trans-styrylsilane) and then with diisobutylaluminum deuteride (1.0 ml, 5.4 mmol) for 25 hr at 8°. However, in the final hydrolysis product (>98% of *trans*-β-styrylsilane), no deuterium was incorporated [NMR (neat) δ 0.14 (s, Me_3Si); 6.38 (d, CH=, J = 19 Hz), 6.88 (d, CH=, J = 19 Hz), 7.07-7.41 (m, 5 H)].

Infrared and NMR Spectral Study of Mixtures of Diisobutylaluminum Hydride and Trimethyl(phenylethynyl)silane. In 1:1 Ratio. By means of a gas-tight syringe, the silylacetylene (1.90 g, 10.9 mmol) was added dropwise to the neat hydride (1.50 g, 10.5 mmol) at 0°. After ca. 5 min of reaction, the C=C stretch at 1530 cm^{-1}, characteristic of the trans hydralumination adduct, was already prominent. As the reaction progressed, the Al-H and C≡C bands at 1760 and 2160 cm^{-1}, respectively, slowly disappeared, but these bands did not appear to be shifted from their usual positions in the pure components.

The NMR spectrum of the neat trans adduct displayed peaks at (δ, ppm): 0.17 (d, 4 H, J = 6.5 Hz), 0.18 (s, 9 H), 0.88 (d, 12 H, J = 6.5 Hz), 1.70 (m, 2 H), 7.23 (s, 5 H), and 7.84 (s, 1 H) (Figure 4).

In 2:1 Ratio. Admixture of 0.515 g (3.0 mmol) of the silylacetylene with 0.80 g (5.6 mmol) of the hydride was performed slowly and carefully in an NMR tube (Caution: exothermic reaction). The progress of the hydralumination was then monitored by NMR spectroscopy at a probe temperature of 0°. After ca. 15 min, new sharp singlets appeared at δ 7.84 and 0.18 ppm because of the vinylic proton and the Me_3Si group, respectively, of the trans adduct. Also, a new, broad singlet centered at 3.90 ppm developed because of a mixed 1:1 complex of the trans adduct with diisobutylaluminum hydride. When the starting acetylene was consumed, the peak at 7.84 bore a 1:5 ratio to the now sharp singlet at 7.23 ppm (C_6H_5). The methyl protons of the isobutyl groups gave rise to a triplet, which seemed to be due to the overlap of two different doublets centered at 0.98 and 0.88 ppm, respectively. The ratio of broad peaks at 3.90 and 2.93 ppm, arising from the hetero- and homohydride complexes of i-Bu_2AlH, varied with temperature. At −10°, the ratio of the heterocomplex absorption [PhCH=C($SiMe_3$)Al(i-Bu_2) with i-Bu_2AlH] to that of the homocomplex, (i-$Bu_2AlH)_3$, was 29:71 and became 19:81 at 38° (Figure 5).

Acknowledgments. The authors express their gratitude to the Public Health Service and to the National Science Foundation for the support of this research through Grants GM-20304 and GP-28209, respectively.

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Intramolecular Cycloaddition Reactions of Vinyl-Substituted 2*H*-Azirines[1]

Albert Padwa,* Joel Smolanoff, and Alan Tremper

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.
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Abstract: The scope of the thermal and photochemical ring expansion reactions of a number of 2-vinyl-substituted 2*H*-azirines has been examined. The azirine derivatives undergo photochemical rearrangement to 2,3-disubstituted pyrroles via transient nitrile ylide intermediates which can be trapped with external dipolarophiles. The thermal reactions proceed by a different pathway involving rupture of the azirine C-N single bond giving a butadienyl nitrene which cyclizes to a 2,5-disubstituted pyrrole. That the photocycloadditions proceed via the excited singlet state of the azirine is indicated by the failure of triplet sensitizers and quenchers to sensitize or quench the reaction. Photolysis of 3-phenyl-2-styryl-2*H*-azirine proceeds by a seven-membered transition state and gives 1-phenyl-3*H*-2-benzazepine as the major product. A study of the quantum yield for product formation as a function of added dipolarophile shows that the photocyclization to give a seven-membered azepine is significantly faster than cyclization to the five-membered pyrrole ring.

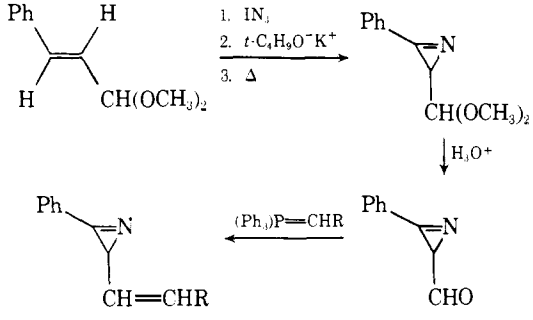
Several in-depth studies from these laboratories have demonstrated that arylazirines undergo photocycloaddition with electron-deficient olefins to give Δ^1-pyrroline derivatives.[2-4] The formation of the adducts was interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate. As a 1,3-dipole, this species can be intercepted with a variety of dipolarophiles to form five-membered heterocyclic rings.[5-9] The cleavage of the C-C bond of the azirine ring was shown to proceed from the n-π* singlet state[2] and was rationalized in terms of an electrocyclic transformation[10-12] analogous to the cyclopropyl → allyl cation rearrangement.[13] That the photocycloadditions proceed via the excited singlet state of the azirine was indicated by our inability to quench or sensitize the cycloaddition with a variety of triplet quenchers and sensitizers.[2,6] In the cases reported previously, the nitrile ylide intermediate generated from the azirine was trapped by an external dipolarophile. As a continuation of our investigations in this area, we were particularly interested in determining whether the cycloaddition reaction

would occur when the dipolarophile and the azirine ring were constrained to be within the same molecule. In this paper, we report that the intramolecular photochemical and thermal cycloaddition reactions of a variety of 2-vinyl-substituted 2*H*-azirines do indeed take place, the reactions providing clean transformations of broad scope for the synthesis of five-membered nitrogen-containing heterocycles. The findings also provide further insight into the chemical behavior of this reactive three-membered heterocyclic ring.

Results and Discussion

Synthesis of 3-phenyl-2*H*-azirines containing vinyl substituents at the 2-position of the ring was desired. A convenient starting material for the preparation of such systems is 2-formyl-3-phenyl-2*H*-azirine (**1**). This material was readily prepared by the addition of iodine azide to the dimethyl acetal of cinnamaldehyde followed by dehydrohalogenation, thermolysis, and aqueous hydrolysis. Reaction of this aldehyde with various Wittig reagents gave the desired 2-vinyl-substituted 2*H*-azirines in good yield. The synthesis is outlined in Chart I.

Chart I. Synthesis of 2-Vinyl-Substituted 2*H*-Azirines

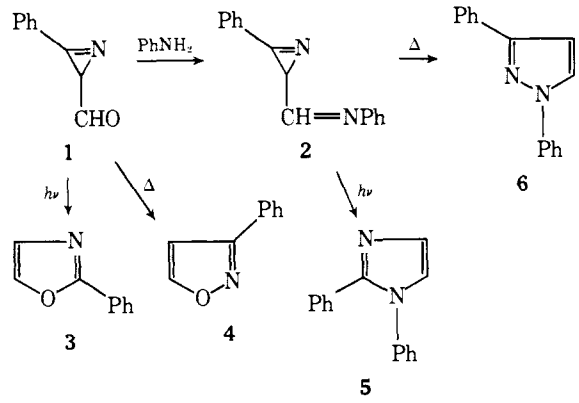


1

With the desired 2-vinyl-substituted 2*H*-azirines in hand, attention was turned to the chemical behavior of these systems. We initially examined the photochemistry of the 2-formyl-3-phenyl-2*H*-azirine (**1**) system. It was found that irradiation of **1** in benzene using a 450-W Hanovia immersion apparatus equipped with a Vycor filter sleeve led to the complete consumption of reactant in 1.2 hr. The only product obtained (70% isolated yield) was 2-phenyloxazole (**3**). Heating azirine **1** for 24 hr in toluene at 200° afforded 3-phenylisoxazole (**4**) in high yield (80%). The photolysis of the corresponding *N*-phenylimine (**2**) proceeded similarly and gave 1,2-diphenylimidazole (**5**) as the exclusive photoproduct. This stands in marked contrast to the thermal reaction of **2**, which afforded 1,3-diphenylpyrazole (**6**) as the only thermal product. The observed chemistry of these two systems is summarized in Chart II.

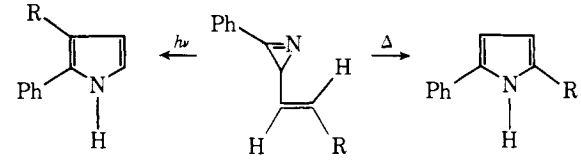
Attention was next turned to the thermal and photochemical behavior of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**). This material was formed in quantitative yield from the reaction of **1** with carbomethoxymethylenetriphenylphosphorane in benzene at 60°. A similar set of Wittig reactions gave azirines **8–10** all bearing *E* stereochemistry in the vinyl moiety. Photolysis of azirine **7** in benzene afforded 2-phenyl-3-carbomethoxypyrrole (**11**) as the only identifiable product in 85% yield. The structure of **11** is based on analytical and infrared, ultraviolet, NMR, and mass spectral data (see Experimental Section). Thermolysis of azirine **7** was found to give 2-phenyl-5-carbomethoxypyrrole (**15**) as the exclusive thermal product. In an analogous manner, photolysis of azirines **8–10** afforded 2,3-disubstituted pyrroles (**12–14**), while thermolysis of these compounds in xylene gave 2,5-disubstituted pyrroles (**16–18**).

