4–8.4 (6 H, m), 6.0–7.0 (3 H, m), 4.28 (3 H, s), 4.9–5.2 (2 H, m), 3.8–4.6 (1 H, m), 2.2–2.7 (5 H, m); UV (cyclohexane) 243 nm (ϵ 17 900); *m/e* 285, 104 (base), and 77.

Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.75; H, 8.12; N, 4.91. Found: C, 75.74; H, 8.16; N, 4.89.

The same nitrile ylide could be trapped with dimethyl acetylenedicarboxylate. The photolysis and workup conditions used in this case were identical to those outlined above. The major component isolated from the chromatography was a pale yellow oil (340 mg, 78%) and was assigned the structure of dimethyl 2-methyl-2-(4-pentenyl)-5-phenyl-2*H*-pyrrole-3,4-dicarboxylate (**6**) on the basis of the following data: IR (neat) 3.47, 5.83, 6.18, 7.04, 7.94, 7.99, 8.94, 9.55, 9.92, 10.91; 12.52, 13.80, and 14.50 μ; UV (cyclohexane) 232 nm (ϵ 18 900); NMR ($CDCl_3$) τ 8.44 (3 H, s), 7.6–8.2 (6 H, m), 6.3 (1 H, s), 6.17 (5 H, s), 4.9–5.3 (2 H, m), 4.2—4.6 (1 H, m), and 2.2–2.7 (5 H, m); *m/e* 341, 287 (base), and 77.

Anal. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.40; H, 6.62; N, 4.07.

Photolysis of 2-Methyl-3-phenyl-2*H*-azirine-2-butyraldehyde. A solution containing 232 mg of azirinyl aldehyde **10** in 250 ml of benzene was irradiated through a Corex filter sleeve for 30 min. Removal of the solvent under reduced pressure left a dark oil which was purified by thick-layer chromatography using a 1:4 ether–cyclohexane mixture as the eluent. The light-yellow oil obtained (163 mg, 70%) was identified as a mixture (3:5) of the cis and trans isomers of 3a,5,6,6a-tetrahydro-3a-methyl-2-phenyl-4*H*-cyclopentoxazole (**11**). All attempts to separate the mixture into its component parts failed; consequently the mixture was analyzed without separation: IR (neat) 3.45, 6.11, 6.24, 6.94, 7.28, 7.44, 7.79, 8.06, 8.16, 8.44, 8.97, 9.42, 9.55, 9.74, 9.94, 10.48, 11.38, 11.50, 11.80, 12.28, 12.58, 12.94, and 14.34 μ; UV

(cyclohexane) 243 nm (ϵ 11 700); NMR ($CDCl_3$) τ 8.37 (3 H, s), 7.7–8.5 (6 H, m), 5.4–5.5 and 4.7–4.8 (1 H, m), 2.1–2.7 (m, 5 H); *m/e* 201, 172 (base), 159, 144, 131, 105, and 77.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.39; H, 7.70; N, 6.71.

An attempt was made to independently synthesize **11** by irradiating a sample of 3-phenyl-4,5,6,6a-tetrahydro-3a-methylcyclopenta-[*d*]isoxazole, according to the procedure of Schmid.[46] This material was prepared according to the procedure of Barbulescu and coworkers.[88] All attempts to obtain characterizable products from the photolysis of this compound failed, and consequently this independent synthesis was abandoned.

Photolysis of Methyl (*E*)-6-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-hexenoate. A solution containing 350 mg of azirine **17** in 480 ml of benzene was irradiated through a Corex filter sleeve for 40 min. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum showed a broad multiplet from τ 7.4–8.8 (10 H), a singlet at 6.40 (3 H), a doublet at 6.18 (1 H, d, J = 3.0 Hz), and a multiplet for the aromatic protons at 2.2–2.8 (5 H). The crude photolysate was chromatographed on a thick layer plate using a 1:4 ether–cyclohexane mixture as the eluent. The major fraction (339 mg) solidified on standing, mp 132–133 °C, and was assigned the structure of methyl 4,5,6,6a-tetrahydro-3-hydroxy-6a-methyl-2-phenylcyclopenta[*b*]pyrrole-3-carboxylate (**20**) on the basis of the following data: IR (KBr) 3.18, 3.44, 5.82, 6.21, 6.99, 7.34, 7.76, 8.02, 8.14, 8.42, 8.58, 8.87, 9.08, 9.59, 9.90, 10.52, 10.79, 10.98, 11.24, 12.50, 12.84, 13.22, 14.44, and 14.53 μ; UV (cyclohexane) 245 nm (ϵ 13 400); NMR ($CDCl_3$) τ 8.36–8.60 (8 H, m), 7.4–8.1 (2 H, m), 6.35 (3 H, s), 2.1–2.7 (5 H, m); *m/e* 263 m, 228, 214, 186, 170 (base), 155, 111, and 77.

