# Effect of Substituents in Controlling the Rate of the Intramolecular Cycloaddition Reaction of Allyl-Substituted 2H-Azirines[1]

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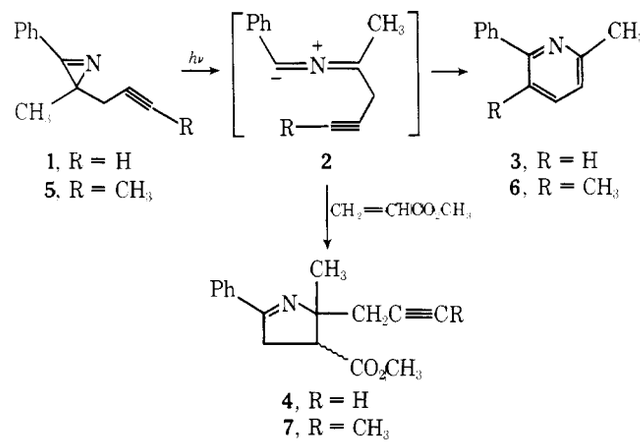
The intramolecular photocycloaddition reactions of a number of allyl-substituted 2H-azirines have been investigated in mechanistic detail. Irradiation of these systems gives rise to 2-azabicyclo[3.1.0]hex-2-enes which are readily oxidized to 2,6-disubstituted pyridines. The rearrangements proceed via a nitrile ylide intermediate which can be intercepted with added dipolarophiles to give $\Delta^1$-pyrroline derivatives. A kinetic investigation, involving Stern–Volmer plots and relative reactivity studies, shows that the internal cycloadditions are controlled by interaction of the HOMO of the dipole with the LUMO of the dipolarophile. Thus, methyl (*E*)-4-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (**14**) was found to undergo internal cycloaddition at a faster rate (tenfold) than 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**8**). The relative reactivity studies show that there is a marked leveling of the rate profile associated with these internal cycloadditions when compared with their bimolecular counterparts. The data suggest that the internal cycloaddition reactions involve appreciable interaction of both the in-plane and out-of-plane $\pi$-unoccupied orbitals of the dipole with the dipolarophile-filled orbitals. This secondary orbital interaction significantly enhances the rate of internal cycloaddition of the simple olefinic azirines and can account for the marked leveling effect noted with these systems.

In earlier papers we have shown that there are two pathways by which nitrile ylides react with multiple $\pi$ bonds.[2-5] The most frequently encountered path involves a "parallel-plane approach of addends" [6] and can be considered to be an orbital symmetry allowed [4 + 2] concerted process.[7] With this path, the relative reactivity of the nitrile ylide toward a series of dipolarophiles will be determined primarily by the extent of stabilization afforded the transition state by interaction of the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) orbitals.[8-12] Substituents which lower the dipolarophile LUMO energy will accelerate the 1,3-dipolar cycloaddition reaction.[13] Nitrile ylides are known to react most rapidly with electron-deficient alkenes since such a pair of addends possesses a narrow dipole HOMO–dipolarophile LUMO gap.[14,15] Bimolecular reactions of nitrile ylides with electron-rich olefins have never been observed, thereby indicating that the dipole LUMO–dipolarophile HOMO 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.[16-18]

The other path by which nitrile ylides react with $\pi$ bonds occurs only in certain intramolecular cases and has been designated as a 1,1-cycloaddition reaction.[2-5] It occurs when the p orbitals of the olefinic group have been deliberately constrained to attack perpendicular to the nitrile ylide plane. Houk and Caramella have suggested that the 1,1-cycloaddition reaction is initiated by interaction of the terminal carbon of the olefin with the second LUMO of the nitrile ylide.[19] The second LUMO of the dipole is perpendicular to the ylide plane and presents a large vacancy at $C_1$ of the dipole for attack by the terminus of the neighboring double bond, without the possibility of simultaneous bonding at the $C_3$ carbon. In fact, the HOMO and second LUMO of the bent nitrile ylide bear a strong resemblance to the HOMO and LUMO of a singlet carbene. According to this argument, the effect of substituents upon the rate of the intramolecular carbene-like cycloaddition should be controlled by the interaction of the alkene HOMO and the second LUMO of the nitrile ylide. Since electron-releasing substituents raise both the HOMO and LUMO orbital energies of ethylene,[9] one might expect that attachment of alkyl groups on the double bond would facilitate the rate of the 1,1-cycloaddition reaction. Electron-withdrawing substituents, on the other hand, would be expected to diminish the rate of the 1,1-cycloaddition reaction. In order to assess the effect of substituents on the rate of the 1,1-cycloaddition reaction, we have examined the photochemistry of a series of olefinic 2H-azirines containing unsaturation two bonds away from the azirine ring. We report here the results of these studies.

## Results

**Product Studies.** As a continuation of our studies dealing with the carbenic behavior of nitrile ylides, we became interested in examining the photochemistry of 2-propargylic 2H-azirines in order to determine whether internal cycloaddition of the nitrile ylide would take place across the acetylenic $\pi$ bond. Our initial experiments revealed that the 2-propargylic-substituted 2H-azirines were highly photochemically reactive. Thus, direct irradiation of 2-methyl-2-propargyl-3-phenyl-2H-azirine (**1**) with light of wavelength >250 nm for




**1**, R = H
**5**, R = $CH_3$

**2**

**3**, R = H
**6**, R = $CH_3$

**4**, R = H
**7**, R = $CH_3$

15 min resulted in the formation of 2-phenyl-6-methylpyridine (**3**; 48% isolated yield). Similar irradiation of 2-(2-butynyl)-2-methyl-3-phenyl-2H-azirine (**5**) afforded the analogous pyridine **6** in good yield. Chemical confirmation of these structures was obtained by comparison with authentic samples. Photolysis of **1** (or **5**) in the presence of methyl acrylate resulted in the trapping of nitrile ylide **2** and produced cycloadduct **4** (or **7**) in high yield. Under these conditions, the formation of pyridine **3** (or **6**) is completely suppressed. This result implicates nitrile ylide **2** as an intermediate in the formation of the pyridine ring. The formation of **3** (or **6**) can be postulated to arise by attack of the terminal carbon atom of the acetylene onto the nitrile ylide followed by a 1,2-hydrogen shift of the resulting carbene intermediate.