Chart II. Photochemical and Thermal Behavior of 2-Formyl-3-phenyl-2*H*-azirine (**2**) and Its Corresponding *N*-Phenylimine



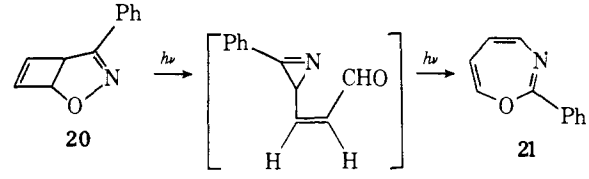
1 2 6 3 4 5

The structures of the disubstituted pyrroles were readily established by examination of their characteristic NMR spectra (see Experimental Section).



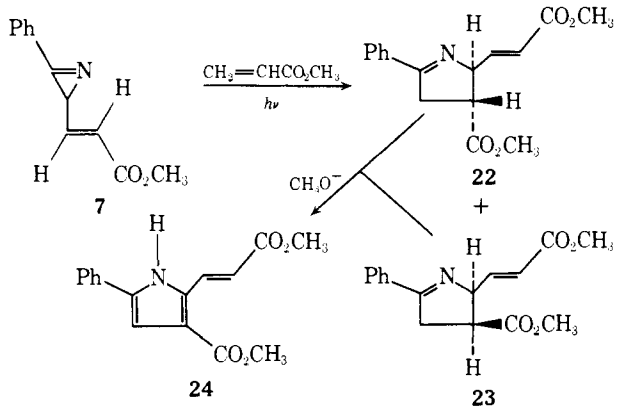
11, R = CO_2CH_3	**7**, R = CO_2CH_3	**15**, R = CO_2CH_3
12, R = CN	**8**, R = CN	**16**, R = CN
13, R = -C(=O)Ph	**9**, R = C(=O)Ph	**17**, R = -C(=O)Ph
14, R = CHO	**10**, R = CHO	**18**, R = CHO

The photochemical rearrangement of azirine **10** to 2-phenyl-3-formylpyrrole (**14**) is particularly noteworthy since the corresponding *Z* isomer **19** has been suggested as an intermediate in the photoconversion of 4-phenyl-2,3-oxazabicyclo[3.2.0]hepta-3,6-diene (**20**) to 2-phenyl-1,3-oxazepine (**21**).[15] All of our attempts to synthesize azirine **19**, to verify this claim, have failed. Mukai and coworkers, however, have recently isolated small quantities of pyrrole **14** from the irradiation of **20**.[16] This would suggest that partial photoisomerization of **19** → **10** occurs during the photorearrangement of **20** → **21**. It is also interesting to note that the corresponding 2,5-disubstituted pyrrole **18** was formed during the vapor-phase pyrolysis of **20**.[17]



20 19 21

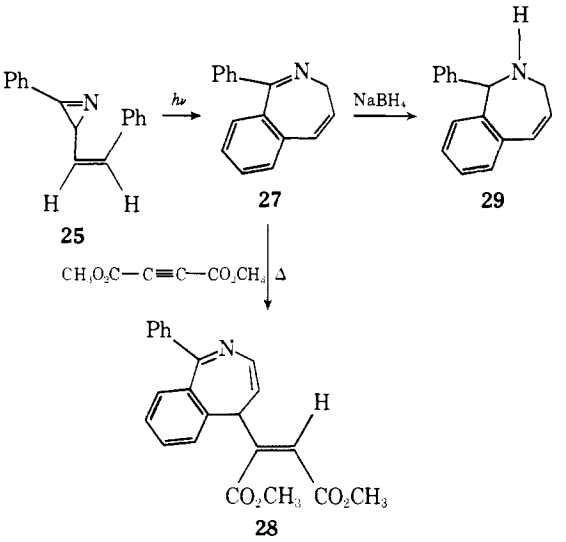
The best available evidence indicates that the photorearrangement of arylazirines **7–10** proceeds by a mechanism which involves a nitrile ylide intermediate. This conclusion was reached by carrying out the irradiation of azirine **7** in the presence of a trapping reagent. Photolysis of a mixture of **7** and excess methyl acrylate in benzene gave cycloadducts **22** and **23** in high yield. Under these conditions, the formation of 2-phenyl-3-carbomethoxypyrrole (**8**), which is formed in high yield in the absence of a trapping reagent, is entirely suppressed. Compounds **22** and **23** could be readily separated by liquid–liquid partition chromatography. The minor adduct **22** was assigned the structure of *trans*-4-carboxy-2-phenyl-(*E*)-Δ^1-pyrroline-5-acrylic acid dimethyl ester, mp 90–91°, while the major adduct **23** was identified as the corresponding cis isomer. The stereochemical assignments were made on the basis of the NMR data. The carbo-



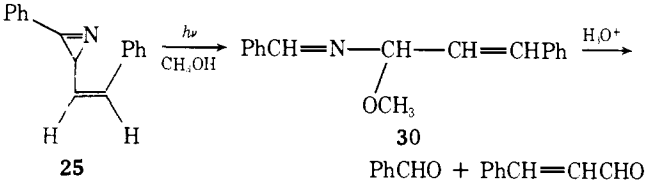
methoxy signals appear at τ 6.25 and 6.22 in **22** and τ 6.34 and 6.30 in **23**. The chemical shifts are in the same direction as was previously observed for *cis*- and *trans*-2,5-diphenyl-4-carbomethoxy-Δ^1-pyrrolines.[2] In addition, proton H_4 in *trans*-Δ^1-pyrroline **22** is shielded by the neighboring vinyl group. This proton appears at higher chemical shift (τ 4.90) in the trans isomer than it does in the corresponding cis isomer (**23**) (τ 4.76), providing further support for the assigned stereochemistry. The base-catalyzed reaction of compounds **22** and **23** did not afford an equilibrium mixture of the Δ^1-pyrrolines but instead gave 4-carboxy-2-phenyl-(*E*)-pyrrole-5-acrylic acid dimethyl ester (**24**), mp 125–126°, in good yield. Pyrrole formation from Δ^1-pyrrolines in the presence of base has been observed in other systems and provides good chemical precedent for this oxidation.[18]

An unusual aspect of the intramolecular photocyclization of unsaturated azirines was uncovered during our study of the photochemistry of (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25**). This compound was the major isomer isolated from the reaction of **1** with benzylidenetriphenylphosphorane in ether at 25°. The preferential formation of the *Z* isomer **25** is in accord with literature reports on the geometric course of the Wittig reaction.[19] The corresponding *E* isomer **26** could not be obtained as a crystalline solid since we were not able to separate it completely from the *Z* isomer. Irradiation of (*Z*)-azirine **25** in benzene with Corex filtered light gave rise to one major product (80%) which was identified as 1-phenyl-3*H*-2-benzazepine (**27**) on the basis of its spectral properties and chemical behavior. The elemental analysis of this material indicated that this substance was isomeric with **25**. The colorless liquid showed an intense absorption at 6.20 μ in the infrared; its ultraviolet spectrum had an absorption maximum at 228 nm (ϵ 17,500). The NMR spectrum consisted of a doublet at τ 6.20 (2 H, J = 7.0 Hz), a doublet of triplets at τ 3.60 (1 H, J = 10.0 and 7.0 Hz), a doublet at τ 3.10 (1 H, J = 10.0 Hz), and aromatic signals at τ 2.80–2.40 (9 H). These spectral features were totally consistent with the benzazepine assignment (**27**). The coupling constants observed with this compound are essentially identical with those reported for closely related systems.[20] Chemical support for the structure of **27** was obtained by heating equimolar quantities of **27** and dimethyl acetylenedicarboxylate. The major product isolated was a crystalline solid, mp 171–172°, whose structure was identified as dimethyl (1-phenyl-5*H*-benzazepin-5-yl)maleate (**28**) on the basis of its spectral properties (see Experimental Section). The formation of **28** may be considered as proceeding via a concerted "ene" reaction. Further support for the structure of benzazepine **27** was provided by its reduction with sodium borohydride to 2,3-dihydro-1-phenyl-1*H*-2-benzazepine (**29**).

The cyclization of azirine **25** to benzazepine **27** was substantially retarded when the irradiation was carried out in

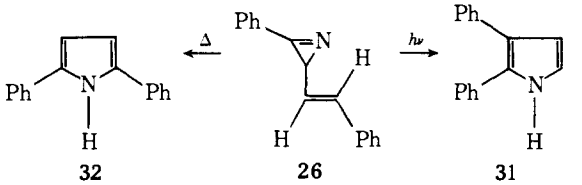


methanol. Under these conditions, the major product isolated (90%) was an oil which exhibited signals at τ 6.50 (s, 3 H), 4.40 (d, 1 H), 2.90 (dd, 1 H), 2.40 (d, 1 H), and 1.40 (s, 1 H) in its NMR spectrum. The infrared spectrum of the oil showed an intense absorption at 6.12 μ which is characteristic of a C–N double bond. This material was assigned the structure of *N*-(1-methoxy-3-phenyl-2-propylidene)-benzalimine (**30**) on the basis of its spectral properties and



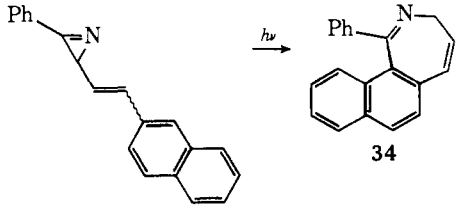
chemical behavior. Treatment of **30** with aqueous acid gave an equimolar mixture of benzaldehyde and cinnamaldehyde. The formation of methanol adduct **30** and the substantial reduction in the yield of benzazepine **27** (i.e., ~5%) strongly argue for the involvement of a transient nitrile ylide in the photorearrangement of **25** → **27**.