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.13. Found: C, 70.02; H, 6.97; N, 5.13.

The initially formed methyl 3,4,5,6,6a-pentahydro-6a-methyl-2-phenylcyclopenta[*b*]pyrrole-3-carboxylate (**19**) which contains a doublet at τ 6.18 (J = 3.0 Hz) could not be isolated since it is rapidly oxidized to **20**. This was experimentally verified by photolyzing a 60-mg sample of **17** and rapidly removing the solvent. The initial photolysate showed a doublet at τ 6.18. This material was taken up in 10 ml of benzene which contained a trace of *p*-toluenesulfonic acid. Oxygen was bubbled through the solution for 5 h at room temperature. Removal of the solvent left a white solid, mp 132–133 °C, which was identical with the material obtained from the thick-layer chromatography and which was devoid of a signal at τ 6.18.

The structure of **20** was further verified by borohydride reduction. A 30-mg sample of sodium borohydride was added to a solution containing 60 mg of **20** in 10 ml of absolute methanol, and the mixture was allowed to stand at room temperature for 1 h. The solution was diluted with water, acidified with hydrochloric acid, and extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The yellow residue was purified by thick-layer chromatography to give 50 mg of methyl octahydro-3-hydroxy-6a-methyl-2-phenylcyclopenta[*b*]pyrrole-3-carboxylate (**21**) as a white solid: mp 136–137 °C; IR (KBr) 3.40, 5.82, 6.96, 7.43, 8.17, 9.01, 9.41, 9.53, 9.93, 10.23, 10.95, 11.07, 11.38, 14.31, and 14.35 μ; UV (cyclohexane) 245 nm (ϵ 2800); NMR τ 8.2–8.6 (9 H), 7.2–7.9 (2 H), 6.8–7.0 (1 H, broad s), 6.60 and 6.30 (3 H, s), 5.40 (1 H, s), 2.4–2.8 (5 H, m); *m/e* 275, 216, 187, 170, 147, 106 (base), 91, and 77.

Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.52; H, 7.61; N, 4.83.

Photolysis of (*E*)-6-(2-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-hexenenitrile. A solution containing 300 mg of **18** in 500 ml of benzene was irradiated through a Corex filter sleeve for 35 min. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum showed a multiplet from τ 8.0–8.8 (9 H), a triplet at 6.80 (1 H, J = 3.5 Hz), a doublet at 6.10 (1 H, J = 3.5 Hz), and a multiplet from 2.1–2.9 (5 H). The crude photolysate was purified by thick-layer chromatography using a 1:4 ether–cyclohexane mixture as the eluent. The major component obtained was a white crystalline solid (280 mg), mp 138–139 °C, whose structure was assigned as 4,5,6,6a-tetrahydro-3-cyano-3-hydroperoxy-6a-methyl-2-phenylcyclopenta[*b*]pyrrole (**23**) on the basis of the following spectral data: IR (kBr) 3.32, 3.41, 3.66, 6.17, 6.96, 7.19, 7.64, 7.84, 8.40, 8.54, 8.79, 9.21, 9.46, 10.58, 10.76, 12.10, 12.68, 13.78, and 14.56; UV (95% ethanol) 250 nm (ϵ 10 800); NMR ($CDCl_3$) τ 7.6–8.7 (9 H); 6.84 (1 H, t, J = 4.0 Hz), 5.60 (1 H, broad s, exchanged with D_2O), 2.05–2.92 (5 H, m); *m/e* 213, 185, 104, 82, and 77.

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.37; H, 6.34; N, 10.85.