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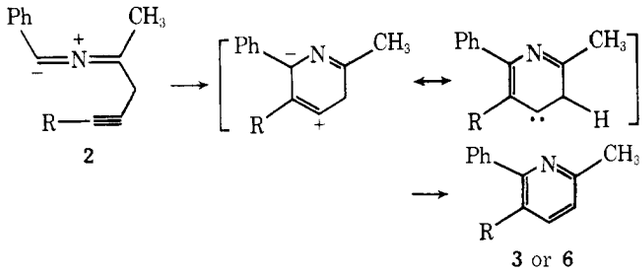
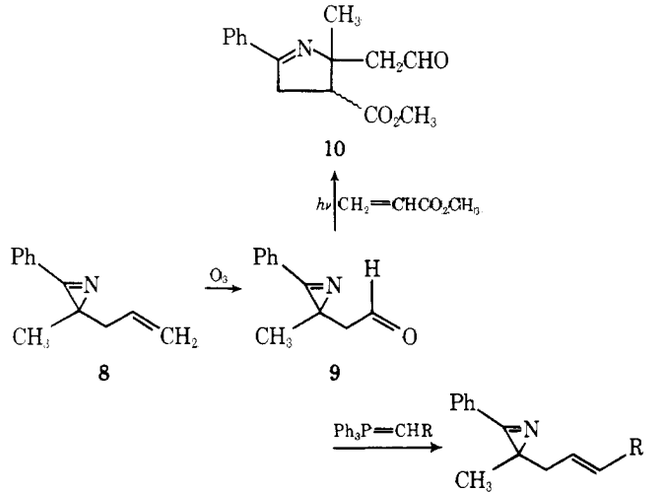


2 3 or 6

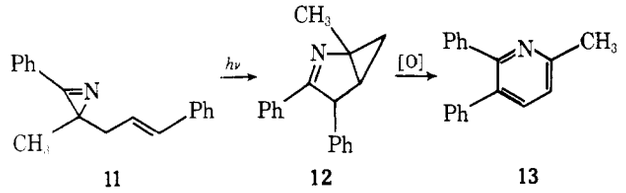
Attention was next turned to the synthesis of 2-allyl-substituted 2*H*-azirines which contain electron-withdrawing groups on the double bond. A convenient method for preparing these systems involved ozonization of the parent 2-allyl-substituted 2*H*-azirine followed by reaction of the resulting aldehyde with various Wittig reagents. All attempts to detect an intramolecular cycloadduct from the photolysis of aldehyde **9** failed. The initially generated nitrile ylide de-



**8** **9** **10**

rived from **9** could be trapped, however, with methyl acrylate to afford the normal $\Delta^1$-pyrroline adduct **10** as a mixture of stereoisomers.

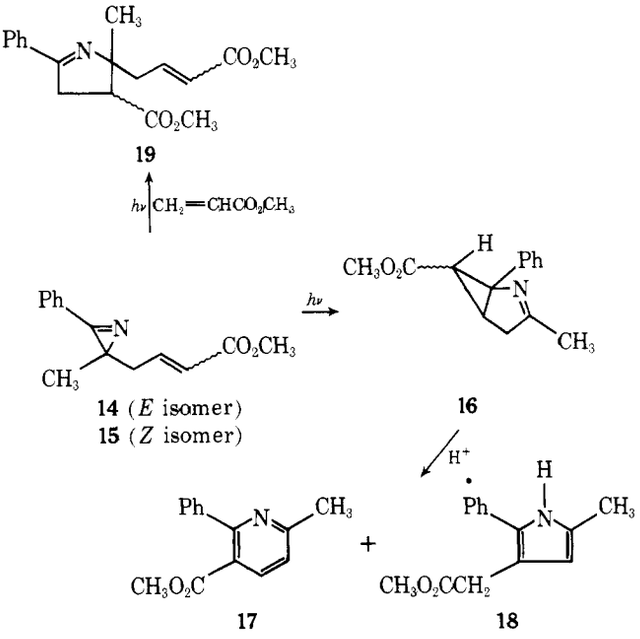
When a thoroughly deaerated solution of (*E*)-2-cinnamyl-2-methyl-3-phenyl-2*H*-azirine (**11**) was irradiated in cyclo-



**11** **12** **13**

hexane, an extremely rapid conversion to *exo*-3,4-diphenyl-1-methyl-2-azabicyclo[3.1.0]hex-2-ene (**12**) occurred. The identity of azabicyclohexene **12** was determined by its straightforward NMR spectrum ($CCl_4$, 60 MHz), which showed signals at $\tau$ 9.76 (t, 1 H, $J$ = 4.5 Hz), 9.07 (dd, 1 H, $J$ = 8.0 and 4.5 Hz), 8.31 (s, 3 H), 7.72 (dd, 1 H, $J$ = 8.0 and 4.5 Hz), 5.83 (s, 1 H), and 2.8 (m, 5 H). Upon standing or on chromatographic separation, the initially produced azabicyclohexene was converted to 2,3-diphenyl-6-methylpyridine (**13**) in quantitative yield. It is interesting to note that the irradiation of **11** resulted in the exclusive formation of cycloadduct **12**. This result stands in marked contrast to the photochemistry of the related 2-allyl-substituted 2*H*-azirine system **8**, which produced a mixture of azabicyclohexenes.[2]

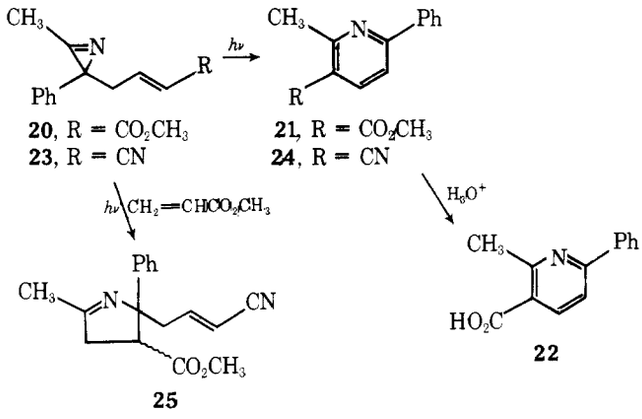
The intramolecular photocycloaddition reaction of methyl (*E*)-4-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (**14**) was also studied in order to assess the effect of electron-withdrawing groups on the double bond. Irradiation of **14** in cyclohexane using a 450-W Hanovia immersion apparatus



**19** **14** (*E* isomer) **15** (*Z* isomer) **16** **17** **18**

equipped with a Vycor filter sleeve led to the complete consumption of reactant in 20 min and produced a mixture of *endo*- and *exo*-6-carbomethoxy-3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**16**) in high yield. The same epimeric mixture of isomers was produced from the irradiation of the corresponding *Z* isomer **15**. The epimeric mixture of azabicyclohexenes was converted to 2-phenyl-3-carbomethoxy-6-methylpyridine (**17**; 60%) and methyl (2-phenyl-5-methylpyrrol-3-yl)acetate (**18**; 40%) on silica gel chromatography. It should be pointed out that no equilibration of the starting azirines was detected, and the only product that was formed when methyl acrylate was used as the trapping agent was the usual $\Delta^1$-pyrroline **19**.

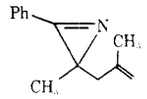
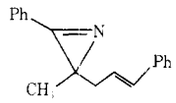
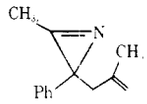
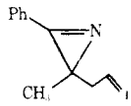
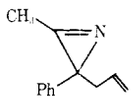
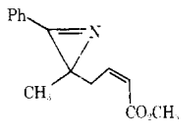
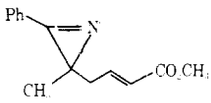
The photochemical behavior of the closely related methyl (*E*)-4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (**20**)



**20**, R = $CO_2CH_3$ **21**, R = $CO_2CH_3$
**23**, R = CN **24**, R = CN
**25** **22**

was also studied in order to assess the generality of the internal cycloaddition reaction. Photolysis of **20** gave 2-methyl-3-carbomethoxy-6-phenylpyridine (**21**) as the only characterizable material. The structure of **21** was verified by hydrolysis to the known carboxylic acid **22**.[20] With this system there were no detectable quantities of a 2-azabicyclohexene in the crude reaction mixture. It would appear as though the initially formed azabicyclohexene is rapidly converted to pyridine **21** during photolysis. We also studied the photochemistry of the closely related butenonitrile **23** and found that it was converted to 2-methyl-3-cyano-6-phenylpyridine (**24**) in high yield. Chemical support for structure **24** was obtained by its hydrolysis to carboxylic acid **22**. Irradiation of **23** in the presence of methyl acrylate was found to afford $\Delta^1$-pyrroline **25** in excellent yield.