The photolysis of the slightly impure (*E*)-3-phenyl-2-styryl-2*H*-azirine (**26**) took an entirely different course giving 2,3-diphenylpyrrole (**31**) as the major product (85%). It should be pointed out that this pyrrole was formed in low yield (ca. 4%) in the irradiation of the *Z* isomer (**25**). Both the (*Z*)-(**25**) and (*E*)-(**26**) azirines, however, gave 2,5-diphenylpyrrole (**32**) in excellent yield on heating in benzene.

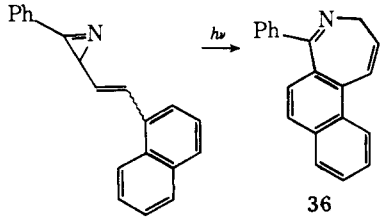


We have found that the photoconversion of 2-vinyl-2*H*-azirines to the seven-membered azepine ring is a general phenomenon when the substituent attached to the double bond contains a *cis*-aryl group. Thus, irradiation of (*Z*)- and/or (*E*)-2-[2-(β-naphthyl)vinyl]-3-phenyl-2*H*-azirine (**33**) gave a single crystalline product (85%) whose structure was identified as 1-phenyl-3*H*-naphth[1,2-*c*]azepine (**34**) on the basis of its spectral properties (see Experimental Section).[21] Similarly, irradiation of (*Z*)- and/or (*E*)-2-[2-(α-naphthyl)vinyl]-3-phenyl-2*H*-azirine (**35**) gave 1-phenyl-3*H*-naphth[2,3-*c*]azepine (**36**) as a crystalline solid in high yield (80%). It is interesting to note that, with the naphthyl systems (i.e., **33** and **35**), both the *Z* and *E* iso-

mers afford the seven-membered azepine on irradiation. This stands in marked contrast to the results obtained with the styryl-2*H*-azirine system where each isomer gave rise to a different photoproduct. This would suggest that, under the irradiation conditions, isomerization about the C-C double bond of the 2-vinyl-substituted azirine is faster than cyclization when the attached substituent is a naphthyl moiety. Cyclization of the styryl-2*H*-azirine system, however, seems to proceed at a faster rate than isomerization about the C-C double bond. These suggestions were experimentally verified by the observation that the photostationary state of the (*Z*/*E*)-naphthyl-2*H*-azirine system (**33**) was



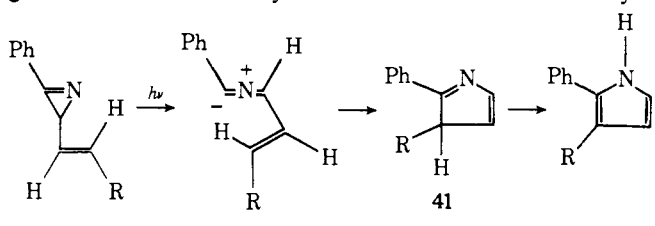
33 **34**



35 **36**

rapidly established (2.0/1) before cyclization to azepine **34** occurred. In the partial irradiation of **25**, however, no detectable quantities of **26** were found. One rationale which is in accord with these observations is that the excitation energy of these 2-vinyl-substituted 2*H*-azirines is localized on the vinylnaphtho (or vinylbenzo) end of the molecule. This is not unreasonable since these moieties would be expected to have lower energies of excitation than the n-π^* singlet state of the azirine ring.[2] Although the excitation energy in the reactant is probably localized on the vinyl end of the molecule, it is the other end of the system which initiates the photoreaction (i.e., C-C bond scission of the azirine ring). In order for the reaction to proceed, it is necessary to transfer the excitation from the vinyl moiety to the azirine portion of the molecule. This is less easily accomplished with the lower energy naphtho system and consequently the molecule has sufficient opportunity to undergo energy dissipation by rotation about the C-C double bond. This rationale is also compatible with the lower quantum yield observed for cyclization of the naphthylazirine (Φ(**33** → **34**) = 0.35) when compared with the styrylazirine system (Φ(**25** → **27**) = 0.82).

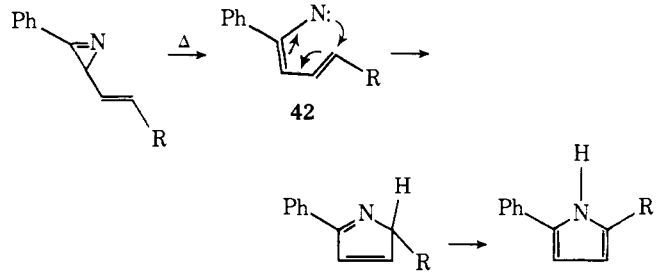
Considerable information has now been accumulated about the intramolecular cyclization reactions of unsaturated 2*H*-azirines. The formation of a 2,3-disubstituted pyrrole from the irradiation of a 2-vinyl-substituted 2*H*-azirine can be interpreted in terms of a mechanism which involves a nitrile ylide intermediate. Intramolecular reorganization of the nitrile ylide intermediate **40** followed by a



40 **41**

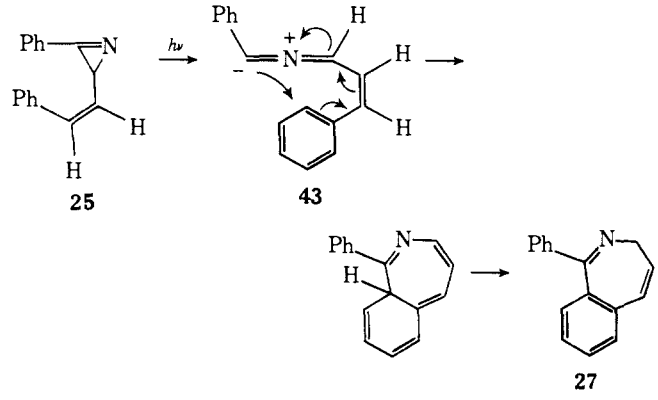
1,3-sigmatropic hydrogen shift of the initially formed five-membered ring **41** readily rationalizes the formation of the final product. This mechanism is supported by the observation that the nitrile ylide can be trapped by the addition of an external dipolarophile (i.e. **7** → **22** + **23**). Photochemical cleavage of the C-C bond of the azirine ring also accounts for the formation of oxazole **3** and imidazole **5** from the irradiation of 2-formyl-3-phenyl-2*H*-azirine (**1**) and its corresponding *N*-phenylimine (**2**).

The thermal transformations observed with these systems, on the other hand, can best be rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene (**42**) which subsequently rearranges to the final product. Nishiwaki and coworkers have recently demonstrated that a vinyl nitrene can be generated and trapped during the thermolysis of a substituted 2*H*-azirine.[22] Several examples are also available in the literature which provide good analogy for the cyclization of a butadienyl nitrene to a five-membered ring.[23,24]



42

The photoisomerization of (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25**) to 1-phenyl-3*H*-2-benzazepine (**27**) represents a novel reaction and merits some comment. In simplest valence bond terms, this transformation is explicable on the basis of a ring opening of **25** to a nitrile ylide intermediate (**43**) which subsequently undergoes intramolecular reorganization to a seven-membered ring followed by a 1,5-sigmatropic shift. In the presence of methanol, the nitrile ylide intermediate can be trapped to give methoxyimine **30**. The preference for cyclization to a seven-membered ring can be attributed to stereoelectronic factors. Recent work in our laboratory[12] as well as some ab initio calculations by Salem[25] on the ground and excited state energy surfaces of the 2*H*-azirine molecule indicates that the photochemical opening of the azirine ring will lead to an intermediate with linear geometry (i.e., **43**). Cyclization of the linear dipolar intermediate obtained from **25** can occur more easily through a seven-membered transition state, thus leading to the preferential formation of benzazepine **27**. With the corresponding (*E*)-2-styryl-2*H*-azirine isomer (**26**), cyclization of the nitrile ylide to a seven-membered ring is precluded on structural grounds, and formation of 2,3-diphenylpyrrole (**31**) occurs instead.



25 **43** **27**

Another point requiring consideration is the reaction

Table I. Quantum Yield and Kinetic Data from the Stern–Volmer Analysis of the Photocyclizations of 2-Vinyl-Substituted 2*H*-Azirines 7 and **25**

Ylide precursor	Dipolarophile	Slope	Intercept	Φ	k_d/k_r	k_2/k_1
Carboxyazirine 7	Methyl acrylate	98	2.95	0.34	1.95	33
Carboxyazirine 7	Dimethyl maleate	113	2.97	0.34	1.97	38
Carboxyazirine 7	Acrylonitrile	197	3.02	0.33	2.02	65
Carboxyazirine 7	Dimethyl acetylenedicarboxylate	598	2.92	0.34	1.92	205
Styrylazirine **25**	Methyl acrylate	2.62	1.22	0.82	0.22	2.1
Styrylazirine **25**	Dimethyl maleate	2.88	1.25	0.80	0.25	2.3
Styrylazirine **25**	Acrylonitrile	4.32	1.20	0.83	0.20	3.6
Styrylazirine **25**	Dimethyl acetylenedicarboxylate	11.1	1.21	0.82	0.21	9.2
N-Phenylimine 2				0.54		

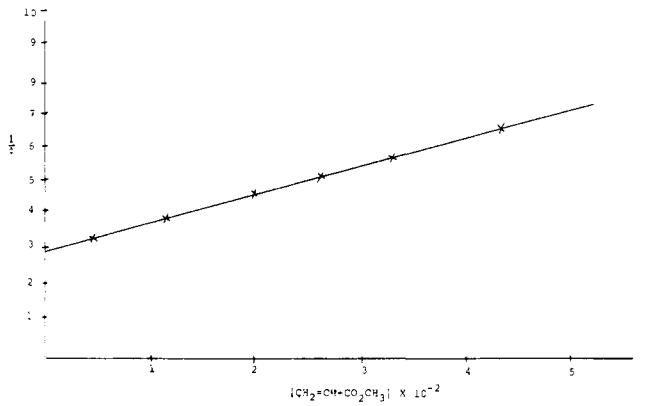


Figure 1. Plot of [quantum yield of cyclization]$^{-1}$ against [methyl acrylate] for methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**).