The structure of **23** was further confirmed by treating 100 mg of **23** with 0.8 ml of a 1 M stannous chloride in 2 M hydrochloride acid solution at 0 °C for 30 min.[58] At the end of this time a 1 N aqueous sodium hydroxide solution was added until the solution became basic. The aqueous solution was extracted with ether, and the ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was filtered through a Florisil column with a 1:3 ether–pentane mixture. The light-yellow oil obtained (80 mg) was assigned the structure of 4,5,6,6a-tetrahydro-6a-methyl-2-phenylcyclopenta[*b*]pyrrol-3(3a*H*)-one (**24**) on the basis of its spectral properties: IR (neat) 3.44, 3.80, 6.28, 6.39, 6.75, 6.95, 7.35, 7.62, 8.08, 8.30, 8.57, 8.90, 9.21, 9.32, 9.82, 10.48, 10.80, 11.98, 12.72, 13.28, and 14.48 μ; UV (cyclohexane) 270 nm (ϵ 7500); NMR ($CDCl_3$) τ 8.45 (s, 3 H), 7.5–8.4 (7 H, m), 2.5–2.7 (3 H, m), 1.7–1.9 (2 H, m); *m/e* 213, 185, 104, 82 (base), and 77.

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.51; H, 7.03; N, 6.45.

Preparation of 2-(3-Butenyl)-2-methyl-3-phenyl-2*H*-azirine (26). A 134-g sample or propiophenone was added to a slurry of 45.3 g of 56% sodium hydride in 1 l. of dimethyl sulfoxide. After the evolution of hydrogen had ceased, 100 g of 4-bromo-1-butene was added dropwise. The reaction mixture was allowed to stir at room temperature for 12 h. At the end of this time, the brown mixture was poured onto 1 l. of water and the aqueous solution neutralized with hydrochloric acid. The solution was extracted with ether, and the combined ether extracts were washed with water. The solvent was dried over magnesium sulfate and removed under reduced pressure. The residue was distilled at 75 °C (0.01 mm) to give 31.8 g (23%) of 2-methyl-1-phenyl-5-hexen-1-one: IR (neat) 3.33, 3.43, 3.48, 5.96, 6.13, 6.31, 6.39, 6.96, 7.34, 8.17, 10.02, 10.32, 11.00, 12.61, 14.20, and 14.30 μ; NMR ($CDCl_3$) τ 8.81 (3 H, d, J = 7.0 Hz), 7.70–8.60 (4 H, m), 6.48 (1 H, hept, J = 6.6 Hz), 3.85–5.20 (3 H, m), and 1.99–2.64 (5 H, m).

A mixture of 14.0 g of 2-methyl-1-phenyl-5-hexen-1-one, 12.0 g of unsymmetrical dimethylhydrazine, 0.15 g of acetic acid, 9.0 g of sodium acetate, and 9.0 of anhydrous magnesium sulfate was heated at 120 °C for 3 days in a sealed Carius tube. To the cooled mixture was added 50 ml of ether, and the undissolved salts were filtered. The solution was concentrated under reduced pressure, and the residue was distilled at 83–85 °C (1.2 mm) to give 15.0 g (88%) of the *N,N*-dimethylhydrazone of 2-methyl-1-phenyl-5-hexen-1-one: IR (neat) 3.28, 3.50, 3.60, 6.17, 6.80, 6.91, 7.01, 7.38, 8.35, 8.75, 9.38, 9.83, 10.10, 10.32, 11.03, 12.93, and 14.36 μ; NMR ($CDCl_3$) τ 8.92 (3 H, d, J = 7.0 Hz), 7.82–8.64 (4 H, m), 7.67 (5 H, s), 7.49 (1 H, s), 6.97–7.40 (1 H, m), 3.87–5.19 (3 H, m), and 2.57–2.94 (5 H, m).

A solution containing 15.0 g of 2-methyl-1-phenyl-5-hexen-1-one *N,N*-dimethylhydrazone and 13.8 g of iodomethane in 15 ml of absolute ethanol was refluxed for 7 h. The solvent was removed under reduced pressure, and the remaining residual oil was identified as the trimethylhydrazonium iodide of 2-methyl-1-phenyl-5-hexen-1-one: IR (neat) 2.94, 3.37, 3.40, 5.92, 6.07, 6.74, 6.84, 6.92, 8.14, 9.24, 9.52, 9.94, 10.44, 10.54, 10.86, 11.32, 12.88, 13.84, and 14.10. A solution of sodium isopropoxide, prepared from 1.50 g of sodium and 200 ml of isopropyl alcohol, was added over a 30-min period to the above trimethylhydrazonium iodide in 180 ml of isopropyl alcohol. After stirring for an additional 45 min, the solvent was removed under reduced pressure. The residue was extracted with hexane and then concentrated to give a yellow oil which was distilled at 69–71 °C (0.04 mm) to give 13.5 g (92%) of 3-phenyl-2-methyl-2-(3-butenyl-2*H*-azirine (**26**) as a clear liquid: IR (neat) 3.36, 3.52, 5.86, 6.17, 6.80, 6.98, 7.36, 8.38, 8.62, 9.41, 10.10, 11.00, 13.11, and 14.54 μ; NMR ($CDCl_3$) τ 8.61 (3 H, s), 7.69–8.30 (4 H, m), 3.98–5.20 (3 H, m), and 2.11–2.73 (5 H, m); UV (cyclohexane) 243 and 287 nm (ϵ 14 000 and 910); *m/e* 185 (M^+), 184, 170, 157, 144, 105, 104 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.16; H, 8.18; N, 7.52.