**Table I. Kinetic Data from the Stern–Volmer Analysis of the Internal Photocycloaddition Reactions of 2-Allyl-Substituted 2*H*-Azirines**

| Compd | No. | $\Phi_o$ | Slope | Intercept | Slope/intercept | $k_{rel}$ |
|---|---|---|---|---|---|---|
|  | 26 | 0.11 | 2200 | 9.1 | 233 | 1.0 |
|  | 11 | 0.014 | 9160 | 70 | 130 | 1.8 |
|  | 27 | 0.21 | 212 | 4.9 | 43 | 5.4 |
|  | 8 | 0.26 | 152 | 3.8 | 40 | 5.8 |
|  | 28 | 0.30 | 112 | 3.3 | 34 | 6.8 |
|  | 15 | 0.049 | 960 | 20 | 48 | 4.9 |
|  | 14 | 0.06 | 73 | 17.5 | 4.2 | 55.4 |

**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.[21] Degassed and sealed quartz tubes containing solutions of the azirines were irradiated 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 were determined by quantitative NMR analysis. The quantum yield for product formation as a function of the concentration of added methyl acrylate was also studied. The results of the quantum yield measurements for the seven azirines studied are given in Table I. Several features become apparent upon examination of the data. 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 internal cycloaddition varies between 0.014 and 0.30. The relatively high quantum efficiencies observed with these systems indicate that a significant path from the electronically excited state of the unsaturated azirine involves bond rupture and formation of a nitrile ylide. The initially generated 1,3 dipole is either trapped internally by the adjacent $\pi$ bond or else undergoes bimolecular cycloaddition with the added dipolarophile.

The results obtained using these unsaturated azirines as nitrile ylide precursors are consistent with the mechanism outlined in Scheme I. In this scheme, $A_o$ = unsaturated azirine, NY = nitrile ylide, P = product, and O = dipolarophile (i.e., methyl acrylate). By making the usual steady state assumption, we can write eq 1, where $k_d$ represents the nonradiative

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

**Scheme I**

$$A_o \xrightarrow{h\nu} A^*$$

$$A^* \xrightarrow{k_d} A_o$$

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

$$NY \xrightarrow{k_1} P$$

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

decay of excited azirine, $k_r$ is the rate of C–C bond cleavage of the excited azirine ring, $k_1$ is the rate of internal cycloaddition, $k_2$ is the rate of 1,3-dipolar cycloaddition with methyl acrylate, and $\Phi_p$ is the quantum yield of product formation.

From the slope and intercept of the Stern–Volmer analysis for product formation with a given azirine, we find that the slope/intercept = $k_2/k_1$. Thus, for the case of azirine **8**, $k_2/k_1$ = 40, while with azirine **14**, $k_2/k_1$ = 4.2. These values indicate that the nitrile ylide intermediate obtained from azirine **8** is much more easily trapped with an added dipolarophile than the 1,3 dipole derived from the carbomethoxy-substituted 2*H*-azirine **14**. If we assume that the rate of cycloaddition (i.e., $k_2$) of both nitrile ylides with methyl acrylate is the same, we can obtain the relative rate difference for internal cycloaddition of these two azirines (eq 2). It should be pointed out that

$$[k_2/k_1 \text{ (for azirine 8)}/k_2/k_1 \text{ (for azirine 14)}] = k_{14}/k_8 = k_{rel} = 9.5 \quad (2)$$

previous work in our laboratory has shown that the relative reactivities of nitrile ylides generated from 2*H*-azirine precursors are very similar toward a given dipolarophile.[22,23] This observation provides strong support for the assumption that the absolute rate constants for bimolecular cycloaddition (i.e., $k_2$) are extremely similar.

**Scheme II**

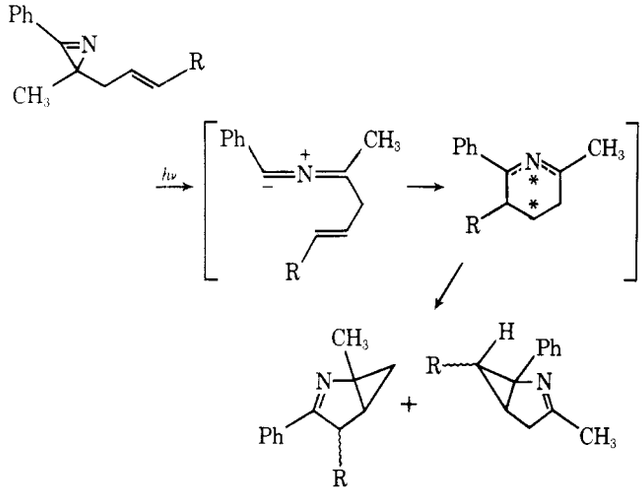


Table I gives a list of the relative rate constants for internal cycloaddition of the seven azirines examined. To facilitate comparison, all of the $k_1$ values are related to that for 2-methyl-2-(2-methylallyl)-3-phenyl-2*H*-azirine (**26**), which is taken as unity. The data presented in the table show that the rate of cycloaddition is affected by both electronic and steric factors. Attachment of electron-withdrawing substituents to the double bond facilitates the internal cycloaddition reaction relative to the alkyl-substituted olefinic azirines (i.e., **8** or **26**). Interestingly, internal cycloaddition of the (*Z*)-carbomethoxy-substituted 2*H*-azirine **15** is eleven times slower than of the corresponding *E* isomer **14**.

## Discussion

Previous papers from this laboratory have established that the irradiation of allyl-substituted 2*H*-azirines produces 2-azabicyclo[3.1.0]hex-2-enes as primary photoproducts.[2-5] The photoreaction has been proposed to proceed via C–C bond cleavage and generation of a bent nitrile ylide intermediate (carbene-like). Attack of the carbene carbon of the dipole onto the terminal position of the neighboring double bond generates a six-membered ring trimethylene intermediate which subsequently collapses to the observed 2-azabicyclohexene ring system. It should be noted that the cycloaddition sequence shown in Scheme II proceeds in a nonconcerted manner and bears a strong resemblance to the stepwise diradical mechanism suggested by Firestone[25,26] to account for bimolecular 1,3-dipolar cycloadditions.

