Carbenic Reactions of Nitrile Ylides. An Example of a Stepwise 1,3-Dipolar Cycloaddition[1]

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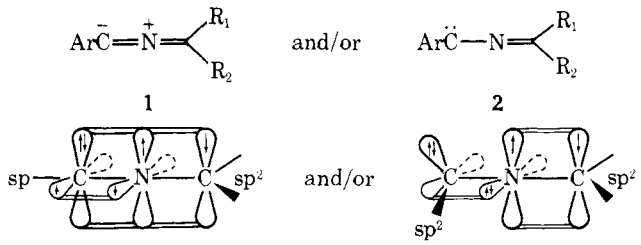
Abstract: The intramolecular photocycloaddition reaction of a number of 3-phenyl-2-methyl-2-allyl substituted 2*H*-azirines has been examined in mechanistic detail. Upon irradiation with ultraviolet light, these systems undergo rearrangement to azabicyclo[3.1.0]hex-2-enes via transient nitrile ylides. These reactive 1,3-dipoles can be intercepted with added dipolarophiles to give five-membered heterocyclic rings. Irradiation of the isomeric 3-methyl-2-phenyl-2-allyl-2*H*-azirine system gave similar results. Inspection of molecular models of these 2-allyl substituted nitrile ylides indicates that the normal "two-plane orientation approach" is impossible as a result of the geometric restrictions imposed on the system. With these nitrile ylides, attack by the alkene is constrained to occur perpendicular to the CNC plane of a bent nitrile ylide. The second LUMO, which is perpendicular to the CNC plane, is low lying and presents a large vacancy at C-1 for attack by the more nucleophilic terminus of the alkene, without the possibility of simultaneous bonding at the C-3 carbon atom. Attack by the carbene carbon on the terminal position of the neighboring double bond generates a trimethylene derivative which subsequently collapses to a mixture of azabicyclohexenes. This cycloaddition sequence proceeds in a nonconcerted manner and bears a strong resemblance to the stepwise diradical mechanism suggested by Firestone to account for bimolecular 1,3-dipolar cycloadditions.

Huisgen, in 1958, was the first to recognize fully the general concept and scope of 1,3-dipolar cycloadditions and since that time, largely due to his efforts, it has become a most valuable method for the synthesis of a great variety of five-ring heterocycles.[2-4] 1,3-Dipolar cycloadditions are generally bimolecular in nature and involve the addition of a 1,3-dipole to a multiple bond system. The independence of solvent polarity, the very negative entropies of activation,[6] and the high stereospecificity and regiospecificity[7] point to a highly ordered transition state. The mechanism that has emerged from Huisgen's group is that of a single-step, four-center, "no-mechanism" cycloaddition, in which the two new bonds are both partially formed in the transition state, although not necessarily to the same extent.[7] The concerted mechanism is an orbital symmetry-allowed [$\pi_4 s + \pi_2 s$] cycloaddition wherein the 1,3-dipole with its allyl anion type MO functions as a 4π reactant and the dipolarophile as a 2π reactant.[8] The concerted mechanism of 1,3-dipolar cycloadditions was recently challenged by Firestone,[9] who proposed an alternative two-step process involving a spin-paired diradical intermediate. Firestone's arguments, however, were rebutted by Huisgen who concluded that the available evidence is only compatible with a concerted process.[7]

All 1,3-dipoles have in common a three atomic orbital π system containing four electrons analogous to an allyl anion. An element of variation of 1,3-dipoles is provided by the incorporation of an additional π bond in the plane perpendicular to the allyl anion MO. These 1,3-dipoles always contain nitrogen as the middle atom, since only this element can supply an unshared electron pair while in the trivalent neutral state. Systematic variation of the elements, carbon, oxygen, and nitrogen, leads to six "1,3-dipoles with double bond", which fall into two groups, nitrilium and diazonium betaines.[2] The most extensively studied member of the nitrilium betaine class of 1,3-dipoles are the nitrile ylides. Access to this group of dipoles can be realized by (a) treatment of imidoyl halides with base,[10] (b) thermal or photochemical elimination of phosphoric acid ester from 4,5-dihydro-1,3,5-oxazaphospholes,[11] and (c) photolysis of 2*H*-azirines.[12,13] The greatest opportunity for structural variation is offered by the latter route.

Among the possible geometric forms of a nitrile ylide, a carbene structure (**2**) can be envisaged which makes conceivable a 1,1-cycloaddition of this 1,3-dipole. Huisgen has argued[3] that the bent geometric form of a nitrile ylide would be less stable than the linear form (**1**), since allyl resonance would be



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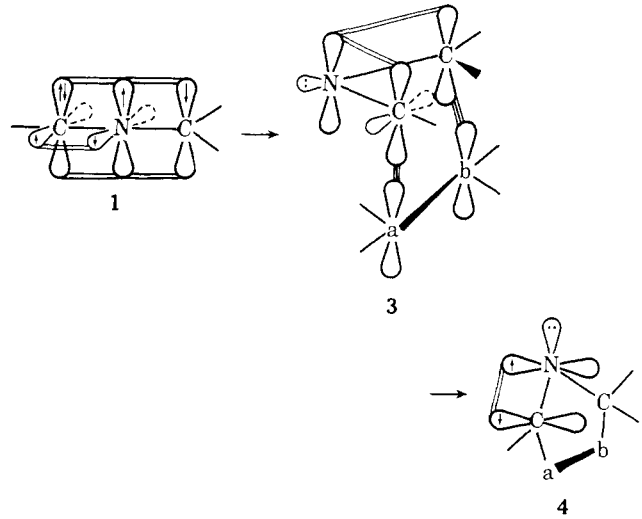
at a maximum with the linear arrangement. The bent form would have a lone pair of electrons in an orbital with some s character, but this was postulated to be of lesser importance. The extensive literature dealing with nitrile ylide cycloadditions has generally been explained in terms of the linear arrangement of this 1,3-dipole. Thus, dipolar cycloadditions of nitrile ylides have been suggested to proceed via a "two-plane" orientation complex in which the dipole and dipolarophile approach each other in parallel planes.[2] Formula **3** depicts the orientation



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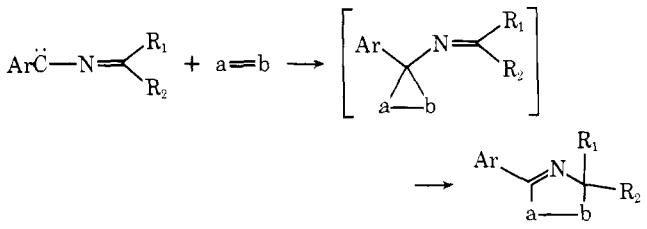
complex involved in the addition of the linear nitrile ylide (**1**) with a dipolarophile. During the activation process, the linear bond system of the nitrile ylide must bend. This involves disruption of the orthogonal π bond at some modest energy cost but leaves the allyl anion π system undisturbed. The loss of π bond energy with **1** is partly compensated by a gain in energy resulting from rehybridization and accomodation of a lone pair of electrons in an orbital of high s character.

Another mechanism which could also account for the products obtained on dipolar cycloaddition of nitrile ylides with π bonds involves an initial 1,1 addition of the supposedly higher



energy bent nitrile ylide (carbene form) with the dipolarophile to give a transient three-membered ring. This would be followed by a rapid intramolecular rearrangement to the five-membered heterocycle. This alternate possibility was discounted by Huisgen, however, who showed that three-membered rings are not primary products in the 1,3-dipolar additions leading to five-membered heterocycles with both nitrilium and diazonium betaines.[14]

Previous papers from this laboratory have established that 2*H*-azirines undergo irreversible opening on electronic excitation to give nitrile ylides.[12] The initially generated 1,3-dipoles were intercepted with a variety of dipolarophiles to form five-membered rings.[12,13] More recently, we have found that nitrile ylides undergo ready intramolecular cycloadditions, the reactions providing clean transformations for the synthesis of five-membered nitrogen containing heterocycles.[15] In order to probe the generality of the intramolecular dipolar cycloaddition of nitrile ylides,[16] we chose to investigate the photochemistry of a series of 2-allyl substituted 2*H*-azirines.[17] Our initial observations indicated that this system differed dramatically from heretofore observed azirine photochemistry, in that the photochemically generated nitrile ylide was found to undergo a 1,1-cycloaddition with the neighboring double bond. The present publication describes our preliminary findings in detail and delineates the significant role played by a bent nitrile ylide intermediate (carbene-form **2**) in the overall cycloaddition process. Our results also provide the first example of a dipolar cycloaddition which occurs by a process which bears a more than superficial resemblance to Firestone's two-step mechanism.