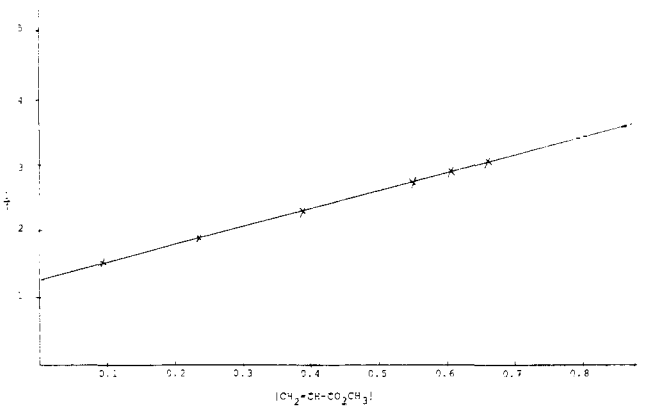


Figure 2. Plot of [quantum yield of cyclization]$^{-1}$ against [methyl acrylate] for (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25**).

multiplicity. To establish the nature of the reactive state involved in these photocyclization reactions, quenching and sensitization experiments were carried out. Identical 2-vinyl-substituted 2*H*-azirine solutions containing 1,3-cyclohexadiene or piperylene were irradiated. Neither the rate of azirine disappearance nor that of product formation was affected by the quenchers, each of which was present in concentrations known to diminish markedly the rates of established triplet processes.[26] Attempts to sensitize the photocyclization reaction were carried out using benzophenone as a triplet sensitizer. The concentrations were adjusted so that benzophenone absorbed more than 98% of the light. Under these conditions, no photocyclization was detected. The quenching and sensitization experiments suggest that the primary photochemistry of the 2-vinyl-substituted 2*H*-azirine system occurs from the excited singlet manifold.

Quantum yields for product formation were determined using benzophenone–benzhydrol as the chemical actinometer.[27] Degassed and sealed Pyrex tubes containing solutions of the 2*H*-azirines 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 results of the quantum yield measurements are given in Table I. 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 both the methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**) and (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25**) 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 2-vinyl-substituted azirine used. At zero dipolarophile concentration, the quantum yield for cyclization is 0.34 for azirine **7** and 0.82 for azirine **25**. The magnitude of the intercept indicates that cyclization of the nitrile ylide to the pyrrole is ca. 40% less efficient than cyclization to the azepine ring. The high quantum efficiencies observed with these systems demonstrate that a significant path from the electronically excited singlet state of the 2-vinyl azirine system involves bond rupture and formation of a nitrile ylide intermediate.

The results obtained using these vinyl-substituted azirines as nitrile ylide precursors are consistent with the mechanism outlined in Scheme I. In this scheme, A_0 = 2-vinyl-

Scheme I

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

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

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

$$NY \xrightarrow{k_1} P$$

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

substituted 2*H*-azirine (**7** or **25**), NY = nitrile ylide, P = product (pyrrole or azepine), and O = dipolarophile (i.e., methyl acrylate). By making the usual steady state assumption, we can write

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

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.

Ratios of rate constants involved in the kinetic scheme can be determined from the slopes and intercepts of the plots. The values are summarized in Table I. For the carbomethoxyazirine system (i.e., **7**), decay is twice as fast as ring opening (i.e., $k_d = 2k_r$). With the styrylazirine system (**25**), however, the decay rate is one-fifth the ring opening rate (i.e., $k_d = 0.2k_r$). This reactivity difference may be related to the relative stabilities expected for the photochemically generated nitrile ylides. In the 2-styryl system, the initially generated 1,3 dipole has a positive charge which can be extensively delocalized over the aromatic ring. Charge delocalization of the nitrile ylide generated from azirine **7** is not as favorable, and consequently the ring opening reaction of **7** will not proceed as readily.

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 carbomethoxyazirine **7**, we find $k_2/k_1 = 33$ while, with azirine **25**, $k_2/k_1 = 2.1$. These values indicate that the nitrile ylide intermediate obtained from azirine **7** is much more easily trapped than the 1,3 dipole derived from the styrylazirine system **25**. We have already offered a qualitative explanation to account for the preference of seven-membered ring cyclization. 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 seven-membered vs. five-membered ring cyclization.

$$[k_2/k_{1(\text{pyrrole})}/k_2/k_{1(\text{azepine})}] = k_{\text{azepine}}/k_{\text{pyrrole}} = k_{\text{rel}} \sim 16/1$$

In order to test this assumption [i.e., $k_2(7) \simeq k_2(25)$], we have studied the variation of the quantum yield for product formation for azirines **7** and **25** as a function of the concentration of several different dipolarophiles (see Table II). Since k_1 is constant for a given azirine series, we can determine the relative reactivities of various dipolarophiles toward the photochemically generated nitrile ylide by determining the magnitude of their slopes and intercepts in a Stern–Volmer plot.

$$[k_{2A}/k_1]_{\text{olefinA}}/[k_{2B}/k_1]_{\text{olefinB}} = k_{2A}/k_{2B}$$

Table II lists the relative rate constants for the cycloaddition of various dipolarophiles with the nitrile ylides generated from azirines **7** and **25**. To facilitate comparison, all the k_2 values are related to that of methyl acrylate, which is taken as unity. It is apparent from the data in Table II that the reactivities in dipolar cycloadditions of the nitrile ylides generated from **7**, **25**, and diphenylazirine are very similar (i.e., the reactivities differ by less than a factor of 2). This suggests that the absolute rate constants for reaction of the nitrile ylides with a particular dipolarophile are similar, and that the assumption (vide supra) that $k_2(7) \approx k_2(25)$ is a reasonable one.[28] The conclusion that cyclization to the azepine is 16 times faster than the cyclization to a pyrrole is in excellent agreement with the ratio of yields of benzazepine **27** and 2,3-diphenylpyrrole (**31**) (i.e., 80 vs. 4%) observed in the direct irradiation of styrylazirine **25**.

Table II. Relative Reactivity of a Series of Olefins toward Nitrile Ylides Generated from Azirines 7 and 25

Dipolarophile	Rel rate with azirine 7	Rel rate with azirine 25	Rel rate with diphenylazirine[a]
Dimethyl acetylenedicarboxylate	6.2	4.4	3.4
Acrylonitrile	1.97	1.72	1.13
Dimethyl maleate	1.15	1.10	1.04
Methyl acrylate	1	1	1

Experimental Section[29]

Preparation of 2-Formyl-3-phenyl-2*H*-azirine (1). A solution containing 81 g of cinnamaldehyde dimethyl acetal[30] in 50 ml of acetonitrile was added to a suspension of iodine azide (85 g) in 450 ml of acetonitrile at 0°. The reaction mixture was allowed to stir at room temperature for 12 hr. The resulting red-brown mixture was poured onto 500 ml of water and was extracted with ether. The combined organic extracts were washed successively with 700 ml of 5% aqueous sodium thiosulfate and 1 l. of water. The solvent was then dried over magnesium sulfate and removed under reduced pressure to give 150 g (97%) of a light-yellow oil whose structure was assigned as 1-azido-3,3-dimethoxy-2-iodo-1-phenylpropane on the basis of the following data: ir (neat) 4.60 μ; NMR ($CDCl_3$, 100 MHz) τ 6.52 (3 H, s), 6.44 (3 H, s), 5.50 (1 H, d, J = 4.0 Hz), 5.52 (1 H, dd, J = 9.0 and 4.0 Hz), 5.12 (1 H, d, J = 9.0 Hz), and 2.48 (5 H, s).

A solution containing 150 g of 1-azido-3,3-dimethoxy-2-iodo-1-phenylpropane in 1500 ml of anhydrous ether was treated with excess potassium *tert*-butoxide (20 mol %) at −10° and was allowed to stir at 0° for an additional 5 hr. The crude reaction mixture was washed twice with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil was filtered through a neutral alumina column with petroleum ether to give 90 g of a pale-yellow oil. The structure of this material was assigned as 1-azido-3,3-dimethoxy-1-phenyl-1-propene on the basis of the following data: ir (neat) 4.75 and 6.09 μ; NMR ($CDCl_3$, 100 MHz) τ 6.64 (6 H, s), 5.18 (1 H, d, J = 8.0 Hz), 4.36 (1 H, d, J = 8.0 Hz), and 2.40 (5 H, s).

A solution of 90 g of 1-azido-3,3-dimethoxy-1-phenyl-1-propene in 1000 ml of chloroform was heated at reflux for 12 hr. After this time, the solvent was evaporated under reduced pressure, and the residual oil was distilled under reduced pressure [bp 103–105° (0.27 mm)] to afford 78 g of 3-phenyl-2-(dimethoxymethyl)azirine as a colorless liquid: ir (neat) 5.70 μ; NMR ($CDCl_3$, 100 MHz) τ 7.58 (1 H, d, J = 3.0 Hz), 6.60 (3 H, s), 6.48 (3 H, s), 5.52 (1 H, d, J = 3.0 Hz), and 1.80–2.40 (5 H, m).