The nonconcerted 1,1-cycloaddition reaction occurs only when the p orbitals of the dipolarophile are constrained to attack perpendicular to the bent[27] nitrile ylide plane. The fact that the irradiation of these electron-deficient allyl-substituted azirines gives rise to azabicyclohexenes and products derived from them (i.e., **21** or **24**) suggests that a similar series of intermediates are involved here. This pathway is distinctly different from that encountered in the bimolecular 1,3-dipolar cycloaddition reactions of nitrile ylides.[14,15,28] The bimolecular path involves a "parallel plane approach of addends" and is an orbital symmetry allowed [3 + 2] concerted process.[7]

As was mentioned earlier, the 1,1-cycloaddition reaction has been suggested to be initiated by interaction of the terminal carbon of the olefin with the second LUMO of the nitrile ylide. Placement of an electron-withdrawing substituent on the $\pi$ bond will lower both the HOMO and LUMO orbital energies of the olefin, and therefore a diminution in the rate of the intramolecular 1,1-cycloaddition reaction might be expected relative to the unsubstituted olefinic azirine system **8**. Using this rationale, the relative reactivity prediction for the second LUMO controlled intramolecular cycloaddition reaction of these allyl-substituted 2*H*-azirines proves to be incorrect. Thus, the internal cycloaddition of the nitrile ylide derived from the carbomethoxy-substituted 2*H*-azirine **14** proceeds at a faster rate (10-fold) than that derived from azirine **8**. Furthermore, the 2-methylallyl-substituted azirines **26** and **27** undergo internal cycloaddition at a slower rate than azirines **8** and **28** (see Table I). Alkylethylenes generally have ionization potentials 1–2 eV lower than ethylene, depending on the type and number of alkyl substituents. Also, the $\pi$–$\pi^*$ transition energies of alkylethylenes are 0.6–1.0 eV lower in energy than that of ethylene.[29] These findings indicate that alkyl groups should raise both the HOMO and LUMO orbital energies of ethylene and therefore should facilitate the rate of the intramolecular carbene-like 1,1-cycloaddition if the reaction is controlled by the second LUMO of the nitrile ylide. This is clearly not the case.

The relative reactivity pattern exhibited by these allyl-substituted azirines seems more consistent with a HOMO controlled intramolecular cycloaddition reaction. Houk's latest MINDO calculations show that the parent nitrile ylide is definitely bent with an HCN angle of 114–116°.[27] Although the highest occupied molecular orbital of the ylide was found to be heavily localized at $C_1$, it still resembles the normal three-orbital, four-electron $\pi$ system present in other 1,3 dipoles. As was pointed out earlier, nitrile ylides will react most rapidly with electron deficient alkenes in bimolecular cycloadditions since such a pair of addends possesses a narrow dipole HOMO–dipolarophile LUMO gap.[14] The same effect seems to be operating in the internal cycloadditions reported here, even though these systems cannot achieve a strictly parallel plane approach of addends. It should be noted, however, that the rate difference for the internal cycloaddition of azirines **8** and **14** is relatively small (i.e., only 10-fold). The rate constants associated with bimolecular dipolar cycloadditions of nitrile ylides generally range over many powers of 10. For example, fumaronitrile undergoes cycloaddition at a rate which is 189 000 times faster than methyl crotonate.[29] 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.

Bimolecular cycloadditions exhibit large negative entropies of activation[7] 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 since the smaller the steric requirements of the transition state the less sensitive the system is toward disturbance. Thus, the high degree of order already present in the transition state for these intramolecular nitrile ylide cycloadditions could readily account for the leveling of the rate profile.

Another factor which undoubtedly plays an important role in the intramolecular 1,1-cycloaddition reaction involves the interaction of the secondary orbitals of the dipole and dipolarophile. With nitrile ylides, the in-plane vacant orbital is of lower energy than the vacant $\pi$ orbital.[10] Consequently, stabilization of the transition state can be enhanced by interaction of this in-plane orbital with the dipolarophile HOMO orbital. For this to occur, a contortion away from the strictly parallel plane approach of the dipole and dipolarophile would be necessary. With these allyl-substituted 2*H*-azirines, the transition state actually involves a geometry where the p orbitals of the olefinic group have been deliberately constrained to attack perpendicular to the nitrile ylide plane. Thus, the 1,1-cycloaddition reaction will involve appreciable interaction of both the in-plane and out-of-plane $\pi$-unoccupied orbitals of the dipole with the dipolarophile-filled orbitals. This secondary orbital interaction would be expected to significantly enhance the rate of the intramolecular 1,1-cycloaddition with

unactivated olefins and could readily account for the leveling effect observed. It should be pointed out that while the secondary orbital effect is important, the relative reactivities toward internal 1,1-cycloaddition will still be controlled by the highest occupied molecular orbital of the nitrile ylide.

## Experimental Section

All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Jeolco-ML-100 and a Varian XL-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV.

**Preparation and Photolysis of 2-Methyl-2-propargyl-3-phenyl-2*H*-azirine (1).** A sample of azirine 1 was prepared by the method previously outlined[2] in 38% yield: NMR ($CDCl_3$, 60 MHz) $\tau$ 8.50 (s, 3 H), 7.95 (t, 1 H, $J$ = 3.0 Hz), 7.55 (dd, 1 H, $J$ = 17.5 and 3.0 Hz), 7.27 (dd, 1 H, $J$ = 17.5 and 3.0 Hz), and 2.0–2.6 (m, 5 H); IR (neat) 3300, 2128, 1740, 1600, 1585, 1495, 1450, 1375, 1235, 1200, 1075, 1010, 985, 952, 766, and 690 $cm^{-1}$; UV (cyclohexane) 241 nm ($\epsilon$ 11 500); MS *m/e* 169 ($M^+$), 128 (base), 105, 104, 103, 102, and 77.

Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.08; H, 6.43; N, 8.31.

A solution containing 75 mg of the above azirine in 200 mL of cyclohexane was purged with an argon stream and irradiated for 15 min using a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was subjected to preparative thick-layer chromatography using a 25% acetone–hexane mixture as the eluent. The major product was a clear oil (36 mg, 48%) whose structure was assigned as 2-phenyl-6-methylpyridine (**3**) by comparison with an authentic sample;[30] picrate derivative, mp 131–132 °C (lit.[30] mp 131 °C).

A trapping experiment was also carried out using methyl acrylate as the dipolarophile. A solution containing 50 mg of **1** and 12 mL of methyl acrylate in 175 mL of cyclohexane was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Corex filter sleeve. The polymer which formed was filtered, and the filtrate was evaporated under reduced pressure to give 65 mg of a clear oil which was subjected to preparative thick-layer chromatography using a 15% acetone–hexane mixture as the eluent. The major band contained a 2:3 mixture of *cis*- and *trans*-4-carbomethoxy-5-methyl-2-phenyl-5-propargyl-$\Delta^1$-pyrroline (**4**) as a clear oil: NMR ($CDCl_3$, 100 MHz) $\tau$ 8.74 and 8.34 (singlets, 3 H), 8.05 and 8.02 (t, $J$ = 2.5 Hz, 1 H), 7.49 and 7.24 (t, $J$ = 2.5 Hz, 2 H), 6.30–7.00 (m, 3 H), 6.25 (s, 3 H), 2.50–2.66 (m, 3 H), and 2.10–2.24 (m, 2 H); IR (neat) 3300, 2960, 2140, 1740, 1630, 1585, 1450, 1440, 1345, 1210, 1175, 1125, 1075, 766, and 695 $cm^{-1}$; MS *m/e* 255 ($M^+$), 254, 224, 216 (base), 196, 184, 169, 158, 157, 156, 123, 115, 105, 91, and 77.