Preparation of 2-Methyl-3-phenyl-2*H*-azirine-2-propionaldehyde (28). A solution containing 1.0 g of 2-methyl-3-phenyl-2-(3-butenyl)-2*H*-azirine **26** in 100 ml of methanol was subjected to ozonolysis at −78 °C. The stream of ozone gas was allowed to continue for an additional 2 min after the reaction mixture had undergone a blue color change. At the end of this time 2.0 g of dimethyl sulfide was added to the reaction mixture at −78 °C, and the solution was allowed to stir

for 1 h at −10 °C, 1 h at 0 °C, and for 1 h at 10 °C. The solution was concentrated under reduced pressure, and 50 ml of ether was added to the residue. The solution was subsequently washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.0 g (99%) of 2-methyl-3-phenyl-2*H*-azirine-2-propionaldehyde (**28**) as a colorless oil: IR (neat) 3.53, 3.76, 5.86, 7.07, 7.33, 9.38, 9.39, 11.14, 12.69, 13.06, and 14.50 μ; NMR ($CDCl_3$) τ 8.60 (3 H, s), 7.48–7.93 (4 H, m), 2.20–2.70 (5 H, m), and 0.42 (1 H, d, J = 0.5 Hz).

Preparation of Methyl (*E*)-5-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate (29). A solution containing 1.0 g of 2-methyl-3-phenyl-2*H*-azirine-2-propionaldehyde (**28**) and 1.8 g of carbomethoxymethylenetriphenylphosphorane[86] in 25 ml of methylene chloride was stirred at room temperature under a nitrogen blanket for 12 h. The solution was concentrated to an oil and triturated with hexane. The precipitated triphenylphosphine oxide was filtered, and the hexane solution was concentrated under reduced pressure. The crude residue was purified by liquid–liquid partition chromatography[89] to give 0.9 g (70%) of methyl (*E*)-5-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate (**29**) as a colorless liquid: IR (neat) 3.46, 5.83, 6.05, 6.93, 7.02, 7.60, 7.90, 8.37, 8.58, 9.62, 10.22, 11.72, 13.08, and 14.52 μ; UV (cyclohexane) 243, 279, and 287 nm (ε 13 500, 980, and 800); NMR ($CDCl_3$) τ 8.60 (3 H, s), 7.7–8.20 (4 H, m), 6.33 (3 H, s), 2.86–4.40 (2 H, m), and 2.2–2.6 (5 H, m); *m/e* 243 (M^+), 242, 184, 170, 144, 113, 105, 104 (base), 81, and 77.

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.97; H, 7.26; N, 5.37.

Photochemical Trapping of the Nitrile Ylide Derived from 2-(3-Butenyl)-2-methyl-3-phenyl-2*H*-azirine. A solution containing 177 mg of 2-(3-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**26**) and 50 ml of methyl acrylate in 400 ml of cyclohexane was irradiated through a Vycor filter for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was purified by dry column chromatography using a 1:4 ether–pentane mixture as the eluent. The clear oil obtained amounted to 195 mg and was identified as a mixture of *cis*- and *trans*-2-phenyl-4-carbomethoxy-5-methyl-5-(3-butenyl)-Δ^1-pyrroline **27** on the basis of the following data: IR (neat) 3.50, 5.82, 6.22, 6.42, 6.99, 7.04, 7.55, 8.02, 8.37, 8.63, 9.36, 9.86, 10.07, 11.02, 13.14, and 14.51 μ; NMR ($CDCl_3$) τ 8.84 and 8.44 (3 H, s), 6.6–8.0 (7 H, m), 6.27 (3 H, s, 3.7–5.2) (3 H, m), and 2.1–2.7 (5 H, m).