A 78-g sample of 3-phenyl-2-(dimethoxymethyl)azirine dissolved in 1 l. of dioxane and 1.4 l. of 20% aqueous acetic acid was heated at 85° for 45 min. The reaction mixture was rapidly cooled to 0° and extracted with ether. The combined organic extracts were washed successively with 1 l. of aqueous 5% sodium bicarbonate and 1 l. of saturated sodium chloride. Removal of the solvent (after drying over magnesium sulfate) gave a clear oil which solidified on standing. The crystalline solid formed (38 g, 55%) was collected on a filter and was sublimed at 35° (0.01 mm) to give white crystals of 2-formyl-3-phenyl-2*H*-azirine (**1**): mp 45–47°; ir (KBr) 5.60 and 5.85 μ; uv (95% ethanol) 245 nm (ϵ 15,500); NMR ($CDCl_3$, 100 MHz) τ 7.10 (1 H, d, J = 7.0 Hz), 2.32–1.84 (5 H, m), and 0.80 (1 H, d, J = 7.0 Hz); *m/e* 145 (base), 144, 117, 116, 90, 89, and 77.

Anal. Calcd for C_9H_7NO: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.41; H, 4.91; N, 9.69.

Thermolysis and Photolysis of 2-Formyl-3-phenyl-2*H*-azirine. A solution containing 500 mg of 2-formyl-3-phenyl-2*H*-azirine (**1**) in 30 ml of toluene in a sealed tube was heated at 200° for 72 hr. Removal of the solvent under reduced pressure left a dark oil which was distilled at 40° (0.01 mm) to give 400 mg of 3-phenylisoxazole;[31] ir (KBr) 3.10, 4.74, and 7.58 μ; *m/e* 145, 144, 89, and 77 (base); NMR ($CDCl_3$, 100 MHz) τ 1.61 (1 H, d, J = 1.5 Hz), 1.97–2.90 (5 H, m), and 3.42 (1 H, d, J = 1.5 Hz).

A solution containing 300 mg of **1** in 450 ml of cyclohexane was irradiated through a Vycor filter sleeve for 75 min. Removal of the solvent under reduced pressure gave a dark oil which was purified

by chromatography on a silica gel thick layer plate using a 1:4 ethyl acetate–benzene mixture as the eluent. The clear oil obtained (210 mg) was identical in all respects with an authentic sample of 3-phenyloxazole (**3**).[32]

Preparation of the *N*-Phenylimine of 2-Formyl-3-phenyl-2*H*-azirine. A solution of 1.45 g of **1** and 0.94 g of aniline in 75 ml of benzene which contained a trace of *p*-toluenesulfonic acid was heated at reflux for 1 hr. Removal of the solvent under reduced pressure left 2.1 g of a clear oil whose structure was assigned as 2-formyl-3-phenyl-2*H*-azirine-*N*-phenylimine (**2**): ir (neat) 5.60, 6.10, and 6.24 μ; uv (cyclohexane) 243 nm (ϵ 10,700) and 275 (4000); NMR (100 MHz, $CDCl_3$) τ 1.25–2.43 (11 H, m) and 6.51 (1 H, d, J = 8.0 Hz).

Thermolysis and Photolysis of 2-Formyl-3-phenyl-2*H*-azirine-*N*-phenylimine. A solution containing 300 mg of **2** in 75 ml of xylene was heated at reflux for 15 hr. Removal of the solvent under reduced pressure left an oily solid. Recrystallization of this material from 95% ethanol gave white crystals (260 mg), mp 84–85°, whose structure was identified as 1,3-diphenylpyrazole (**6**): ir (KBr) 6.28, 6.58 μ; uv (cyclohexane) 268 nm (ϵ 23,400); NMR ($CDCl_3$) τ 3.14 (1 H, d, J = 2 Hz) and 1.94–2.80 (11 H, m). This material was further verified by comparison with an authentic sample.[33]

A solution containing 500 mg of *N*-phenylimine **2** in 450 ml of benzene was irradiated through a Corex filter sleeve for 90 min. Removal of the solvent under reduced pressure left a dark oil which was purified by thick layer chromatography. The white solid obtained, mp 80–81°, was assigned as 1,2-diphenylimidazole (**5**) (450 mg): ir (KBr) 6.25 μ; uv (95% ethanol) 270 nm (ϵ 16,700); *m/e* 220, 219 (base), 193, and 77; NMR ($CDCl_3$) τ 2.52–3.00 (12 H, m).

A picrate derivative was prepared, mp 193–194°.

Anal. Calcd for $C_{21}H_{15}N_5O_7$: C, 56.13; H, 3.36; N, 15.59. Found: C, 56.22; H, 3.47; N, 15.60.

Preparation of Methyl (*E*)-3-Phenyl-2*H*-azirine-2-acrylate (7). A solution containing 1.45 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 3.34 g of carbomethoxymethylenetriphenylphosphorane[34] in 100 ml of benzene was heated at 50–60° under a nitrogen blanket for 12 hr. 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 to afford methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**) as a light-yellow oil in quantitative yield: ir (neat) 5.65, 5.78, and 6.05 μ; uv (95% ethanol) 253 and 305 nm (ϵ 15,600 and 6900); NMR ($CDCl_3$, 100 MHz) τ 7.08 (1 H, d, J = 8.0 Hz), 6.28 (3 H, s), 3.80 (1 H, d, J = 16.0 Hz), 3.12 (1 H, dd, J = 16.0 and 8.0 Hz), and 2.00–2.40 (5 H, m); *m/e* 201 (base), 170, 169, 141, 140, 115, and 114.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.45; H, 5.76; N, 6.58.

Irradiation of Methyl (*E*)-3-Phenyl-2*H*-azirine-2-acrylate. A solution containing 0.60 g of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**) in 500 ml of benzene was irradiated through a Corex filter sleeve for 1.5 hr. The solvent was removed under reduced pressure to afford a dark oil. The crude oil was filtered through a silica gel column with a 10% ethyl acetate–benzene mixture to afford a light-orange oil which solidified on standing. Recrystallization of the crude solid from benzene–heptane gave 2-phenyl-3-carbomethoxypyrrole (**11**) (95%) as colorless crystals: mp 96.5–97.5°; ir (KBr) 3.05 and 5.92 μ; uv (95% ethanol) 293 nm (ϵ 12,800); NMR ($CDCl_3$, 100 MHz) τ 6.32 (3 H, s), 3.24 (2 H, AB quartet, J = 3.0 Hz after D_2O exchange), 2.20–2.60 (5 H, m), and 0.72 (1 H, broad s); *m/e* 201, 170 (base), 169, 142, 141, 140, 115, and 77.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.48; H, 5.51; N, 7.03.

Photocycloaddition of Methyl (*E*)-3-Phenyl-2*H*-azirine-2-acrylate with Methyl Acrylate. A solution containing 0.50 g of methyl (*E*)-3-phenyl-2*H*-azirine-2-acrylate (**7**) and 50 ml of methyl acrylate in 500 ml of benzene was irradiated through a Corex filter for 3 hr. Removal of the solvent and excess methyl acrylate under reduced pressure afforded a yellow oil. Scanning liquid–liquid partition chromatography of the residual oil showed the presence of two products.[35] The minor product (31%) was assigned the structure of *trans*-4-carboxy-2-phenyl-(*E*)-Δ^1-pyrroline-5-acrylic acid dimethyl ester (**22**) on the basis of the following data: mp 90–91.5°; ir (KBr) 5.80, 6.00, and 6.18 μ; uv (95% ethanol) 247 nm (ϵ 24,100); NMR ($CDCl_3$, 100 MHz) τ 6.70 (3 H, m), 6.25 (3 H, s), 6.22 (3 H, s), 4.90 (1 H, broad m), 3.80 (1 H, d, J = 18.0 and 2.0 Hz), 2.76 (1 H, dd, J = 18.0 and 6.0 Hz), 2.40 (3 H, m), and 2.10 (2 H, m); *m/e* 287, 256, 255, 228 (base), 214, 196, 168, 116, 115, 98, and 77.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 66.75; H, 5.94; N, 4.72.

The major adduct (69%) was assigned the structure of *cis*-4-carboxy-2-phenyl-(*E*)-Δ^1-pyrroline-5-acrylic acid dimethyl ester (**23**) on the basis of the following data: mp 119–120° (95% ethanol); ir (KBr) 5.80, 6.05, and 6.19 μ; uv (95% ethanol) 248 nm (ϵ 19,200); NMR ($CDCl_3$, 100 MHz) τ 6.68 (3 H, m), 6.34 (3 H, s), 6.30 (3 H, s), 4.76 (1 H, broad m), 3.90 (1 H, dd, J = 18.0 and 2.0 Hz), 3.06 (1 H, dd, J = 18.0 and 6.0 Hz), 2.40 (3 H, m) and 2.10 (2 H, m); *m/e* 287, 256, 255, 227; 214 (base), 196, 169, 168, 115, and 77.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88. Found: C, 66.58; H, 6.06; N, 4.86.

The combined yield of adducts **22** and **23** amounted to 67%.