**Irradiation of 2-(2-Butynyl)-2-methyl-3-phenyl-2*H*-azirine (5).** A solution containing 165 mg of **5**[31] in 150 mL of cyclohexane was irradiated for 15 min using a Corex filter sleeve. The solvent was removed under reduced pressure, and the crude photolysate was subjected to preparative thick-layer chromatography using a 30% acetone–hexane mixture as the eluent. The fastest moving component contained 50 mg (31%) of 2-phenyl-3,6-dimethylpyridine (**6**): NMR (benzene-$d_6$, 100 MHz) $\tau$ 7.97 (s, 3 H), 7.54 (s, 3 H), 3.35 (1 H, d, $J$ = 8.0 Hz), 2.98 (1 H, d, $J$ = 8.0 Hz), 2.70–2.90 (m, 3 H), and 2.32–2.44 (m, 2 H). The structure of this material was further verified by comparison with an authentic sample;[32] picrate derivative, mp 134–135 °C (lit.[32] mp 134 °C).

The nitrile ylide derived from **5** could be trapped using methyl acrylate as the dipolarophile. A solution containing 200 mg of **5** and 10 mL of methyl acrylate in 150 mL of cyclohexane was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Corex filter sleeve. The solvent was removed under reduced pressure, and the resulting residue was purified by preparative thick-layer chromatography. The major component contained 270 mg (91%) of a 1:2 mixture of the cis and trans isomers of 5-(2-butynyl)-4-carbomethoxy-5-methyl-2-phenyl-$\Delta^1$-pyrroline (**7**): NMR ($CDCl_3$, 100 MHz) (isomer with methyl and carbomethoxy groups in a cis relationship) $\tau$ 8.82 (s, 3 H), 8.32 (t, 3 H, $J$ = 2.5 Hz), 7.38 (q, 2 H, $J$ = 2.5 Hz), 6.40–7.10 (m, 3 H), 6.36 (s, 3 H), 2.60–2.76 (m, 3 H), and 2.18–2.32 (m, 2 H); NMR ($CDCl_3$, 100 MHz) (trans isomer) $\tau$ 8.42 (s, 3 H), 8.34 (t, $J$ = 2.5 Hz, 3 H), 7.62 (q, 2 H, $J$ = 2.5 Hz), 6.40–7.10 (m, 3 H), 6.34 (s, 3 H), 2.60–2.76 (m, 3 H), and 2.18–2.32 (m, 2 H); IR (neat) 2940, 1735, 1635, 1585, 1500, 1440, 1330, 1205, 1165, 1125, 1020, 866, 760, and 692 $cm^{-1}$; MS *m/e* 269 ($M^+$), 268, 254, 238, 216 (base), 210, 184, 182, 158, 142, 115, 105, 91, and 77.

**Irradiation of (*E*)-2-Cinnamyl-2-methyl-3-phenyl-2*H*-azirine (11).** A solution containing 100 mg of azirine **11**[31] in 150 mL of cyclohexane was irradiated for 8 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Evaporation of the solvent under reduced pressure left a clear oil whose NMR spectrum indicated it to be a mixture of unreacted starting material (50%) and 3,4-diphenyl-1-methyl-2-azabicyclo[3.1.0]hex-2-ene (**12**): NMR ($CCl_4$, 60 MHz) $\tau$ 9.76 (t, 1 H, $J$ = 4.5 Hz), 9.07 (dd, 1 H, $J$ = 8.0 and 4.5 Hz), 8.31 (s, 3 H), 7.72 (dd, $J$ = 8.0 and 4.5 Hz, 1 H), 5.83 (s, 1 H), and 2.8 (m, 5 H).

Upon standing or on chromatographic workup, the crude photolysate was converted to 2,3-diphenyl-6-methylpyridine (**13**) in 45% yield: NMR ($CF_3CO_2D$, 60 MHz) $\tau$ 7.02 (s, 3 H), 2.40–2.90 (m, 10 H), 2.16 (d, 1 H, $J$ = 8.0 Hz), and 1.50 (d, 1 H, $J$ = 8.0 Hz); IR (neat) 3010, 2900, 1725, 1680, 1626, 1575, 1490, 1440, 1370, 1070, 756, and 697 $cm^{-1}$; MS *m/e* 245 ($M^+$), 244 (base), 202, 86, and 84.

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.31; H, 6.03; N, 5.46.

When the irradiation of **11** was carried out for longer periods of time and was allowed to reflux in the presence of 5% palladium on carbon, a quantitative yield of 2,3-diphenyl-6-methylpyridine (**13**) was obtained.

**Preparation and Photolysis of (2-Methyl-3-phenyl-2*H*-azirin-2-yl)acetaldehyde (9).** A solution containing 150 mg of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**8**)[2] in 200 mL of methanol was ozonized at −78 °C until a blue color persisted. The solution was then flushed with nitrogen, and 20 mL of dimethyl sulfide was added. The mixture was allowed to warm to 0 °C and stirred at this temperature for 4 h. The solvent was removed under reduced pressure, and the residue was extracted with petroleum ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a clear oil which was distilled at 25 °C (0.05 mm) to give (2-methyl-3-phenyl-2*H*-azirin-2-yl)acetaldehyde (**9**) in 91% yield: NMR ($CDCl_4$, 100 MHz) $\tau$ 8.64 (s, 3 H), 7.72 and 6.94 (AB pattern with $J_{AB}$ = 17.0 Hz; each peak was further coupled into doublets with $J$ = 1.5 and 0.5 Hz, respectively), 2.4–2.6 (m, 3 H), 2.0–2.2 (m, 2 H), and 0.24 (dd, 1 H, $J$ = 1.5 and 0.5 Hz); IR (neat) 3010, 2890, 2820, 2690, 1720, 1680, 1600, 1485, 1447, 1370, 1198, 1115, 938, 763, and 690 $cm^{-1}$; UV (cyclohexane) 243 nm ($\epsilon$ 12 500), 278 (1300), and 288 (1000); MS *m/e* 173 ($M^+$, base), 158, 144, 130, 115, 105, 104, 91, and 77. This material was extremely sensitive and was immediately used in the next step.

The direct irradiation of **9** afforded intractable material. The irradiation of **9** was also carried out in the presence of methyl acrylate. A solution containing 100 mg of **9** and 30 mL of methyl acrylate in 130 mL of cyclohexane was irradiated for 8 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure afforded a 98% yield of (4-carbomethoxy-5-methyl-2-phenyl-$\Delta^1$-pyrrolin-5-yl)acetaldehyde (**10**) as a 2:3 mixture of cis and trans isomers: NMR ($CDCl_3$, 100 MHz) (cis isomer) $\tau$ 8.88 (s, 3 H), 7.40 and 7.16 (AB pattern, $J_{AB}$ = 16.0 Hz, further coupled into doublets with $J$ = 1.5 Hz, 2 H), 6.52–7.10 (m, 3 H), 6.32 (s, 3 H), 2.60–2.90 (m, 3 H), 2.16–2.30 (m, 2 H), and 0.24 (t, 1 H, $J$ = 1.5 Hz); NMR ($CDCl_3$, 100 MHz) (trans isomer) $\tau$ 8.44 (s, 3 H), 7.56 and 7.75 (AB pattern, $J_{AB}$ = 16.0 Hz, further coupled into doublets with $J$ = 1.5 Hz, 2 H), 6.52–7.10 (m, 3 H), 6.37 (s, 3 H), 2.60–2.90 (m, 3 H), 2.16–2.30 (m, 2 H), and 0.34 (t, 1 H, $J$ = 1.5 Hz); IR (neat) 3030, 2940, 1736, 1623, 1580, 1450, 1342, 1205, 1170, 1136, 1020, 763, and 692 $cm^{-1}$; MS *m/e* 259 ($M^+$), 231, 230, 184, 172 (base), 170, 156, 144, 115, 105, 91, and 77.