Results

Synthesis of 2-Allyl Substituted 2*H*-Azirines. As a continuation of our studies dealing with intramolecular dipolar cycloadditions of nitrile ylides, we became interested in examining the photochemistry of a series of 2-allyl substituted 2*H*-azirines. These compounds were prepared by a modified Neber reaction in which variously substituted 2-methyl-1-phenyl-4-penten-1-ones were allowed to react with dimethylhydrazine according to the general procedure of Leonard and Zwanenburg.[18] Treatment of the appropriate dimethylhydrazone with methyl iodide followed by reaction with base gave the desired 2-allyl substituted 2*H*-azirines in good yield. The synthesis is outlined in Chart I.

Isolation and Identification of Photoproducts. We initially examined the photochemistry of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**5**) (Chart II). When a thoroughly deaerated solution of **5** was irradiated in cyclohexane with light of wavelength >250 nm for 15 min, an extremely rapid and clean conversion to 1-phenyl-3-methyl-2-azabicyclo[3.1.0]hex-2-ene (**6**) was observed. When the irradiation of **5** was carried out to 20% conversion, however, a 1:1 mixture of **6** and 1-methyl-3-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**7**) was produced. On further irradiation, **7** was quantitatively isomerized to **6**. We also examined the photochemical behavior of the isomeric 2-allyl-2-phenyl-3-methyl-2*H*-azirine (**8**) system.[19] Irradiation of **8** in cyclohexane afforded a quantitative yield of azabicyclohexene **6**. Photolysis of **8** in the presence of the very reactive dipolarophile, methyl trifluoroacetate,[20] resulted in the trapping of a nitrile ylide and gave cycloadduct **9** in high yield. Under these conditions, the formation of **6**, which is produced in quantitative yield in the absence of a trapping agent, is entirely suppressed. Photocycloaddition of **5** with added methyl trifluoroacetate resulted in the formation of cycloadduct **10** in high yield. The isolation of **9** in the external trapping experiment eliminates a path by which **8** is partially isomerized to **5** which then rapidly rearranges to **6** on further excitation. This possibility was initially considered to be a reasonable one since the extinction coefficient of **5** at 254 nm (ϵ 8700) is much larger than that of **8** (ϵ 220). It should be noted that no significant quantities of **7** were detected in a short term irradiation of **8**. This is probably related to the fact that **7** possesses a much larger extinction coefficient than **8** and is optically pumped to **6** even at low conversions.

The identity of azabicyclohexene **6** was determined by its straightforward spectral characteristics [IR (neat) 1640 cm^{-1}; NMR (100 MHz) τ 9.64 (t, 1 H, J = 5.0 Hz), 8.68 (dd, 1 H, J = 8.0 and 5.0 Hz), 8.33 (m, 1 H), 8.13 (s, 3 H), 7.64 (d, 1 H, J = 17.5 Hz), 7.22 (dd, 1 H, J = 17.5 and 8.0 Hz), 2.61-3.10 (m, 5 H)]. Structure **7** could readily be distinguished from **6** by examination of its unique NMR spectrum which showed

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

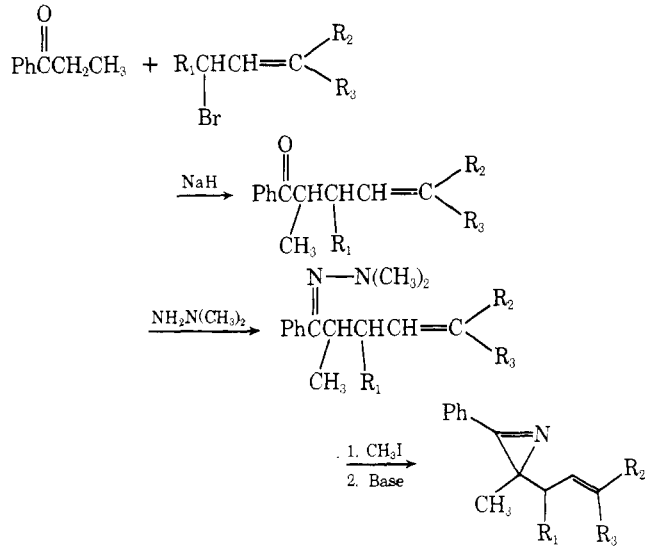
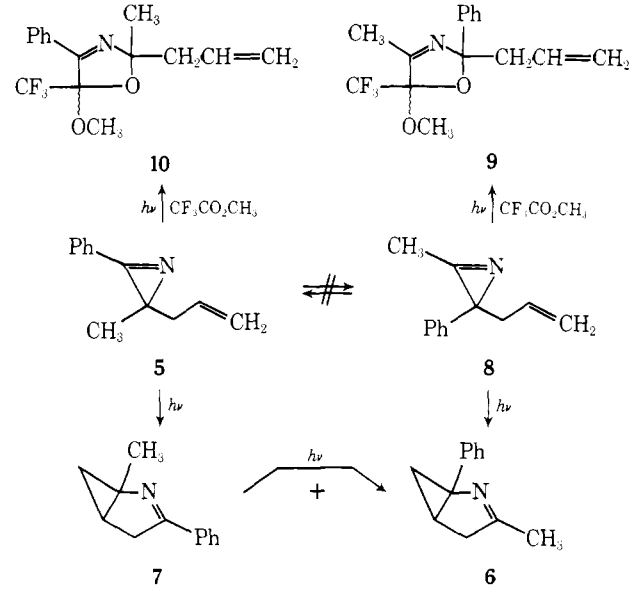


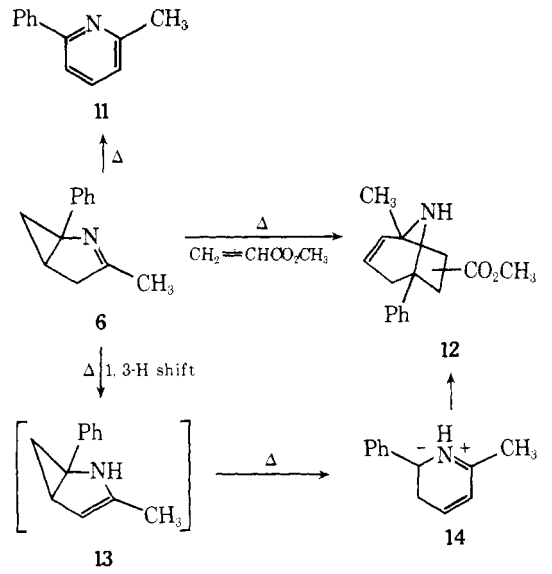
Chart II



a triplet at τ 9.92 (1 H, J = 5.0 Hz), a doublet of doublets at τ 9.10 (1 H, J = 8.0 and 5.0 Hz), a multiplet at 8.20 (1 H), a singlet at 8.38 (3 H), a doublet at 7.60 (1 H, J = 17.5 Hz), a double doublet at 6.78 (1 H, J = 17.5 and 8.0 Hz), and a multiplet at 2.61–3.10 (5 H). In accord with this assignment is the observation that the cyclopropyl protons of **7** appear at a higher chemical shift than those in **6**. Also, the methyl group present in structure **7** (τ 8.38) is located at a higher upfield position than the corresponding methyl group (τ 8.13) of **6**. It was not possible to separate the isomeric azabicyclohexenes (**6** and **7**) since both compounds were readily oxidized on chromatographic separation to the known 2-methyl-6-phenylpyridine (**11**).[21]

Thermolysis of a pure sample of azabicyclohexene **6** in toluene also gave pyridine **11** in quantitative yield (Chart III).