The nitrile ylide derived from the photolysis of 2-(3-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**26**) could also be trapped with dimethyl acetylenedicarboxylate. A solution containing 246 mg of **26** and 1.94 g of dimethyl acetylenedicarboxylate in 450 ml of cyclohexane was irradiated through a Vycor filter sleeve for 30 min. The solvent was removed under reduced pressure, and the residual yellow oil was purified by dry column chromatography using a 1:4 ether–pentane mixture as the eluent. The white crystals obtained (280 mg, 64%) were identified as dimethyl-2-(2-butenyl)-2-methyl-5-phenyl-2*H*-pyrrole-3,4-dicarboxylate: mp 72–73 °C; IR (KBr) 3.49, 5.85, 6.20, 6.98, 7.04, 7.64, 7.92, 8.12, 8.42, 8.96, 9.49, 9.92, 10.96, 12.58, 13.92, and 14.50 μ; UV (cyclohexane) 234 nm (ε 13 100); NMR ($CDCl_3$) τ 8.43 (3 H, s), 7.4–8.2 (4 H, m), 6.14 (6 H, s), 3.7–5.3 (3 H, m), and 2.2–2.7 (5 H, m); *m/e* 327 (M^+), 312, 268, (base) 239, 208, and 104.

Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.47; N, 4.28. Found: C, 69.40; H, 6.48; N, 4.20.

All attempts to isolate a pure product from the photolysis of 2-(3-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**26**) under a variety of photolytic conditions and with different solvents failed.

Photochemical Trapping of the Nitrile Ylide Derived from Methyl (*E*)-5-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate. A solution containing 152 mg of methyl (*E*)-5-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate (**29**) and 1.30 g of dimethyl acetylenedicarboxylate in 250 ml of cyclohexane was irradiated through a Pyrex filter sleeve for 2 h. The solvent was removed under reduced pressure to afford a yellow oil which was purified by dry column chromatography using a 1:4 ether–pentane mixture as the eluent. The clear oil obtained amounted to 225 mg (93%) and was identified as dimethyl (*E*)-2-[4-(methoxycarbonyl)-3-butenyl]-2-methyl-5-phenyl-2*H*-pyrrole-3,4-dicarboxylate (**30**) on the basis of the following data: IR (neat) 3.46, 5.84, 6.19, 7.04, 7.99, 9.50, 9.97, 12.60, 13.95, and 14.50 μ; UV (cyclohexane) 230 nm (ε 14 800); NMR ($CDCl_3$) τ 8.44 (3 H, s), 7.4–8.1 (4 H, m), 6.36 (3 H, s), 6.35 (3 H, s), 6.37 (3 H, s), 2.9–4.4 (3 H, m), and 2.2–2.7 (5 H, m); *m/e* 385 (M^+), 355, 326, 325 (base), 297, 286, and 266.

All attempts to isolate a pure product from the photolysis of methyl (*E*)-5-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate (**29**) under a variety of photolytic conditions failed.

Thermolysis of 2-(3-Butenyl)-2-methyl-3-phenyl-2*H*-azirine. A solution containing 216 mg of azirine **26** in 15 ml of toluene was heated in a sealed tube at 195 °C for 13 days. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a thick-layer plate using a 1:4 ether–pentane mixture as the eluent. The major product (96 mg, 49%) was a colorless oil which was identified as 2-methylbiphenyl (**34**) by comparison with an authentic sample: IR (neat) 3.31, 3.43, 6.26, 6.77, 6.87, 6.98, 7.27, 8.65, 8.84, 9.32, 9.50, 9.66, 9.90, 10.90, 12.84, 13.37, 13.77, and 14.30 μ; NMR ($CDCl_3$) τ 7.95 (3 H, s), 3.01 (4 H, s), and 2.90 (5 H, s); *m/e* 168 (M^+), 167, 144, 105 (base), and 77.

The minor product isolated from the thick-layer plate contained 32 mg (15%) of a pale-yellow liquid whose structure was identified as 2,5-dimethyl-6-phenylpyridine (**35**) by comparison with the spectral data listed in the literature:[62] IR (neat) 3.36, 3.46, 5.88, 6.33, 6.41, 6.76, 6.87, 7.35, 8.94, 9.76, 10.92, 12.21, 12.76, 13.26, 13.62, and 14.36 μ; NMR ($CDCl_3$) τ 7.74 (3 H, s), 7.44 (3 H, s), 2.98 (1 H, d, J = 8.0 Hz), 2.4–2.7 (6 H, m); *m/e* 183, 182 (base), 167, 105, and 77.