**Preparation of Methyl 4-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate.** To a solution containing 1.73 g of (2-methyl-3-phenyl-2*H*-azirin-2-yl)acetaldehyde (**9**) in 20 mL of methyl chloride was added 3.5 g of carbomethoxymethylenetriphenylphosphorane.[33] The mixture was stirred for 24 h at room temperature, and then the solvent was removed under reduced pressure. The resulting oil was triturated with cyclohexane to remove the precipitated triphenylphosphine oxide. After filtration, the solution was concentrated under reduced pressure and the resulting oil was chromatographed on silica gel using a 10% acetone–hexane mixture as the eluent to give the *Z* (0.35 g, 17%; **15**) and *E* (1.54 g, 67%; **14**) isomers of methyl 4-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate. The *Z* isomer **15** was identified on the basis of its characteristic spectral properties: NMR ($CCl_4$, 100 MHz) $\tau$ 8.64 (s, 3 H), 7.04 (ddt, 1 H, $J$ = 16.0, 7.0, and 1.5 Hz), 6.86 (ddt, 1 H, $J$ = 16.0, 7.0, and 1.5 Hz), 6.42 (s, 3 H), 4.28 (dt, 1 H, $J$ = 11.0 and 1.5 Hz), 3.86 (dt, 1 H, $J$ = 11.0 and 7.0 Hz), and 2.1–2.6 (m, 5 H); IR (neat) 3010, 2940, 1715, 1645, 1430, 1400, 1365, 1175, 1010, 820, 766, and 690 $cm^{-1}$; UV (cyclohexane) 243 nm ($\epsilon$

16 700); MS *m/e* 229 ($M^+$), 186, 170 (base), 105, and 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.12; H, 6.66; N, 6.03.

The corresponding *E* isomer **14** showed the following spectral properties: NMR ($CCl_4$, 100 MHz) $\tau$ 8.61 (s, 3 H), 7.67 (dd, 1 H, $J$ = 14.0 and 8.0 Hz), 7.38 (dd, 1 H, $J$ = 14.0 and 8.0 Hz), 6.36 (s, 3 H), 4.20 (d, 1 H, $J$ = 16.0 Hz), 3.12 (dt, 1 H, $J$ = 16.0 and 8.0 Hz), 2.48 (m, 3 H), and 2.28 (m, 2 H); IR (neat) 3010, 2940, 1725, 1667, 1490, 1440, 1380, 1330, 1265, 1180, 1075, 1042, 982, 930, 766, and 690 $cm^{-1}$; UV (cyclohexane) 243 nm ($\epsilon$ 14 300); MS *m/e* 229 ($M^+$), 170 (base), 105, and 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.05; H, 6.77; N, 5.77.

**Irradiation of Methyl (*E*)-4-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (14).** A solution containing 170 mg of **14** in 200 mL of cyclohexane was irradiated for 17 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent left a yellow residue whose NMR spectrum revealed it to be a 1:1 mixture of *exo*- and *endo*-6-carbomethoxy-3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**16**): NMR ($CDCl_3$, 100 MHz) $\tau$ 7.94 and 7.84 (singlets, 3 H), 8.44 (d, 1 H, $J$ = 4.0 Hz), 7.50–7.80 (m, 2 H), 7.24 (d, 1 H, $J$ = 17.5 Hz), 6.60–7.00 (m, 1 H), 6.53 and 6.38 (singlets, 3 H), and 2.4–2.8 (m, 5 H); IR (neat) 1755, 1680, 1625, 1430, and 1160 $cm^{-1}$.

When the crude photolysate was subjected to preparative thick-layer chromatography, it was not possible to isolate the azabicyclohexenes. Instead, two new compounds were isolated and were derived by an acid-catalyzed rearrangement of **16**. The faster moving component (60%) was identified as 2-phenyl-3-carbomethyoxy-6-methylpyridine (**17**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) $\tau$ 7.34 (s, 3 H), 6.32 (s, 3 H), 2.74 (1 H, d, $J$ = 8.0 Hz), 2.46 (m, 5 H), and 1.90 (1 H, d, $J$ = 8.0 Hz); IR (neat) 3030, 2940, 1715, 1590, 1430, 1380, 1290, 1236, 1217, 1135, 1110, 1055, 818, 803, 769, 743, and 700 $cm^{-1}$; MS *m/e* 227 ($M^+$), 212 (base), 196, and 153; UV (cyclohexane) 255 nm ($\epsilon$ 22 800).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.06; H, 5.68; N, 6.04.

The minor component (40%) isolated from the thick-layer plate was assigned the structure of methyl (2-phenyl-5-methylpyrrol-3-yl)-acetate (**18**) on the basis of its characteristic spectra: NMR ($CCl_4$, 100 MHz) $\tau$ 7.80 (s, 3 H), 6.60 (s, 2 H), 6.38 (s, 3 H), 4.24 (s, 1 H), 2.6–2.9 (m, 5 H), and 2.08 (broad s, 1 H, exchanged with $D_2O$); IR (neat) 3380, 2910, 1755, 1600, 1520, 1430, 1260, 1200, 1015, 795, 765, and 700 $cm^{-1}$; UV (ethanol) 293 nm ($\epsilon$ 5800) and 217 (2700); MS *m/e* 229 ($M^+$), 217, 170 (base), 155, 129, 105, and 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.18; H, 6.46; N, 6.17.

The irradiation of azirine **14** was also carried out in the presence of a trapping agent. A solution containing 100 mg of **14** and 15 mL of methyl acrylate in 150 mL of cyclohexane was irradiated for 20 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left 135 mg (98%) of an oil whose NMR spectrum indicated it to be a 1:1 mixture of the cis and trans isomers of methyl (*E*)-4-(4-carbomethoxy-5-methyl-2-phenyl-$\Delta^1$-pyrrolin-5-yl)-2-butenoate (**19**). The mixture of isomers could not be separated but showed the following properties: NMR ($CCl_4$, 100 MHz) $\tau$ 8.86 and 8.48 (singlets, 3 H), 7.80 (dd, 1 H, $J$ = 16 and 8.0 Hz), 7.28 (dd, 1 H, $J$ = 16.0 and 8.0 Hz), 6.30–7.06 (m, 3 H), 6.30 (s, 3 H), 7.26 and 6.24 (singlets, 3 H), 4.16 (d, 1 H, $J$ = 16.0 Hz), 3.10 (dt, 1 H, $J$ = 16.0 and 8.0 Hz), and 2.10–2.76 (m, 5 H); IR (neat) 2915, 1725, 1655, 1600, 1570, 1430, 1330, 1265, 1198, 1010, 763, and 693 $cm^{-1}$; UV (cyclohexane) 243 nm ($\epsilon$ 17 200); MS *m/e* 315 ($M^+$), 284, 256, 216, 212, 170, 156, 119, 117, 105 (base), and 77.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.90; H, 6.91; N, 4.13.