Chart III



When the thermolysis of **6** was carried out in toluene in the presence of methyl acrylate, azabicyclo[3.2.1]octene **12**, mp 87–88 °C, was isolated in good yield. The formation of this adduct is readily interpreted if it is assumed that **6** undergoes an initial 1,3-proton shift to give 1-phenyl-3-methyl-2-azabicyclo[3.1.0]hex-3-ene (**13**) which subsequently undergoes cycloaddition with the added dipolarophile. Tanny and Fowler[22] have recently shown that the 2-azabicyclo[3.1.0]-hex-3-ene ring system will undergo thermal cycloaddition reactions with electron-deficient olefins, thereby providing good analogy for the last step of the proposed sequence. In the absence of an added dipolarophile, the transient 1,3-dipole **14** undergoes a 1,2-proton shift followed by air oxidation to give 2-methyl-6-phenylpyridine (**11**).

The formation of azabicyclohexenes **6** and **7** from the irradiation of azirine **5** clearly proceeds via a nitrile ylide intermediate since the formation of these compounds are entirely suppressed when the irradiation is carried out in the presence of an added dipolarophile (Chart IV). For example, when dimethyl acetylenedicarboxylate is used, cycloadduct **15**, mp 58–60 °C, was the only product isolated. Similar results were obtained when methyl acrylate was employed as the trapping agent.[23] The fact that the photolysis of **5** produces a nitrile ylide intermediate which could be trapped by an added dipolarophile (i.e., as **15** or **16**) eliminates a [2 + 2] cycloaddition of the azirine C=N double bond with the olefin and subsequent rearrangement of a hypothetical azabicyclo[2.1.1.$0^{2,5}$]hexane intermediate (**17**) as the mechanism for the formation of the azabicyclo[3.1.0]hex-2-ene system.

Attention was next turned to the photochemical behavior of the closely related 2-(2-methylallyl)-2*H*-azirines **18** and **19**

Chart IV

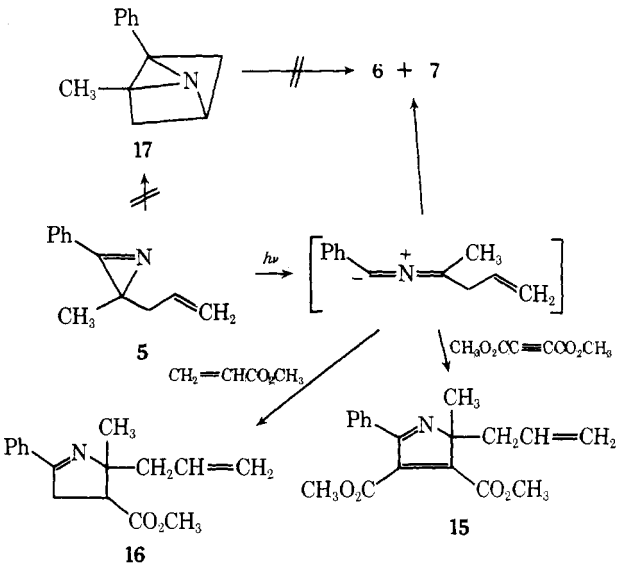
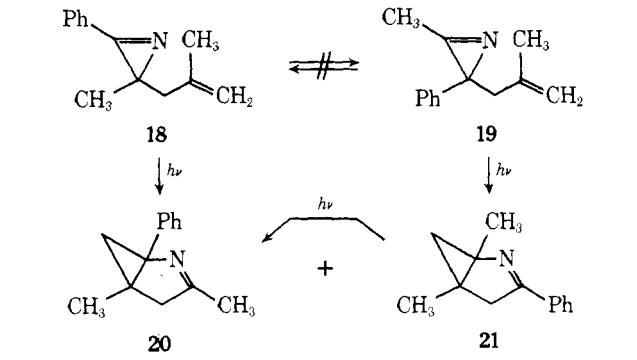


Chart V



(Chart V). Irradiation of **18** in cyclohexane (80% conversion) produced a mixture (2:1) of azabicyclohexenes **20** and **21** in high yield. A short term photolysis (40% conversion) of the isomeric 2-methyl-2*H*-azirine **19** afforded the same two products in a 4:1 ratio. On further irradiation, **21** was converted into **20** in quantitative yield. A control experiment showed that **18** and **19** were not photochemically interconverted. The formation of azabicyclohexenes **20** and **21** was completely suppressed when the irradiation of **18** was carried out in the presence of methyl trifluoroacetate. The only product formed under these conditions was the usual 2,5-dihydro-1,3-oxazine.[20] The analytical and spectral data support the formulation of the photoproducts (i.e., **20** and **21**) as azabicyclo[3.1.0]hex-2-enes. A distinction between the two isomers can be readily made on the basis of the location of the methyl and cyclopropyl hydrogens in the NMR spectrum (see Experimental Section). It is interesting to note that the irradiation of **19** produced a mixture of azabicyclohexenes (**20** and **21**), since the related 2-allyl substituted 2*H*-azirine system **8** gave a single photoproduct. This observation provides support for our contention that the initially formed 3-phenyl-2-azabicyclohexene **7**, is optically pumped to **6**, even at low conversions.

The intramolecular photocycloaddition reaction of the analogous 2-(1-methylallyl)-2*H*-azirine (**22**) system was also studied in order to assess the generality of the cyclization (Chart VI). A long-term irradiation of **22** afforded a quantitative yield of 1-phenyl-3,4-dimethyl-2-azabicyclo[3.1.0]-hex-2-ene (**24**) as a mixture of endo (25%) and exo (75%) isomers. When (*E*)-2-(2-butenyl-2-phenyl-3-methyl-2*H*-azirine (**23**) was irradiated in cyclohexane (100% conversion), a mixture of the endo (25%) and exo (75%) isomers of **24** were the only products formed. This same epimeric mixture of iso-

Chart VI.

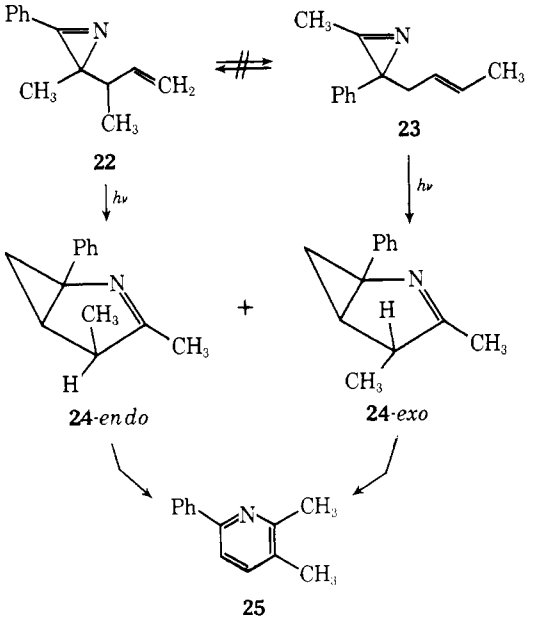
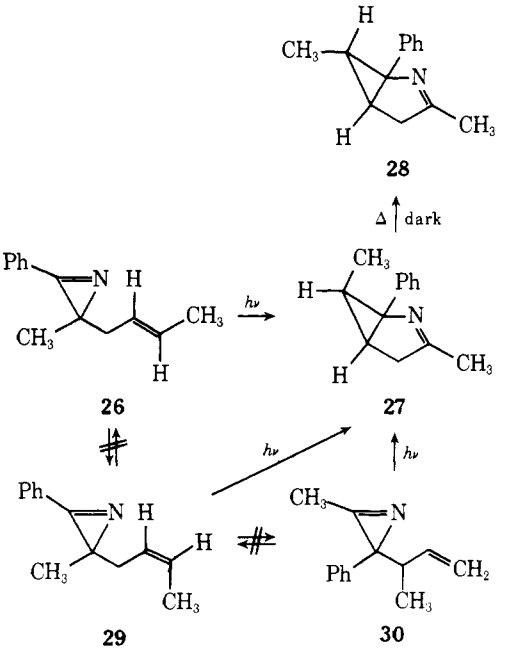


Chart VII.