Attempted Base-Catalyzed Epimerization of *cis*- or *trans*-4-Carboxy-2-phenyl-(*E*)-Δ^1-pyrroline-5-acrylic Acid Dimethyl Ester (22 and 23). A solution containing 0.065 g of *cis*- or *trans*-Δ^1-pyrroline (**22** or **23**) and a catalytic quantity of sodium methoxide in 25 ml of absolute methanol was refluxed under a nitrogen atmosphere for 1 hr. The solvent was removed under reduced pressure, and the residual oil obtained was dissolved in ether. The ethereal layer was washed with water and dried over magnesium sulfate to give 0.055 g (87%) of a compound whose structure is assigned as 4-carboxy-2-phenyl-(*E*)-pyrrole-5-acrylic acid dimethyl ester (**24**) on the basis of the following data: mp 125–126°; ir (KBr) 2.98, 5.80, and 5.85 μ; uv (95% ethanol) 222 and 284 (ϵ 28,000 and 21,900); NMR ($CDCl_3$, 100 MHz) τ 6.40 (3 H, s), 6.28 (3 H, s), 3.34 (1 H, d, J = 2.0 Hz), 2.80 (7 H, m), and 0.60 (1 H, broad s); *m/e* 285 (base).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.27; H, 5.28; N, 4.77.

A similar reaction of *cis*- or *trans*-Δ^1-pyrroline (**22** or **23**) with sodium methoxide in methanol at room temperature under a nitrogen atmosphere for 12 hr afforded pyrrole **24** in 75% yield.

Thermolysis of Methyl (*E*)-3-Phenyl-2*H*-azirine-2-acrylate. A solution containing 0.30 g of methyl (*E*)-phenyl-2*H*-azirine-2-acrylate (**7**) in 50 ml of toluene was heated at reflux for 12 hr. Removal of the solvent gave off-white crystals of 2-phenyl-5-carbomethoxypyrrole (**15**) in quantitative yield: mp 142–143.5°; ir (KBr) 3.02 and 5.95 μ; uv (95% ethanol) 220 and 317 nm (ϵ 12,200 and 27,900); NMR ($CDCl_3$, 100 MHz) τ 6.16 (3 H, s), 3.40 (1 H, d, J = 4.0 Hz), 3.00 (1 H, d, J = 4.0 Hz), 2.80–2.20 (5 H, m), and −0.20 (1 H, broad s); *m/e* 201, 170, 169 (base), 141, 140, 115, and 114.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.49; H, 5.51; N, 6.86.

Synthesis of (*E* and *Z*)-3-Phenyl-2*H*-azirine-2-acrylonitrile. A solution of 1.45 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 3.31 g of cyanomethylenetriphenylphosphorane[36] in 100 ml of benzene was heated at 50–60° under a nitrogen atmosphere for 12 hr. The solvent was removed under reduced pressure, and the residual oil was triturated with hexane in order to precipitate triphenylphosphine oxide. Concentration of the hexane solution afforded 1.26 g (75%) of a mixture of (*E*)- and (*Z*)-3-phenyl-2*H*-azirine-2-acrylonitrile (**8**) as a yellow oil. All attempts to separate the mixture into its separate components failed; consequently, the mixture was analyzed without separation: ir (neat) 4.50, 5.65, and 6.10 μ; NMR ($CDCl_3$, 100 MHz) τ 7.10 (1 H, d, J = 7.0 Hz), 6.70 (1 H, d, J = 9.0 Hz), olefinic multiplets at τ 4.48, 3.88, 3.40, and aromatic absorptions at τ 1.80–2.60 (5 H, m); *m/e* 168 (base), 141, 140, 115, 114, and 77.

Irradiation of (*E* and *Z*)-3-Phenyl-2*H*-azirine-2-acrylonitrile. A solution containing 1.26 g of (*E*)- and (*Z*)-3-phenyl-2*H*-azirine-2-acrylonitrile (**8**) in 500 ml of benzene was irradiated through a Corex filter sleeve for 1 hr. The solvent was removed under reduced pressure, and the residual oil was chromatographed on a silica gel column with a 10% ethyl acetate–benzene mixture to afford 0.70 g (55%) of a solid whose structure was assigned as 2-phenyl-3-cyanopyrrole (**12**) on the basis of the following data: mp 153–154°; ir (KBr) 3.10 and 4.48 μ; uv (95% ethanol) 288 nm (ϵ 10,800); NMR ($CDCl_3$, 100 MHz) τ 3.32 (2 H, AB quartet, J =

3.0 Hz after D_2O exchange), and 2.00–2.70 (5 H, m); *m/e* 168 (base), 141, and 140.

Anal. Calcd for $C_{11}H_8N_2$: C, 77.98; H, 4.79; N, 16.66. Found: C, 77.67; H, 4.79; N, 16.54.

Synthesis of (*E*)-3-(3-Phenyl-2*H*-azirin-2-yl)acrylophenone. A solution containing 1.01 g of 3-phenyl-2-formyl-2*H*-azirine (**1**) and 2.66 g of benzoylmethylenetriphenylphosphorane[37] in 75 ml of benzene was heated at 50° under a nitrogen atmosphere for 12 hr. The benzene was removed under reduced pressure to afford a yellow oil which was purified by filtration through a Florisil column with a 10% ethyl acetate–benzene mixture. Subsequent crystallization of the oil from ether gave azirine **9** as a white crystalline solid: mp 113–114°; ir (KBr) 5.72, 6.05, and 6.28 μ; uv (95% ethanol) 273 and 350 nm (ϵ 18,900 and 8900); NMR ($CDCl_3$, 100 MHz) τ 7.00 (1 H, d, J = 8.0 Hz), 3.16 (1 H, dd, J = 16.0 and 8.0 Hz), 2.88 (1 H, d, J = 16.0 Hz), and aromatic multiplets centered at τ 2.50 and 2.10.

Anal. Calcd for $C_{15}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.52; H, 5.41; N, 5.63.

Thermolysis and Photolysis of (*E*)-3-(3-Phenyl-2*H*-azirin-2-yl)-acrylophenone (9). A solution containing 0.120 g of 3-(3-phenyl-2*H*-azirin-2-yl)acrylophenone (**9**) in 50 ml of toluene was heated at reflux for 3 hr. Removal of the solvent and recrystallization of the residue from 95% ethanol gave 0.108 g (90%) of 2-phenyl-5-benzoylpyrrole (**17**). The structural assignment is in complete accord with the data outlined below: mp 164–166°; ir (KBr) 3.08 and 6.21 μ; uv (95% ethanol) 255 and 350 nm (ϵ 11,900 and 31,800); NMR ($CDCl_3$, 100 MHz) τ 3.40 (1 H, d, J = 5.0 Hz after D_2O exchange), 3.00 (1 H, d, J = 5.0 Hz), and 2.80–2.00 (10 H, m); *m/e* 246 (base), 170, 115, and 77.

Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.56; H, 5.41; N, 5.61.

A solution containing 0.50 g of (*E*)-3-(3-phenyl-2*H*-azirin-2-yl)acrylophenone (**9**) in 500 ml of benzene was irradiated through a Corex filter for 1.5 hr. Removal of the solvent afforded a dark oil. The crude NMR spectrum showed the presence of 2-phenyl-3-benzoylpyrrole (**13**) (ca. 50%) as judged by absorptions at τ 3.56 (1 H) and 3.48 (1 H). All attempts to obtain a pure sample of pyrrole **13** failed.

Synthesis of (*E*)-3-(3-Phenyl-2*H*-azirin-2-yl)acrolein (10). A solution containing 1.31 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 3.40 g of formylmethyltriphenylphosphorane[38] in 100 ml of benzene was heated at 40° for 96 hr under a nitrogen atmosphere. Removal of the solvent under reduced pressure left a dark oil. This material was taken up in 20 ml of ether, and the resulting mixture was filtered to remove the triphenylphosphine oxide which had precipitated. The ethereal solution was concentrated, and the crude residue was chromatographed through a Florosil column using 10% ethyl acetate–benzene as the eluent. The yellow oil obtained was distilled at 35° (0.005 mm) to give 0.8 g (60%) of (*E*)-3-(3-phenyl-2*H*-azirin-2-yl)acrolein (**10**) as a clear oil: ir (KBr) 5.67, 5.94, and 6.14 μ; uv (95% ethanol) 256 nm (ϵ 42,800) and 249 (42,500); NMR ($CDCl_3$, 100 MHz) τ 0.50 (1 H, d, J = 7.0 Hz), 1.94–2.68 (5 H, m), 3.38–3.86 (2 H, m), and 7.01 (1 H, d, J = 8.0 Hz).

Thermolysis and Photolysis of (*E*)-3-(3-Phenyl-2*H*-azirin-2-yl)-acrolein. A solution containing 100 mg of azirine **10** in 50 ml of toluene was heated at reflux for 5 hr. Removal of the solvent under reduced pressure gave a yellow oil which solidified on standing. This material was sublimed at 60° (0.05 mm) to give 92 mg (92%) of 2-phenyl-5-formylpyrrole (**18**) as a pale-yellow solid: mp 137–138°; ir (KBr) 6.06, 6.61 μ; uv (95% ethanol) 318 nm (ϵ 29,000); *m/e* 171 (base), 170, 116; NMR ($CDCl_3$, 100 MHz) τ −0.8 to 0.2 (1 H, m), 0.40 (1 H, s), 2.02–2.70 (5 H, m), 2.90 (1 H, m), and 3.30 (1 H, m).

Anal. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.32; N, 8.25.