**Irradiation of Methyl (*Z*)-4-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (15).** A solution containing 80 mg of **15** in 150 mL of cyclohexane was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent afforded a 1:1 mixture of the same *exo*- and *endo*-2-azabicyclo[3.1.0]hex-2-enes **16** as was obtained from the irradiation of the *E* isomer. Preparative thick-layer chromatography of the mixture afforded pyridine **17** and pyrrole **18**.

The irradiation of the (*Z*)-azirine **15** was also carried out in the presence of methyl acrylate. A solution containing 75 mg of **15** and 10 mL of methyl acrylate in 150 mL of cyclohexane was irradiated for 15 min with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure followed by preparative thick-layer chromatography using a 25% acetone–hexane mixture as the eluent gave 95 mg (91%) of a mixture (2:3) of the cis and trans isomers of methyl (*Z*)-4-(4-carbomethoxy-5-methyl-2-phenyl-$\Delta^1$-pyrrolin-5-yl)-2-butenoate (**19**) which could not be separated: NMR ($CDCl_3$, 100 MHz) $\tau$ 8.78 and 8.40 (singlets, 3 H), 6.28–7.20 (m, 5 H), 6.28 and 6.24 (s, 3 H), 6.22 and 6.20 (s, 3 H), 4.08 and 3.96 (d, 1 H, $J$ = 12.0 Hz), 3.52 (dt, 1 H, $J$ = 12.0 and 8.0 Hz), and 2.0–2.56 (m, 5 H); IR (neat) 2960, 1730, 1640, 1590, 1445, 1350, 1190, 1045, 831, 769, and 695 $cm^{-1}$; UV (cyclohexane) 243 nm ($\epsilon$ 16 400); MS *m/e* 315 ($M^+$), 284, 256, 216, 184, 170, 157, 156, 115, 113, 105 (base), and 77.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.37; H, 6.64; N, 4.38.

**Preparation of (3-Methyl-2-phenyl-2*H*-azirin-2-yl)acetaldehyde.** A solution containing 150 mg of 2-allyl-3-methyl-2-phenyl-2*H*-azirine[2] in 200 mL of methanol was ozonized at −78 °C until a blue color persisted. The solution was flushed with nitrogen, and 20 mL of dimethyl sulfide was added. The mixture was allowed to warm to 0 °C and stirred at this temperature for 4 h. The solvent was removed under reduced pressure, and the residue was extracted with ether, washed with water, and dried over sodium sulfate. The remaining oil was quite labile to atmosphere conditions and was immediately used in a Wittig reaction. The crude azirinyl aldehyde exhibited the following spectral properties: NMR ($CDCl_3$, 100 MHz) $\tau$ 7.58 (s, 3 H), 7.24 (d, 1 H, $J$ = 18.0 Hz), 6.84 (d, 1 H, $J$ = 18.0 Hz), 2.6–3.0 (m, 5 H), and 0.30 (s, 1 H); IR (neat) 3010, 2950, 2700, 1730, 1590, 1495, 1450, 1370, 1100, 770, and 698 $cm^{-1}$; MS *m/e* 158 ($M^+$ and base).

**Preparation of Methyl (*E*)-4-(3-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (20).** Treatment of 175 mg of (2-phenyl-3-methyl-2*H*-azirin-2-yl)acetaldehyde with 400 mg of carbomethoxymethylenetriphenylphosphorane in an analogous fashion to that used to prepare **14** gave 181 mg (79%) of methyl (*E*)-4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (**20**): NMR ($CCl_4$, 100 MHz) $\tau$ 7.64 (s, 3 H), 7.24 (ddt, 1 H, $J$ = 15.5, 6.5, and 1.5 Hz), 7.04 (ddt, 1 H, $J$ = 15.5, 6.5, and 1.5 Hz), 6.42 (s, 3 H), 4.22 (dt, 1 H, $J$ = 16.0 and 1.5 Hz), 3.26 (dt, 1 H, $J$ = 16.0 and 6.5 Hz), and 2.7–3.0 (m, 5 H); IR (neat) 3030, 2910, 2800, 1754, 1710, 1650, 1600, 1495, 1430, 1265, 1205, 1160, 1075, 1020, 980, 770, and 693 $cm^{-1}$; UV (cyclohexane) 253 nm ($\epsilon$ 12 600); MS *m/e* 229 ($M^+$), 214, 170 (base), 157, 130, 115, 91, and 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.21; H, 6.46; N, 6.08.

**Irradiation of Methyl (*E*)-4-(3-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (20).** A solution containing 120 mg of azirine **20** in 150 mL of cyclohexane was irradiated for 7.5 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum showed a complex pattern from $\tau$ 6.0–9.0. Purification of the crude photolysis mixture by thick-layer chromatography resulted in the isolation of 45 mg of 2-methyl-3-carbomethoxy-6-phenylpyridine (**21**): NMR ($CCl_4$, 100 MHz) $\tau$ 7.16 (s, 3 H), 6.06 (s, 3 H), 2.60–2.74 (m, 3 H), 2.48 (d, 1 H, $J$ = 8.0 Hz), 1.96–2.08 (m, 2 H), and 1.88 (d, 1 H, $J$ = 8.0 Hz); IR (neat) 2900, 1720, 1575, 1430, 1370, 1265, 1190, 1150, 1087, 768, and 694 $cm^{-1}$; MS *m/e* 227 ($M^+$, base), 212, 196, 169, 168, 167, 141, 115, 91, and 77. When a mixture of the crude photolysate and 5% palladium on carbon in benzene was heated at reflux, the only product obtained in 74% yield was 2-methyl-3-carbomethoxy-6-phenylpyridine (**21**).

The structure of this material was further verified by aqueous hydrolysis to the known carboxylic acid.[20] A solution containing 25 mg of the above pyridine in 10 mL of a 50% dioxane-water mixture containing 100 mg of potassium hydroxide was heated at reflux for 4 h. The solution was cooled, acidified with hydrochloric acid, and extracted with chloroform. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give a quantitative yield of 2-methyl-3-carboxy-6-phenylpyridine (**22**): mp 194–196 °C (lit.[20] mp 196 °C); NMR ($Me_2SO$-$d_6$, 100 MHz) $\tau$ 7.18 (s, 3 H), 2.40–2.52 (m, 3 H), 1.76–1.90 (m, 2 H), and 1.72 and 2.08 (AB doublet, $J$ = 8.0 Hz, 2 H); IR (KBr) 3300–2100, 1680, 1610, 1495, 1395, 1280, 1188, 1149, 1090, 1070, 930, 855, 775, 755, 706, 694, and 687 $cm^{-1}$; MS *m/e* 213 ($M^+$, base), 196, 195, 169, 168, 157, 115, 105, and 93.