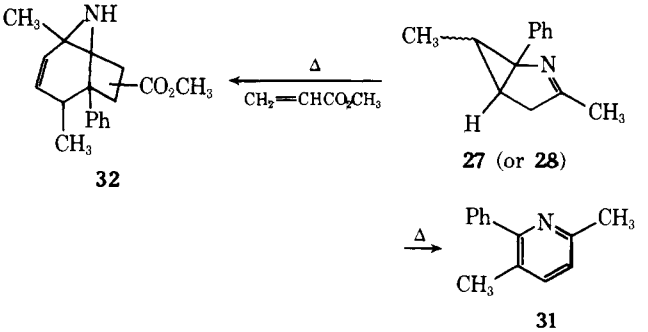


mers was produced from azirine **22.** Both epimers were smoothly converted to 2,3-dimethyl-6-phenylpyridine (**25**) on heating. Structure **25** was verified by comparison with an authentic sample.[24] Again, no photoequilibration of the starting azirines was detected, and the only product formed when methyl acrylate was used as a trapping agent was the usual Δ^1-pyrroline.[12] With these systems, the irradiations were carried out for extended periods of time, and consequently only the 1-phenyl substituted azabicyclohexene was present in the reaction mixture.

The stereochemical assignments of the epimeric azabicyclohexenes were made on the basis of the NMR data (see Experimental Section). The major isomer exhibited a quartet for proton H_4 (J = 8.0 Hz) while the minor isomer exhibited a pentuplet (J = 8.0 Hz) for proton H_4. The absence of coupling between H_4 and H_5 with the major isomer implies trans vicinal coupling and fixes the C(4) methyl group in the exo position. In support of this conclusion is the observation of other workers that the magnitude of trans C(4)–C(5) vicinal coupling of bicyclo[3.1.0]hex-2-enes is close to zero,[25-27] while that for cis vicinal coupling is ca. 8 Hz.[28] This is to be expected since molecular models show that the dihedral angle for the trans C(4)–C(5) protons is about 110°, while that for the cis protons is approximately 0°.

An unusual aspect of the intramolecular photocyclization of allyl substituted 2*H*-azirines was uncovered during our study of the photochemistry of (*E*)-2-(2-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**26**). Irradiation of **26** in cyclohexane gave rise to one major product (>95%) which was assigned as *endo*-3,6-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**27**) on the basis of its spectral properties and chemical behavior (Chart VII). The NMR spectrum of **27** consisted of a methyl doublet at τ 9.24 (J = 6.0 Hz), a one proton doublet of quartets at τ 8.42 (J = 8.0 Hz and 6.0 Hz), a triplet at τ 8.13 (J = 8.0 Hz), a singlet at τ 8.00 (3 H), a doublet at τ 7.80 (1 H, J = 18.0 Hz), a well-defined doublet of doublets at τ 7.26 (1 H, J = 18.0 and 8.0 Hz), and a multiplet for the aromatic protons at τ 2.4–3.0 (5 H). *Most importantly, the magnitude of the cyclopropyl hydrogen coupling (J = 8.0 Hz) indicates a cis relationship of the protons and thus requires that the 6-methyl group in* **27** *be endo.*[29,30] The initial photoproduct slowly epimerized to the thermodynamically more stable exo isomer **28** at room temperature. The NMR of the exo isomer **28** showed a 4.5 Hz trans coupling constant for the cyclopropyl hydrogens after double irradiation. The formation of the thermodynamically less favored endo isomer (i.e., **27**) corresponds to a complete inversion of stereochemistry about the π system in the cycloaddition process. In order to obtain a better understanding of the stereochemical course of the cycloaddition, we investigated the photochemistry of the isomeric (*Z*)-2-(2-butenyl)-2*H*-azirine system **29.** This compound was prepared by the modified Neber route outlined in Chart I. The only product obtained on irradiation of **29,** however, was azabicyclohexene **27.** Photoisomerization about the C–C double bond of starting azirine (**26** or **29**) did not occur during the course of the irradiation. Thus, azabicyclohexene **27** is the exclusive product obtained with both the *E* and *Z* isomers. To further clarify the stereochemical nature of the cycloaddition process, the photochemistry of 2-phenyl-2-(1-methylallyl)-3-methyl-2*H*-azirine (**30**) was studied. Irradiation of **30** in cyclohexane (100% conversion) also gave **27** as the exclusive photoproduct. When the irradiation of these azirines were carried out in the presence of excess methyl acrylate, the usual 1,3-dipolar cycloadducts (i.e., Δ^1-pyrrolines) were obtained. The above irradiations were carried out for extended periods of time in order to avoid dealing with a mixture of 1-methyl- and 1-phenylazabicyclohexenes.

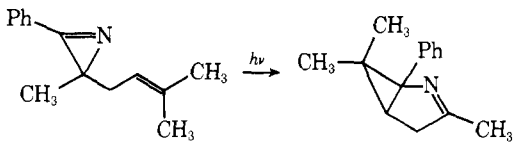
Further verification for the structure of azabicyclohexenes **27** and **28** comes from thermolysis experiments, in which both isomers were converted to 2,5-dimethyl-6-phenylpyridine (**31**) on heating in chloroform. Structure **31** was unequivocably



established by comparison with an authentic sample.[24] Thermolysis of **27** (or **28**) in the presence of methyl acrylate gave azabicyclo[3.2.1]octene **32.** The spectral data for this compound are summarized in the Experimental Section.

One additional system which was studied involved the photochemistry of 2-methyl-2-(3-methyl-2-butenyl)-3-phe-

nyl-2*H*-azirine (**33**). Intramolecular cycloaddition of this material gave 3,6,6-trimethyl-1-phenyl-2-azabicyclo[3.1.0]-hex-2-ene (**34**) in quantitative yield.



33 **34**

Multiplicity Studies. To establish the nature of the reactive state involved in these photocyclization reactions, quenching and sensitization experiments were carried out. Identical 2-allyl 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.[31] Attempts to sensitize the photocyclization reactions were also 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, formation of the usual azabicyclohexenes occurred when 3-phenyl substituted 2*H*-azirines **5, 18, 22,** and **29** were used as substrates. That energy transfer from benzophenone to the azirine ring was occurring was shown by quenching the known triplet reaction of benzophenone with cyclohexanol to form benzpinacol and cyclohexanone.[32] In contrast with the above results, benzophenone failed to sensitize the rearrangement of the isomeric 3-methyl-2*H*-azirine system. These observations suggest that the triplet energy levels of the 3-methyl substituted azirine system are located above 68 kcal/mol while the 3-phenyl substituted azirines have triplet levels low enough to quench benzophenone's triplet. In a further attempt to document the multiplicity of the reactive state produced on direct irradiation, solutions of azirine, methyl acrylate, and benzophenone were irradiated with 3130 Å light. The concentration of benzophenone was such that it absorbed over 96% of the light. The triplet state of the azirine gave no bimolecular cycloadduct. This stands in marked contrast to the results obtained on direct irradiation where smooth bimolecular cycloaddition occurred. The failure of benzophenone to sensitize bimolecular cycloaddition and the inability of piperylene or 1,3-cyclohexadiene to quench the unimolecular rearrangements suggest that the primary photochemistry of the 2-allyl substituted 2*H*-azirine system proceeds from the excited singlet manifold. The photochemical cyclization reactions were reasonably efficient, with quantum yield values close to 0.3.