A solution containing 80 mg of the above azirine (**10**) in 100 ml of hexane was irradiated at 2537 Å for 40 min. The solution was concentrated and the brown solid that formed was collected and recrystallized from benzene–hexane to give 70 mg of 2-phenyl-3-formylpyrrole (**14**): mp 171–173°; ir (KBr) 3.16 and 6.13 μ; NMR ($CDCl_3$, 100 MHz) τ 0.08 (1 H, s), 2.18–2.76 (5 H, m), 3.02 (1 H, m), 3.32 (1 H, m), and 7.18 (1 H, NH); *m/e* 171, 170 (base), and 115.

Synthesis of (*E*)- and (*Z*)-3-Phenyl-2-styryl-2*H*-azirine (25 and 26). To a slurry of 4.33 g of triphenylbenzylphosphonium bromide[39] in 200 ml of anhydrous ether was added 4.1 ml of a 2.4 *M* phenyllithium solution at room temperature under a nitrogen atmosphere. The orange solution obtained was allowed to stir at 25° for 15 min prior to the addition of 1.45 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) in 50 ml of ether. The mixture was allowed to stir for an additional hour and then filtered to remove the triphenylphosphine oxide. Concentration of the filtrate afforded 1.70 g (78%) of a mixture of (*E*)- and (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25** and **26**) as a light-yellow oil. The NMR spectrum of the crude reaction mixture revealed a (*Z*)/(*E*) azirine ratio of 1.5/1. The *Z* isomer was obtained in pure form by allowing the mixture to stand in the cold for several days. The solid obtained was sublimed at 40° (0.05 mm) and recrystallized from hexane to give (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**25**) (60%): mp 56–58°; ir (KBr) 5.75 μ; uv (95% ethanol) 258 nm (ϵ 14,100); NMR ($CDCl_3$, 100 MHz) τ 6.80 (1 H, d, J = 10.0 Hz), 4.94 (1 H, dd, J = 10.0 and 11.0 Hz), 3.50 (1 H, d, J = 11.0 Hz), and 3.00–2.10 (10 H, m).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.58; H, 6.02; N, 6.40.

The above filtrate was a light-yellow oil enriched in the (*E*)-azirine. Its NMR spectrum ($CDCl_3$, 100 MHz) had signals attributable to the *E* isomer **26** at τ 7.24 (1 H, d, J = 7.0 Hz), 4.00 (1 H, dd, J = 18.0 and 7.0 Hz), and 3.28 (1 H, d, J = 18.0 Hz). All attempts to obtain a pure sample of the *E* isomer **26** were unsuccessful.

Irradiation of (*E*)- and (*Z*)-3-Phenyl-2-styryl-2*H*-azirine (25 and 26). A solution containing a mixture of (*Z*)- and (*E*)-styrylazirine (**25** and **26**) (4:1) (0.50 g) in 500 ml of benzene was irradiated through a Corex filter sleeve for 2 hr. The solvent was evaporated under reduced pressure, and the residual oil was analyzed by VPC using a 5 ft × 0.25 in. column of 5% SE-30 on Chromosorb P at 5°. The GLC trace showed the presence of one major component. Molecular distillation of the crude reaction mixture at 150° (0.001 mm) gave a colorless viscous oil (0.40 g) (80%) whose structure was assigned as 1-phenyl-3*H*-2-benzazepine (**27**) on the basis of the following data: ir (neat) 6.20 μ; uv (95% ethanol) 228 nm (ϵ 17,500); NMR ($CDCl_3$, 100 MHz) τ 6.20 (2 H, d, J = 7.0 Hz), 3.60 (1 H, dt, J = 10.0 and 7.0 Hz), 3.10 (1 H, d, J = 10.0 Hz), and 2.80–2.40 (9 H, m); *m/e* 219 (parent).

A picrate derivative was prepared and recrystallized from 95% ethanol to give an analytical sample, mp 208–211°.

Anal. Calcd for $C_{22}H_{15}N_4O_7$: C, 58.93; H, 3.60; N, 12.50. Found: C, 58.84; H, 3.79; N, 12.53.

The structure of 1-phenyl-3*H*-2-benzazepine was further established by heating it in the presence of dimethyl acetylenedicarboxylate. A solution containing 0.438 g of 1-phenyl-3*H*-2-benzazepine (**27**) and 0.284 g of dimethyl acetylenedicarboxylate in 50 ml of benzene was heated at reflux for 2 hr. The solvent was removed under reduced pressure to afford a dark oil which was recrystallized from 95% ethanol to give 0.15 g (24%) of a crystalline solid whose structure is assigned as dimethyl (1-phenyl-5*H*-2-benzazepin-5-yl)maleate (**28**) on the basis of the following data: mp 171–172°; ir (KBr) 5.70, 5.88, and 6.22 μ; uv (95% ethanol) 258, 292, and 312 nm (ϵ 23,800, 22,000, and 18,000); NMR ($CDCl_3$, 100 MHz) τ 6.94 (3 H, s), 6.36 (3 H, s), 6.08 (1 H, d, J = 4.0 Hz), 4.20 (1 H, s), 4.10 (1 H, dd, J = 10.0 and 4.0 Hz), 3.40 (1 H, d, J = 10.0 Hz), and 3.10–2.40 (9 H, m); *m/e* 361, 302, 270, 269, 244, 243 (base), 242, 241, 240, 215, 204, 203, and 202.

Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.11; H, 5.30; N, 3.88. Found: C, 72.87; H, 5.29; N, 3.93.

Further proof for the structure of **27** was obtained by sodium borohydride reduction. A solution containing 0.80 g of 1-phenyl-3*H*-2-benzazepine (**27**) in 50 ml of absolute methanol was treated with a slight excess (10%) of sodium borohydride. The mixture was allowed to stir for an additional hour at room temperature, and then the solvent was removed under reduced pressure. The residual oil was dissolved in ether, and the ethereal solution was washed several times with water and then dried over magnesium sulfate. Concentration of the ethereal solution under reduced pressure gave 0.79 g (100%) of a viscous oil whose structure was assigned as 2,3-dihydro-1-phenyl-1*H*-2-benzazepine (**29**) on the basis of its spectral properties: ir (neat) 2.95 μ; uv (95% ethanol) 258 nm (ϵ 9400); NMR ($CDCl_3$, 100 MHz) τ 6.50 (2 H, m), 4.92 (1 H, s), 4.24 (1 H, dt, J = 12.0 and 3.0 Hz), 3.60 (1 H, dt, J = 12.0 and 1.0 Hz), and 3.40–2.70 (9 H, m); *m/e* 221, 220, 219, 218, 193, 192, 191,

178, 144 (base), 117, 116, 115, 91, and 77.

A picrate derivative was prepared and recrystallized from 95% ethanol to afford an analytical sample, mp 215–218°.

Anal. Calcd for $C_{22}H_{17}N_4O_7$: C, 58.66; H, 4.03; N, 12.44. Found: C, 58.43; H, 4.11; N, 12.58.

The minor component isolated from the irradiation of 3-phenyl-2-styryl-2*H*-azirine was assigned the structure of 2,3-diphenylpyrrole (**31**) on the basis of its characteristic NMR absorptions at τ 3.64 (1 H, d, J = 4.0 Hz) and 3.28 (1 H, d, J = 4.0 Hz). The amount of this pyrrole increased as the concentration of the (*E*)-styrylazirine was increased in the starting material. Irradiation of a pure sample of (*Z*)-azirine **25** gave benzazepine **27** with only small quantities of 2,3-diphenylpyrrole (**31**) (4%).

The photolysis took a different course when methanol was used as a solvent. A solution containing 0.30 g of (*Z*)-azirine in 250 ml of absolute methanol was irradiated through a Corex filter sleeve for 1 hr. Removal of the solvent under reduced pressure afforded a light-yellow oil. NMR analysis of the crude oil revealed the presence of two components in the ratio of 9:1. The minor product (10%) was identified as 1-phenyl-3*H*-2-benzazepine (**27**) on the basis of absorptions at τ 6.20, 3.60, and 3.10 in the NMR, while the major product (90%) exhibited signals at τ 6.50, 4.40, 2.90, 2.40, and 1.40. The ir spectrum (neat) showed an intense absorption at 6.12 μ characteristic of a carbon–nitrogen double bond chromophore. This structure was assigned as *N*-(methoxystyrylmethyl)benzalimine (**30**) on the basis of the above data and on its behavior on acid-catalyzed hydrolysis. Treatment of **30** in aqueous dioxane with a small amount (2 drops) of concentrated hydrochloric acid afforded a mixture of benzaldehyde and cinnamaldehyde as judged by ir and NMR comparison with authentic samples. All attempts to purify benzalimine **30** were unsuccessful as this material is extremely acid labile and underwent extensive hydrolysis on attempted purification.

Thermolysis of (*E*)- and (*Z*)-3-Phenyl-2-styryl-2*H*-azirine. A solution containing 0.5 g of (*E*)- and (*Z*)-3-phenyl-2-styryl-2*H*-azirine in 75 ml of benzene was heated at reflux for 12 hr. Removal of the solvent under reduced pressure left a semisolid which was recrystallized from hexane to give 0.4 g (80%) of 2,5-diphenylpyrrole (**32**): mp 142–143°; ir (KBr) 2.89, 6.20 μ; NMR ($CDCl_3$, 100 MHz) τ 3.40 (1 H, m), and 2.83–2.10 (11 H, m). This material was unambiguously established by comparison with an authentic sample.[40] A mixture melting point was undepressed at 142–143°.