**Preparation of 4-(3-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenonitrile (23).** The method used to prepare this azirine was essentially identical with that used to prepare **20**. To a solution containing 9 mmol of the aldehyde in 27 mL of methylene chloride was added 3.6 g of cyanomethylenetriphenylphosphorane[34] in 10 mL of methylene chloride. After stirring for 25 h, the solvent was removed and the crude reaction mixture was subjected to silica gel chromatography using a 5% acetone–hexane mixture as the eluent. The major product obtained in 27% yield was identified as (*E*)-4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenonitrile (**23**): bp 85 °C (0.02 mm); NMR ($CCl_4$, 100 MHz) $\tau$ 7.64 (s, 3 H), 7.34 (ddd, 1 H, $J$ = 16.5, 6.5, and 1.6 Hz), 7.07 (ddd, 16.5, 6.5, and 1.6 Hz), 4.70 (dt, 1 H, $J$ = 16.0 and 1.6 Hz), 3.52 (dt, 1 H, $J$ = 16.0 and 6.5 Hz), and 2.72–3.16 (m, 5

H); IR (neat) 3010, 2900, 2217, 1755, 1630, 1590, 1490, 1440, 1420, 1360, 1253, 971, 770, and 696 $cm^{-1}$; UV (cyclohexane) 255 nm ($\epsilon$ 2090); MS *m/e* 196 ($M^+$), 195, 181, 169, 168 (base), 154, 144, 127, 115, 103, and 93.

Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.28. Found: C, 79.34; H, 6.01; N, 14.03.

The minor product (23%) obtained from the column was identified as the *Z* isomer: NMR ($CCl_4$, 100 MHz) $\tau$ 7.62 (s, 3 H), 7.20 (ddd, 1 H, $J$ = 15.5, 7.0, and 1.3 Hz), 4.72 (dt, 1 H, $J$ = 11.0 and 1.3 Hz), 3.67 (dt, 1 H, $J$ = 11.0 and 7.0 Hz), and 2.72–3.04 (m, 5 H); IR (neat) 3030, 2940, 2230, 1779, 1630, 1610, 1505, 1450, 1430, 1355, 1250, 1165, 1075, 760, and 699 $cm^{-1}$; UV (cyclohexane) 255 nm ($\epsilon$ 1750); MS *m/e* 196 ($M^+$), 181, 169, 168 (base), 154, 144, 103, and 92.

Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.28. Found: C, 79.51; H, 6.19; N, 14.28.

**Irradiation of 4-(3-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenonitrile (23).** A solution containing 50 mg of either the *E* or *Z* isomer of azirine **23** in 150 mL of benzene was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum contained a series of bands from $\tau$ 7.2 to 9.0. The crude photolysate was dissolved in 5 mL of benzene, 25 mg of 5% palladium on carbon was added, and the mixture was heated at reflux for 4 h. Filtration of the crude reaction mixture and evaporation of the solvent under reduced pressure left a yellow-brown solid which was recrystallized from pentane to give 38 mg (76%) of 2-methyl-3-cyano-6-phenylpyridine (**24**): mp 127–128 °C; NMR ($CDCl_3$, 100 MHz) $\tau$ 7.13 (s, 3 H), 2.36–2.48 (m, 3 H), 2.24 (d, 1 H, $J$ = 8.5 Hz). 1.80–1.96 (m, 2 H), and 1.96 (d, 1 H, $J$ = 8.5 Hz); IR (KBr) 2220, 1575, 1550, 1440, 1375, 1300, 1282, 1120, 864, 840, 787, 741, and 693 $cm^{-1}$; MS *m/e* 194 ($M^+$, base), 193, 102, and 77.

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.16; H, 5.50; N, 14.44.

Further support for the structure of pyridine **24** was obtained by its hydrolysis to the known carboxylic acid **22**.[20] A solution containing 70 mg of **24** and 200 mg of potassium hydroxide in 20 mL of a 50% water–dioxane mixture was heated at reflux for 4 h. The solution was then acidified with hydrochloric acid, extracted with chloroform, and dried over magnesium sulfate. Removal of the solvent gave a pure sample of 2-methyl-3-carboxy-6-phenylpyridine (**22**), mp 194–196 °C.

The irradiation of **23** was also carried out in the presence of a trapping agent. A solution containing 35 mg of **23** and 20 mL of methyl acrylate in 50 mL of benzene was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent followed by preparative thick-layer chromatography gave 28 mg of a mixture of the cis and trans (1:1) isomers of 4-(4-carbomethoxy-2-methyl-5-phenyl-$\Delta^1$-pyrrolin-5-yl)-2-butenonitrile (**25**): NMR ($CDCl_3$, 100 MHz) $\tau$ 7.84 (s, 3 H), 7.50 (s, 3 H), 6.52–7.40 (m, 5 H), 6.20 (s, cis), 4.84 (dt, 1 H, $J$ = 17.0 and 2.0 Hz), 4.54 (dt, 1 H, $J$ = 17.0 and 2.0 Hz), 3.44 (dd, 1 H, $J$ = 10.0 and 6.5 Hz), 3.28 (dd, 1 H, $J$ = 10.0 and 6.5 Hz), and 2.50–3.00 (m, 5 H); IR (neat) 2935, 2220, 1725, 1665, 1640, 1495, 1430, 1360, 1258, 1175, 966, 770, and 698 $cm^{-1}$; MS *m/e* 196, 195, 194, 169, 168 (base), 103, 93, and 77.

**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 $5 \times 10^{-3}$ 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,[21] giving a reproducible lamp output of $1.73 \times 10^{17}$ quanta $s^{-1}$. After irradiation, the degree of reaction was determined by quantitative NMR spectroscopy. 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 NMR spectroscopy until optimum conversion times for analysis had been determined. All measurements were made on a "merry-go-round" assembly at room temperature using a 2437-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 NMR spectroscopy after ca. 30% of the starting material had been consumed.

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**Registry No.**—**1**, 66416-62-4; **3**, 46181-30-0; *cis*-**4**, 66416-64-6; *trans*-**4**, 66416-63-5; **5**, 65495-91-2; **6**, 27068-69-5; *cis*-**7**, 66416-66-8; *trans*-**7**, 66416-65-7; **8**, 56434-95-8; **9**, 66416-67-9; *cis*-**10**, 66416-68-0; *trans*-**10**, 66538-26-9; **11**, 65495-83-2; **12**, 66416-42-0; **13**, 66416-43-1; **14**, 66416-61-3; **15**, 66416-60-2; *exo*-**16**, 66416-44-2; *endo*-**16**, 66513-14-2; **17**, 66416-45-3; **18**, 66416-46-4; (*E*)-*cis*-**19**, 66416-47-5; (*E*)-*trans*-**19**, 66416-54-4; (*Z*)-*cis*-**19**, 66416-55-5; (*Z*)-*trans*-**19**, 66416-56-6; **20**, 65495-71-8; **21**, 66416-48-6; **22**, 66416-49-7; (*E*)-**23**, 66416-50-0; (*Z*)-**23**, 66416-51-1; **24**, 66416-52-2; *cis*-**25**, 66416-53-3; *trans*-**25**, 66538-25-8; **26**, 59175-24-5; **27**, 66416-59-9; **28**, 59175-18-7; methyl acrylate, 96-33-3; carbomethoxymethylenetriphenylphosphorane, 2605-67-6; 2-allyl-3-methyl-2-phenyl-2*H*-azirine, 59175-18-7; cyanomethylenetriphenylphosphorane, 16640-68-9.

## References and Notes

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