Discussion

There exists a large body of compelling experimental evidence in the literature which indicates that the cycloaddition of 1,3-dipoles to alkenes are concerted processes.[7] Orbital symmetry considerations have provided additional theoretical support for the concerted mechanism.[33-37] Huisgen's contention[3] that all 1,3-dipolar cycloadditions involve the "parallel-planes approach of addends" still remains the most logical view, since cyclic 1,3-dipoles such as sydnones behave normally in 1,3-dipolar cycloadditions. Thus far, the workers in this field have examined the requirements for 1,3-dipolar cycloadditions strictly from an orbital symmetry standpoint and have neglected any possible spatial factors. Obviously the primary spatial requirement for concerted addition is that the distance between the two reacting centers should be short enough so that effective three-center overlap of the 1,3-dipole with the carbon atoms of the olefin could occur. Also the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the 1,3-dipole. In view of the stringent spatial demands of dipolar cycloadditions, we thought it worthwhile to consider what effect a distortion from the "parallel-plane approach" would have on the mechanism of dipolar addition.

With this in mind, we decided to investigate the intramolecular dipolar cycloadditions of nitrile ylides in systems where significant contortion away from the strictly parallel-plane approach of the dipole and dipolarophile exists. Inspection of molecular models of the above 2-allyl substituted nitrile ylides indicates that the normal "two-plane orientation approach" of the linear nitrile ylide and the allyl π system is impossible as a result of the geometric restrictions imposed on the system. Consequently, the normal mode of 1,3-dipolar cycloaddition cannot occur. The most reasonable mechanism to account for the cycloadditions observed with these systems involves the reaction of a bent nitrile ylide intermediate (carbene-like). Attack of the carbene carbon on the terminal position of the neighboring double bond will generate a six-membered ring trimethylene intermediate. Collapse of this species will result in the formation of the observed azabicyclohexene system. The photoconversion of the azabicyclohexenes (i.e., **7** → **6**) can also be rationalized in terms of a trimethylene derivative.

It is particularly important to note that the cycloaddition sequence shown in Chart VIII proceeds in a nonconcerted manner and bears a strong resemblance to the stepwise diradical mechanism suggested by Firestone to account for bimolecular 1,3-dipolar cycloadditions. It is evident from our data, that unless the dipole and dipolarophile approach each other in parallel planes, an alternate nonconcerted mechanism for dipolar cycloadditions can occur. The possibility that other dipolar cycloadditions of nitrilium betaines occur via a stepwise process now merits serious attention. In fact, the cycloaddition of benzonitrile oxide to the arylidenic double bond of 3-phenyl-4-arylidenisoxazol-5-ones has been proposed to proceed through the phenylnitrosocarbene form.[38] Since our original report of this phenomenon appeared,[17] a related intramolecular carbene type of 1,1-cycloaddition of a nitrile imine has been reported by Garanti and co-workers.[39]

The mechanism shown in Chart VIII also accommodates the unusual stereochemical results observed with azirine **26** (Chart IX). As was pointed out earlier, the formation of the thermodynamically less favored endo isomer **27** from **26** corresponds to a complete inversion of stereochemistry about the π system in the cycloaddition process. The stereochemical results can now be rationalized by assuming that collapse of the trimethylene derivative **35** to the thermodynamically more favored exo isomer **28** will result in a severe torsional barrier on ring closure. Collapse of **35** to the thermodynamically less favored endo isomer **27** moves the phenyl and methyl groups increasingly further apart and accounts for the formation of the less stable product. Supporting evidence for this rationale was obtained from the irradiation of the isomeric *Z*-2-butenyl-2*H*-azirine **29.** Photolysis of this azirine resulted in the quantitative formation of the same *endo*-azabicyclohexene (**27**) and is quite consistent with the preferred kinetic closure of intermediate **35.** The formation of **27** from methyl azirine **30** also provides convincing support for this interpretation.

Remaining for discussion is the unusual reactivity associated with these intramolecular cycloaddition reactions. According to the frontier orbital treatment of 1,3-dipolar cycloadditions,[40-44] the relative reactivity of a given 1,3-dipole toward a series of dipolarophiles will be determined primarily by the extent of stabilization afforded the transition state by interaction of the frontier orbitals of the two reactants. When nitrile ylides are used as 1,3-dipoles, the dipole highest occupied (HO) and dipolarophile lowest unoccupied (LU) interaction will be of greatest importance in stabilizing the transition state. Nitrile ylides are known to react preferentially with electron-deficient alkenes,[12] since such a pair of addends possesses a narrow dipole-HOMO-dipolarophile-LUMO gap.[45] This is the case

Chart VIII

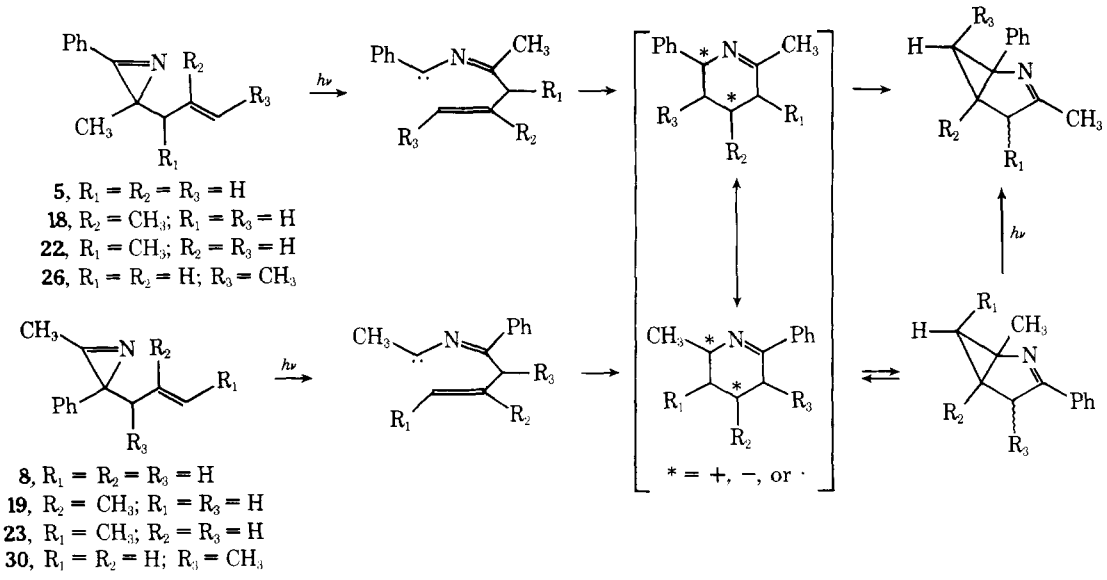
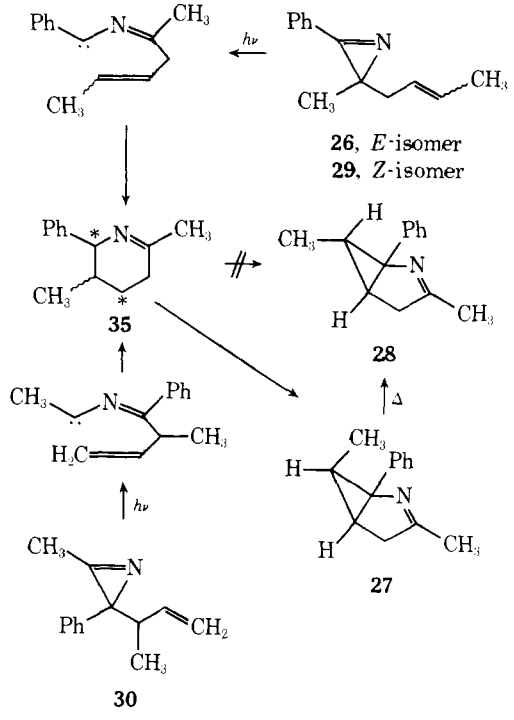


Chart IX



when the above allyl substituted 2*H*-azirines undergo 1,3-dipolar cycloaddition with added dipolarophiles. Thus, fumaronitrile undergoes cycloaddition at a much faster rate (ca. 189 000) than methyl crotonate, and aliphatic olefins were found to be ineffective dipolarophiles. 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.[12,14] Since the above intramolecular cycloadditions involve the use of electron-rich olefins as dipolarophiles, one might inquire why the reaction occurs so readily. The reason is that in these intramolecular reactions, attack by the alkene is constrained to occur perpendicular to the CNC plane of the bent nitrile ylide. The second LUMO, which is perpendicular to the CNC plane, is low lying and presents a large vacancy at C-1 for attack by the more nucleophilic terminus of the alkene, without the possibility of simultaneous bonding at the C-3 carbon atom.[49] In fact, the HOMO and second LUMO of the ylide bear a strong resemblance to the HOMO and LUMO of a singlet carbene. Carbenes are known to react rapidly with electron-rich double bonds.[46]