Synthesis of (*E*)- and (*Z*)-2-[2-(β-Naphthyl)vinyl]-3-phenyl-2*H*-azirine (33). To a slurry of 11.1 g of triphenyl-2-naphthylmethylphosphonium bromide[41] in 100 ml of ether was added 10.0 ml of a 2.3 *M* phenyllithium solution at room temperature under a nitrogen blanket. The dark-red solution that formed was allowed to stir at 25° for an additional 15 min prior to the addition of 2.80 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) in 50 ml of ether. The mixture was allowed to stir for an additional 30 min and was subsequently filtered to remove triphenylphosphine oxide. Concentration of the filtrate under reduced pressure afforded 4.99 g (92%) of a mixture of (*E*)- and (*Z*)-2-[2-(naphthyl)vinyl]-3-phenyl-2*H*-azirine (**33**) as a light-yellow solid, mp 50–80°. The NMR spectrum of the crude mixture revealed a (*Z*)/(*E*) azirine ratio of 1.5/1. All attempts to separate the mixture into its separate components failed; consequently, the mixture was analyzed without separation: ir (KBr) 5.75 and 5.88 μ; uv (95% ethanol) 258, 290, and 300 nm (ϵ 36,000, 13,200, and 11,700); NMR ($CDCl_3$, 100 MHz) τ 6.92 (1 H, d, J = 8.0 Hz), 6.50 (1 H, d, J = 9.0 Hz), 4.60 (1 H, dd, J_Z = 12.0 and 8.0 Hz), 3.72 (1 H, dd, J_E = 16.0 and 9.0 Hz), 3.04 (1 H, d, J_Z = 12.0 Hz), 2.92 (1 H, d, J_E = 16.0 Hz), and 1.70–2.48 (12 H, m).

Irradiation of (*E*)- and (*Z*)-2-[2-β-Naphthyl)vinyl]-3-phenyl-2*H*-azirine (33). A solution containing 0.50 g of (*E*)- and (*Z*)-azirine (**33**) in 500 ml of benzene was irradiated through a Corex filter sleeve for 1 hr. The solvent was removed under reduced pressure to afford a dark oil. Purification of the crude oil was accomplished by the formation of a picrate derivative, mp 198–200°. Decomposition of the picrate in an aqueous sodium hydroxide solution at 50° for 2 hr gave a solid (85%) whose structure was assigned as 1-phenyl-3*H*-naphth[1,2-*c*]azepine (**34**) on the basis of the following data: mp 148–149°; ir (KBr) 6.24 μ; uv (95% ethanol) 224, 238, and 255 nm (ϵ 32,000, 35,900, and 31,800); NMR ($CDCl_3$, 100 MHz) τ 7.20 (1 H, ddd, J = 18.0, 6.0, and 2.0 Hz), 5.76 (1 H, dd, J = 18.0 and 6.0 Hz), 3.92 (1 H, dt, $J \approx$ 10.0 and 6.0 Hz), 3.48 (1 H, d, J = 10.0 Hz), and 2.60–3.40 (11 H, m); *m/e* 269 (base).

Anal. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.86; H, 5.61; N, 5.19.

Thermolysis of 2-[2-(β-Naphthyl)vinyl]-3-phenyl-2*H*-azirine. A solution containing 0.50 g of a mixture of (*E*)- and (*Z*)-azirines (**33**) in 100 ml of toluene was refluxed for 1 hr. Removal of the solvent under reduced pressure gave 0.45 g (90%) of 2-phenyl-5-(2-naphthyl)pyrrole (**37**) as a crystalline solid: mp 162–164°; ir (KBr) 2.90 μ; uv (95% ethanol) 220, 279, 290, and 339 nm (ϵ 27,400, 14,400, 17,100, and 31,500); NMR (Me_2SO-d_6, 100 MHz) τ 3.28 (1 H, d, J = 3.0 Hz after D_2O exchange), 3.20 (1 H, d, J = 3.0 Hz), 3.00–2.00 (12 H, m), and 1.60 (1 H, broad s); *m/e* 269 (base), 165, and 115.

Anal. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.86; H, 5.65; N, 5.20.

Synthesis of (*E*)- and (*Z*)-2-[2-(1-Naphthyl)vinyl]-3-phenyl-2*H*-azirine (35). To a slurry of 11.1 g of triphenyl-1-naphthylmethylphosphonium bromide in 100 ml of ether was added 10.0 ml of a 2.3 *M* phenyllithium solution at room temperature under a nitrogen atmosphere. The dark-red solution that formed was allowed to stir at 25° for an additional 15 min prior to the addition of 2.8 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) in 50 ml of ether. The mixture was allowed to stir for an additional 30 min and was subsequently filtered to remove triphenylphosphine oxide. Concentration of the filtrate under reduced pressure gave 4.20 g (79%) of a mixture of (*E*)- and (*Z*)-2-[2-(1-naphthyl)vinyl]-3-phenyl-2*H*-azirine (**35**) as a light-yellow solid, mp 102–108°. The NMR spectrum of the crude mixture revealed a (*Z*)/(*E*) azirine ratio of 3/1. All attempts to separate the mixture into its separate components failed; consequently, the mixture was analyzed without separation: ir (KBr) 5.72 μ; uv (95% ethanol) 225, 237, 250, and 295 nm (ϵ 28,300, 19,800, 15,700, and 7100); NMR ($CDCl_3$, 100 MHz) τ 7.16 (1 H, d, J = 9.0 Hz), 7.12 (1 H, d, J = 8.0 Hz), 4.88 (1 H, dd, J_Z = 11.0, and J = 9.0 Hz), 4.36 (1 H, dd, J_E = 16.0, and J = 8.0 Hz), 3.32 (1 H, d, J_Z = 11.0 Hz), and 2.20–3.00 (12 H, m).

Irradiation of (*E*)- and (*Z*)-2-[2-(1-Naphthyl)vinyl]-3-phenyl-2*H*-azirine (35). A solution containing 0.60 g of (*E*)- and (*Z*)-azirine (**35**) in 500 ml of benzene was irradiated for 1.5 hr through a Corex filter. The solvent was removed under reduced pressure to afford a dark oil. Purification of the crude oil was accomplished by the formation of a picrate derivative, mp 240–242°. Decomposition of the picrate in an aqueous sodium hydroxide solution at 50° for 2 hr gave a solid (80%) whose structure is assigned as 1-phenyl-3*H*-naphth[2,3-*c*]azepine (**36**) on the basis of the data presented below: mp 113–114.5°; ir (KBr) 6.30 μ; uv (95% ethanol) 240, 250, 290, and 305 nm (ϵ 45,000, 38,200, 7100, and 4900); NMR ($CDCl_3$, 100 MHz) τ 5.50–7.00 (2 H, broad m), 3.80 (1 H, dt, J = 10.0 and 6.0 Hz), and 2.00–3.00 (12 H, m); *m/e* 269 (base).

Anal. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.88; H, 5.69; N, 5.24.

Since the NMR spectrum of compound **36** was indicative of a coalescence point at room temperature, the spectrum of **36** was redetermined at both high and low temperature. The NMR spectrum (benzonitrile, 100 MHz) of **36** at 115° showed a doublet with J = 8.0 Hz while, upon cooling a sample of **36** in hexadeuterioacetone to −30°, two distinct multiplets for the methylene protons were apparent at τ 7.20 (1 H, ddd, J = 18.0, 6.0, and 2.0 Hz) and 5.76 (1 H, dd, J = 18.0 and 6.0 Hz).

Thermolysis of 2-[2-(1-Naphthyl)vinyl]-3-phenyl-2*H*-azirine (35). A solution containing 0.50 g of a mixture of (*E*)- and (*Z*)-azirines (**35**) in 100 ml of toluene was heated at reflux for 1 hr. Removal of the solvent under reduced pressure gave 0.50 g (100%) of 2-phenyl-5-(1-naphthyl)pyrrole (**38**) as a yellow oil. All attempts to obtain an analytically pure sample of pyrrole **38** failed; consequently, it was characterized without further purification. The ir spectrum (neat film) showed a band at 2.90 μ (NH). The NMR spectrum ($CDCl_3$, 100 MHz) exhibited signals at τ 3.60 (1 H, J = 3.0 Hz) and 3.46 (1 H, J = 3.0 Hz), and the aromatic protons and pyrrole hydrogen from τ 3.00 to 1.76 (13 H, m).

Quantum Yield Measurements. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 0.528 g of potassium chromate and 10.0 g of potassium carbonate in 1000 ml of

distilled water.[42] All studies were made at room temperature. Samples were degassed to 5×10^{-3} mm in three freeze-thaw cycles and then sealed. Benzophenone-benzhydrol solutions were used as the chemical actinometer.[28] After the irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions in the azirine series were run to 10% or less. The mass balance in these runs was generally better than 95%. Solutions of the azirine in benzene containing excess piperylene as a standard triplet quencher were irradiated under conditions where more than 98% of the light was absorbed by the azirine. The reaction was monitored by GLC and in no case was the amount of product formed affected by the piperylene. The quencher was present in concentrations sufficiently high to suppress established triplet processes.[27] Sensitization experiments utilized benzophenone as a standard triplet sensitizer. The concentrations were adjusted so that benzophenone absorbed greater than 98% of the light. The reaction was monitored by GLC and, under the conditions employed, no photoreaction occurred.

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 rotating assembly at room temperature using an internal water-cooled mercury arc lamp (450 W). The 3130-Å line was isolated by circulation of a potassium chromate-carbonate solution. 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. 40% of starting material had been consumed.

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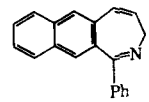

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be more or less equivalent and give rise to a simple doublet for these protons as was observed with benzazepine **27**. Also, cyclization of the nitrile ylide generated from **33** is more likely to occur through attack at the α-position of the naphthalene ring than the β-position since this would result in less disruption of aromaticity.
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(29) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer and at 100 MHz using a Joel-MH-100 spectrometer.
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