Thermolysis of Methyl (*E*)-5-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-pentenoate. A solution containing 154 mg of azirine **29** in 12 ml of toluene was heated at 195 °C in a sealed tube for 13 days. Removal of the solvent under reduced pressure left a yellow oil which contained two components when analyzed by GLC (Chromosorb W, 10%). The two products were isolated by thick-layer chromatography using a 1:4 ether–pentane mixture as the eluent. The minor product contained 18 mg (12%) of a clear oil whose structure was assigned as methyl 6-methylbiphenyl-2-carboxylate (**37**) on the basis of the following data: IR (neat) 3.49, 5.85, 6.32, 7.05, 7.32, 7.81, 8.43, 8.85, 9.18, 9.37, 9.95, 12.61, 13.08, 13.50, and 14.30 μ; NMR ($CDCl_3$) τ 8.01 (3 H, s), 6.48 (3 H, s), and 2.2–3.0 (8 H, m); *m/e* 226 (M^+), 196, 195, 194, 193, 165, 91, and 77. The structure of this thermal product was verified by hydrolysis to 6-methylbiphenyl-2-carboxylic acid.[64] A 8-mg sample of the above ester was hydrolyzed by heating in the presence of 0.5 ml of a 20% aqueous hydroxide solution at 100 °C for 20 min. The reaction mixture was acidified with concentrated hydrochloric acid, and the mixture was extracted with ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a white solid which was recrystallized from methanol–water to give 6 mg of 6-methylbiphenyl-2-carboxylic acid, mp 155–156 °C (lit.[64] mp 154–155 °C). The structure of this acid was further verified by oxidation to 2-phenylisophthalic acid. To a solution containing 5 mg of 6-methylbiphenyl-2-carboxylic acid in 1.0 ml of a 1% aqueous sodium hydroxide solution was added a 5% potassium permanganate solution at 100 °C. The mixture was heated for 2 h and then hydrochloric acid was added to the reaction mixture. The solution was extracted with ether, and the ethereal solution was dried over magnesium sulfate. Removal of the solvent under reduced pressure left a white solid which was recrystallized from chloroform–methanol to give 3 mg of 2-phenylisophthalic acid, mp 269–270 °C (lit.[64] mp 270–271 °C).

The major product isolated from the thick-layer plate was a colorless oil (63 mg, 58%) whose structure was assigned as 3-methyl-2-phenylpyridine (**36**) on the basis of the following data: IR (neat) 3.38, 3.50, 6.96, 7.06, 8.51, 9.01, 9.46, 9.85, 10.93, 12.59, 12.76, 13.39, and 14.31 μ; NMR ($CDCl_3$) τ 7.66 (3 H, s), 2.88 (1 H, dd, J = 7.0 and 5.0 Hz), 2.56 (6 H, m), and 1.68 (1 H, dd, J = 5.0 and 1.0 Hz); *m/e* 169, 168 (base), 167, 134, 115, 105, and 77.

A picrate derivative was prepared and recrystallized from ethanol, mp 164–165 °C (lit.[63] mp 164–165 °C).

Thermolysis of 2-Methyl-3-phenyl-2*H*-azirine-2-propionaldehyde. A solution containing 200 mg of the above azirine in 12 ml toluene was heated at 195 °C in a sealed tube for 11 days. Removal of the solvent under reduced pressure left a dark oil. Chromatography of this material on a thick-layer plate gave 100 mg (55%) of 3-methyl-2-phenylpyridine (**36**). The structure of this material was verified by comparison with an authentic sample.[63]

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 actinometer for which a quantum yield of 0.38 was used,[60] giving a reproducible lamp output

of 1.73×10^{17} quanta s^{-1}. After irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions were run to 15% or less.

Competitive studies were carried out photochemically on mixtures of an arylazirine, an internal standard, and methyl acrylate as an external dipolarophile. Since cycloaddition rates varied considerably between systems, tubes were removed periodically and analyzed periodically by GLC until optimum conversion times for analysis had been determined. All measurements were made on a "merry-go-round" assembly at room temperature using a 2537 Å source. Varying quantities of methyl acrylate were added to solutions of the azirine, and the final peak areas of rearranged product were determined by GLC after ca. 30% of starting material had been consumed.

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