The above considerations suggest that there are two pathways by which nitrile ylides react with multiple π bonds. The most frequently encountered path involves a "parallel-plane approach of addends" and can be considered to be an orbital-symmetry allowed [4 + 2]-concerted process. In this case, the relative reactivity is controlled by the extent of stabilization afforded the transition state by interaction of the frontier orbitals of the two reactants. Electron-withdrawing substituents, which lower the dipolarophile LU energy, will accelerate the reaction. The other path, which operates with the above systems, occurs because the p orbitals of the olefin are constrained to attack perpendicular to the nitrile ylide plane. The effect of substituents upon the rate of the intramolecular carbene-like cycloaddition should be controlled by the interaction of the alkene HOMO with the second LUMO of the nitrile ylide. Alkyl ethylenes generally have ionization potentials 1–2 eV lower than ethylene, depending on the type and number of alkyl substituents. Also, the π–π^* transition energies of alkyl ethylenes are 0.6–1.0 eV lower in energy than that of ethylene.[47] These findings indicate that electron-releasing substituents should raise both the HOMO and LUMO orbital energies of ethylene. Consequently, attachment of alkyl groups on the double bond should facilitate the rate of the intramolecular carbene-like cycloaddition of nitrile ylides.

One final point of importance which warrants discussion relates to the geometry of the nitrile ylide involved in the above cycloaddition processes. Huisgen originally concluded that 1,3-dipoles of the propargyl-allenyl type possess linear geometry.[3,7] Since that time, the extensive nitrile ylide literature has been rationalized in terms of a linear arrangement of this 1,3-dipole.[7] Recently, Salem has carried out some ab initio computations on the ground and excited state energy surfaces of the 2*H*-azirine molecule.[48] His calculations indicate that the ring-opened intermediate should be capable of dual reactivity when it is intercepted by an added dipolarophile. The behavior of the system was predicted to be dependent on the geometry of the transient intermediate generated from the photolysis. Opening of the ring to an intermediate with linear geometry will result in the formation of a 1,3-dipolar species having closed-shell zwitterionic character. Salem's calculations also indicate that if the ring is opened to give an intermediate with bent geometry, a diradical state with partial dipolar character will be obtained and which may undergo reactions different from the linear species. According to Salem's calculations, the lowest energy ground-state geometry of the nitrile ylide has a CNC angle of 156.7° and is ca. 18 kcal/mol more stable than the linear form. A similar conclusion was reached by Houk and Caramella.[49] These authors have carried

out optimizations of the geometries of the parent nitrilium betaines by ab initio LCAO-MO-SCF calculations[50-53] and find that the geometry of the nitrile ylide is appreciably different from that suggested by Huisgen.[3] Their calculations show that the bent nitrile ylide geometry is favored over the linear, but otherwise optimized, geometry by 11.1 kcal/mol. These findings indicate that the most stable form of a nitrile ylide resembles a bent allenyl anion rather than a planar propargyl anion.

In an earlier communication,[17] we postulated that the stable linear form of the nitrile ylide rehybridizes to a higher energy bent (carbene) form which then undergoes a subsequent intramolecular carbene-like addition. The 1,1-cycloaddition process can now be adequately accounted for in terms of the ground-state orbitals of a bent nitrile ylide. No second geometrical ground-state minimum of a nitrile ylide is required. It should also be noted that the bent nitrile ylide geometry correctly rationalizes the regioselectivity encountered with the 1,3-dipolar cycloadditions of nitrile ylides with added dipolarophiles. In order to predict regioselectivity for this process, it is necessary to determine the relative magnitudes of the coefficients in the highest occupied orbital (HO) of the nitrile ylide. The HO coefficients originally calculated using the linear geometry of the ylide were found to be larger at the trivalent carbon (C-3) than at the divalent carbon (C-1).[41] Using these coefficients, the regioselectivity predicted for the HOMO controlled cycloadditions of nitrile ylides proved to be incorrect.[12,41] Houk's latest calculations,[49] however, shows that the bent nitrile ylide HOMO is heavily localized at C-1, but still resembles the normal three-orbital, four-electron π system present in other 1,3-dipoles so that concerted cycloadditions can still occur. As a consequence of the bent geometry, C-1 is the nucleophilic terminus of nitrile ylides rather than C-3 as was found for the linear arrangement. Thus, the regioselectivity of the cycloadditions to electron-deficient alkenes,[12] where C-1 of the nitrile ylide adds to the most electrophilic alkene terminus, is correctly accounted for.[54] Protonation of the nitrile ylide is also known to occur at the C-1 carbon atom.[55] Thus, all the known reactions of nitrile ylides can be adequately accounted for in terms of a bent nitrile ylide.

Experimental Section[56]

General Procedure for the Preparation of 2-Allyl Substituted 2*H*-Azirines. The desired 2-allyl substituted 2*H*-azirines were prepared by a modified Neber reaction in which variously substituted 2-methyl-1-phenyl-4-penten-1-ones (or 3-phenylhex-5-en-2-ones) were treated with *N,N*-dimethylhydrazine according to the method of Leonard and Zwanenburg.[18] The general procedure used for the synthesis of the unsaturated ketones was to react the enolate anion of propiophenone (or 1-phenylpropan-2-one) with a substituted allyl halide. A typical procedure involves adding 1 mol of propiophenone (or 1-phenylpropan-2-one) to a well-stirred slurry of 24 g (1 mol) of sodium hydride in 1 l. of dry dimethyl sulfoxide. The temperature was kept between 25 and 35 °C during the course of the addition. After hydrogen evolution had ceased, 1 mol of the appropriate allyl halide was added. Again, the temperature was never allowed to exceed 35 °C. The mixture was allowed to stand for 3–4 h in order to complete the reaction and was then poured into 2 l. of an ice-water slurry, neutralized with hydrochloric acid, and extracted with ether. The ether extracts were washed with water, a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a yellow oil which was distilled under reduced pressure.

The unsaturated ketone was converted to the corresponding *N,N*-dimethylhydrazone by heating a mixture of the appropriate ketone and *N,N*-dimethylhydrazine in the presence of sodium acetate and acetic acid. Anhydrous magnesium sulfate was added in order to absorb the water. A typical procedure involved mixing 0.1 mol of ketone, 0.2 mol of *N,N*-dimethylhydrazine, 10 g of anhydrous sodium acetate, 5 drops of acetic acid, and 10 g of anhydrous magnesium sulfate in a sealed tube. The tube was heated at 120 °C in an oil bath for 80 h. After cooling to room temperature, the reaction mixture was washed four times with 50 ml of ether. Concentration of the ether extracts under reduced pressure gave the crude product as a yellow oil. Distillation of this material using a 10 in. Vigreux column afforded the pure hydrazone. The product generally appeared as a mixture of syn and anti isomers which were not separated.

The desired trimethylhydrazonium iodides were prepared by stirring a mixture containing 0.01 mol of hydrazone and 0.03 mol of methyl iodide for 16 h at room temperature. After approximately 30 min a clear oil separated from the solution. Upon stirring for longer periods of time, the reaction mixture became homogeneous. The excess methyl iodide was removed under reduced pressure, and the remaining bright yellow oil was washed with ether until crystallization occurred. The crude crystalline hydrazonium salt was pure enough to be used directly in the next step.

A general method (A) used for the preparation of the 2*H*-azirine ring system involved adding 75 ml of 2-propanol (which contained 0.01 mol of sodium hydride) to a well-stirred solution of the appropriate hydrazonium iodide, (0.01 mol) in 25 ml of 2-propanol over a 2-h interval. The reaction mixture was allowed to stir for an additional 4 h. The solvent was then removed under reduced pressure, and the residue was washed with 150 ml of cyclohexane. The filtrate was concentrated under reduced pressure, never allowing the temperature to exceed 35 °C. The 2*H*-azirines obtained were distilled under reduced pressure.

An alternate method (B) that was also used with fairly insoluble hydrazonium salts consisted of dissolving a 0.1 mol sample of the appropriate hydrazonium iodide in 100 ml of dimethyl sulfoxide. To the stirred solution was added 1.0 g of sodium hydride in one portion, and after 30 min an additional 1.0-g sample of sodium hydride was added. The reaction was allowed to stir for 1 h, and another 0.49-g sample of sodium hydride was added. The reaction mixture was then stirred for 5 h at room temperature and was poured into 500 ml of ice water. The aqueous phase was extracted with pentane, and the extracts were washed with water, dried over magnesium sulfate, and evaporated under reduced pressure. The reaction mixture contained the desired azirine in excellent yield and of high purity. The azirines were distilled under reduced pressure before use. Using these procedures the following 2*H*-azirines were synthesized.

2-Allyl-2-methyl-3-phenyl-2*H*-azirine (5) was prepared in 80% yield from the corresponding hydrazonium iodide (mp 147–148 °C) by procedure A: bp, 48–50 °C (0.04 mm); IR (neat) 3075, 2970, 2920, 1725, 1635, 1487, 1450, 1375, 1192, 1165, 990, 913, 763, 660 cm^{-1}; UV (cyclohexane) 243 nm (ϵ 12 000); NMR (CCl_4, 100 MHz) τ 8.64 (s, 3 H), 7.76 (dd, 1 H, J = 15.0 and 7.0 Hz), 7.48 (dd, 1 H, J = 15.0 and 7.0 Hz), 5.0 (m, 2 H), 4.24 (m, 1 H), 2.1–2.6 (m, 5 H); *m/e* 171 (M^+) and 104 (base).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.37; H, 7.92; N, 7.96.

2-Allyl-2-phenyl-3-methyl-2*H*-azirine (8) was prepared in 83% yield from the corresponding hydrazonium iodide (mp 141–142 °C) by procedure B: bp 52–53 °C (0.04 mm); IR (neat) 3080, 3065, 3020, 2970, 2910, 1756, 1630, 1590, 1489, 1440, 1425, 1255, 1060, 991, 913, 769, 696 cm^{-1}; UV (hexane) 226 nm (ϵ 7800) with shoulders at 254 nm (ϵ 2200) and 274 nm (ϵ 700); NMR (CCl_4, 60 MHz) τ 7.70 (s, 3 H), 7.26 (m, 2 H), 4.0–5.2 (m, 3 H), 2.91 (m, 5 H); *m/e* 171 (M^+), 169, 130, 129, 115, and 103.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.12; H, 7.66; N, 8.09.

2-Methyl-2-(2-methylallyl)-3-phenyl-2*H*-azirine (18) was prepared in 93% yield from the corresponding hydrazonium iodide (mp 148–149 °C) by procedure A: bp 49 °C (0.01 mm); IR (neat) 3010, 2875, 1725, 1681, 1640, 1480, 1440, 1370, 1190, 1070, 1015, 893, 763, 687 cm^{-1}; NMR (CCl_4, 100 MHz) τ 8.66 (s, 3 H), 8.24 (s, 3 H), 7.72 and 7.62 (AB pattern, 2 H, J_{AB} = 14.5 Hz), 5.24 (s, 2 H, broad), 2.0–2.6 (m, 5 H); *m/e* 185 (M^+) and 170 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.12; H, 8.18; N, 7.51.

2-(2-Methylallyl)-2-phenyl-3-methyl-2*H*-azirine (19) was prepared in 82% yield from the corresponding hydrazonium iodide (mp 137–138 °C) by procedure B: bp 61–62 °C (0.05 mm); IR (neat) 3050, 3020, 2960, 2900, 1759, 1703, 1640, 1593, 1490, 1440, 1370, 1256, 1060, 1022, 890, 770, 695 cm^{-1}; UV (cyclohexane) 225 nm (ϵ 7220), 256 nm (shoulder, ϵ 2000), 272 nm (shoulder, ϵ 780); NMR (CCl_4, 60 MHz) τ 8.33 (s, 3 H), 7.68 (s, 3 H), 7.57 and 7.14 (AB pattern with J_{AB} = 15.0 Hz, 2 H), 5.26 (s, broad, 2 H), 2.94 (m, 5 H); *m/e* 185 (M^+) and 144 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.27; H, 8.42; N, 7.39.

2-Methyl-2-(1-methylallyl)-3-phenyl-2*H*-azirine (22) was prepared in 68% yield from the corresponding hydrazonium iodide (mp 160–161 °C) by procedure A: bp 96–97 °C (4.0 mm); IR (neat) 3080, 2970, 2923, 2870, 1726, 1685, 1635, 1488, 1450, 1415, 1375, 1195, 1160, 912, 883, 760, 690 cm^{-1}; UV (cyclohexane) 245 nm (ϵ 13 000); NMR (CCl_4, 100 MHz) showed that the product was a 1:1 mixture of diastereomers τ 9.19 (d, J = 7.0 Hz) and 9.08 (d, J = 7.0 Hz) (3 H), 8.73 (s) and 8.70 (s) (3 H), 7.66 (q, J = 7.0 Hz) and 7.49 (q, J = 7.0 Hz) (1 H), 4.7–5.2 (m, 2 H), 3.7–4.5 (m, 1 H), 2.0–2.7 (m, 5 H); *m/e* 185 (M^+) and 67 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.20; H, 8.17; N, 7.56.

(*E*)-2-(2-Butenyl)-2-phenyl-3-methyl-2*H*-azirine (23) was prepared in 95% yield from the corresponding hydrazonium iodide (mp 124–125 °C) by procedure B: bp 66–67 °C (0.05 mm); IR (neat) 3050, 3020, 2905, 1758, 1703, 1594, 1490, 1440, 1360, 1255, 965, 766, 696 cm^{-1}; UV (cyclohexane) 225 nm (ϵ 7440) with shoulders at 256 nm (ϵ 2000) and 273 nm (ϵ 725); NMR (CCl_4, 60 MHz) τ 8.41 (d, J = 5.0 Hz, 3 H), 7.72 (s, 3 H), 7.33 (m, 2 H), 4.71 (m, 2 H), 2.94 (m, 5 H); *m/e* 185 (M^+) and 170 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.14; H, 8.17; N, 7.54.

(*E*)-2-(2-Butenyl)-2-methyl-3-phenyl-2*H*-azirine (26) was prepared in 98% yield from the corresponding hydrazonium iodide (mp 137–138 °C) by procedure A: bp 63–64 °C (0.04 mm); IR (neat) 3060, 3020, 2960, 2910, 1722, 1593, 1575, 1485, 1448, 1372, 1190, 960, 760, 688 cm^{-1}; UV (cyclohexane) 244 nm (ϵ 8000); NMR (CCl_4, 100 MHz) τ 8.68 (s, 3 H), 8.38 (d, 3 H, J = 4.0 Hz), 7.68 (m, 2 H), 4.60 (m, 2 H), 2.1–2.6 (m, 5 H); *m/e* 185 (M^+) and 67 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.08; H, 8.21; N, 7.51.

(*Z*)-2-(2-Butenyl)-2-methyl-3-phenyl-2*H*-azirine (29) was prepared in 65% yield from the corresponding hydrazonium iodide (mp 146–147 °C) by procedure A: bp 61–62 °C (0.1 mm); IR (neat) 3050, 3005, 2960, 2905, 1720, 1680, 1650, 1590, 1575, 1485, 1447, 1370, 1190, 763, 690 cm^{-1}; NMR (CCl_4, 60 MHz) τ 8.67 (s, 3 H), 8.46 (d, 3 H, J = 6.0 Hz), 7.58 (m, 2 H), 4.60 (m, 2 H), 2.1–2.9 (m, 5 H). When $Eu(fod)_3$ chemical shift reagent was added, the multiplet at τ 7.58 appeared as two sets of doublets of doublets with J = 14.0 and 6.0 Hz. The multiplet at τ 4.60, corresponding to the alkene protons, separated into two sets of signals. The upfield corresponded to a quartet of doublets with J = 11.0 and 6.0 Hz, while the downfield signals appeared as a triplet of doublets with J = 11.0 and 7.0 Hz. The coupling constant of 11.0 Hz for the doublet indicates that the olefinic protons must be cis.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.19; H, 8.23; N, 7.32.

2-(1-Methylallyl-2-phenyl-3-methyl-2*H*-azirine (30) was prepared in 82% yield from the corresponding hydrazonium iodide (mp 135–136 °C) by procedure B: bp 54–55 °C (0.05 mm); IR (neat) 3050, 3020, 2960, 2920, 1755, 1680, 1592, 1489, 1440, 1365, 1265, 995, 910, 772, 730, 695 cm^{-1}; UV (cyclohexane) 225 nm (ϵ 7060) with shoulders at 256 nm (ϵ 2010) and 272 nm (ϵ 800); NMR (CCl_4, 60 MHz) showed that the product was a 7:10 mixture of diastereomers with signals at τ 9.19 and 9.08 (d, J = 7.0 Hz, 3 H), 7.70 (two singlets with ~1 Hz spacing), 6.83 and 6.69 (p, J = 7.0 Hz, 1 H), 4.8–5.2 (m, 2 H), 4.0–4.7 (m, 1 H), 2.9 (s, 5 H); *m/e* 185 (M^+) and 170 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.09; H, 8.21; N, 7.49.

2-Methyl-2-(3-methyl-2-butenyl)-3-phenyl-2*H*-azirine (33) was prepared in 94% yield from the corresponding hydrazonium iodide (mp 122–123 °C) by procedure A: bp 60–61 °C (0.02 mm); IR (neat) 3010, 2900, 1725, 1680, 1481, 1450, 1370, 1200, 1174, 1100, 1075, 990, 875, 840, 766, 690 cm^{-1}; NMR (CCl_4, 100 MHz) 8.64 (s, 3 H), 8.42 (s, 3 H), 8.32 (s, 3 H), 7.75 (dd, 1 H, J = 14.0 and 8.0 Hz), 7.50 (dd, 1 H, J = 14.0 and 8.0 Hz), 4.80 (t, 1 H, J = 8.0 Hz), 2.0–2.6 (m, 5 H); *m/e* 199 (M^+) and 184 (base).

Anal. Calcd for $C_{14}H_{17}H$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.28; H, 8.53; N, 7.12.

Irradiation of 2-Allyl-2-methyl-3-phenyl-2*H*-azirine (5). A solution containing 200 mg of **5** in 200 ml of cyclohexane was irradiated for 15 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. After evaporation of the solvent, the photolysate consisted of a single product formed in quantitative yield and was assigned the structure of 3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**6**) on the basis of the following data:[57] IR (neat) 3010, 2900, 2820, 1635, 1600, 1495, 1440, 1375, 1315, 1270, 1225, 1110, 1025, 917, 820, 750, 697 cm^{-1}; UV (cyclohexane) 225 nm (ϵ 9000); NMR (CCl_4, 100 MHz) τ 9.64 (t, 1 H, J = 5.0 Hz), 8.68 (dd, 1 H, J = 8.0 and 5.0 Hz), 8.33 (m, 1 H), 8.13 (s, 3 H), 7.64 (d, 1 H, J = 17.5 Hz), 7.22 (dd, 1 H, J = 17.5 and 8.0 Hz), 2.60–3.10 (m, 5 H).

The structure of azabicyclohexene **6** was further supported by its facile oxidation to 2-methyl-6-phenylpyridine (**11**). This could be accomplished by allowing the photoproduct to stand in 10 ml of chloroform at room temperature for 12 h. The solvent was removed, and the yellow residue was chromotographed on a thick layer plate using chloroform as the eluent. The major component isolated (47%) was identical with an authentic sample of 2-methyl-6-phenylpyridine (**11**)[21] prepared by treating 2-methylpyridine with phenyllithium; picrate derivative, mp 131–132 °C (lit.[21] 131–132 °C).

A solution containing 100 mg of azirine **5** in 30 ml of cyclohexane was also photolyzed to 20% conversion using a low-pressure mercury lamp. At this stage of the reaction, the photolysate contained recovered starting material as well as a mixture of 3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**6**) and another azabicyclohexene in nearly equal amounts. The structure of this new azabicyclohexene was assigned as 1-methyl-3-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**7**) on the basis of its NMR spectrum (60 MHz, CCl_4): τ 9.92 (t, 1 H, J = 5.0 Hz), 9.10 (dd, J = 8.0 and 5.0 Hz, 1 H), 8.20 (m, 1 H), 8.38 (s, 3 H), 7.60 (d, 1 H, J = 17.5 Hz), 6.78 (dd, 1 H, J = 17.5 and 8.0 Hz), 2.61–3.10 (m, 5 H). On further irradiation, this new bicyclic intermediate (i.e., **7**) was completed converted to **6.**

Thermal Cycloaddition of Methyl Acrylate with 3-Methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene. The structure of azabicyclohexene **6** was further verified by a thermal cycloaddition with methyl acrylate. A solution containing 250 mg of **6** and 15 ml of methyl acrylate in 50 ml of toluene was heated at reflux for 22 h. Removal of the solvent left a yellow oil which was purified by thick-layer chromatography. The major component isolated (200 mg) was a white solid, mp 87–88 °C, whose structure is assigned as methyl 1-methyl-5-phenyl-8-azabicyclo[3.2.1]oct-2-ene-6- (or 7) carboxylate (**12**) on the basis of its spectral properties: IR (KBr) 3020, 2910, 2840, 1715, 1640, 1590, 1485, 1425, 1370, 1335, 1190, 1163, 1110, 1095, 873, 837, 706 cm^{-1}; *m/e* 257 (M^+) and 170 (base); NMR ($CDCl_3$, 100 MHz) τ 8.68 (s, 3 H), 7.76 (ddd, 1 H, J = 18.0, 4.0, and 1.5 Hz), 7.56 (m, 2 H), 7.44 (d, J = 13.0 Hz), 7.28 (s, broad, exchanged with D_2O), 6.82 (dd, 1 H, J = 7.5 and 4.0 Hz), 6.36 (s, 3 H), 4.34 (ddd, 1 H, J = 9.5, 4.0 and 2.0 Hz), 4.16 (dt, 1 H, J = 9.5 and 1.5 Hz), 2.4–2.8 (m, 5 H). When $Eu(fod)_3$ chemical shift reagent was added to the NMR sample, the multiplet centered at τ 7.56 separated into two distinct patterns with the following characteristics: dd, 1 H, J = 13.0 and 7.5 Hz, and d, 1 H, J = 18.0 Hz.

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.48. Found: C, 74.53; H, 7.19; N, 5.32.

Trapping of the Nitrile Ylide Derived from 2-Allyl-2-methyl-3-phenyl-2*H*-azirine. A solution containing 450 mg of **5** and 50 ml of methyl acrylate in 500 ml of cyclohexane was irradiated for 10 min using a Vycor filter. Removal of the solvent followed by thick-layer chromatography afforded a 3:5 mixture of the stereoisomers of 5-allyl-5-methyl-4-carbomethoxy-2-phenyl-Δ^1-pyrroline (**16**): NMR ($CDCl_3$, 100 MHz) τ 8.76 (s) and 8.40 (s) (3 H), 7.5 (m, 2 H), 6.8 (m, 3 H), 6.24 (s, 3 H), 4.90 (m, 2 H), 4.20 (m, 1 H), 2.1–2.9 (m, 5 H). It was not possible to separate the mixture into its individual components.

A trapping experiment was also carried out using dimethylacetylene dicarboxylate as the dipolarophile. A solution containing 300 mg of **5** and 3 g of dimethyl acetylenedicarboxylate in 250 ml of cyclohexane was irradiated for 15 min using a Vycor filter. Removal of the solvent followed by dry column chromatography (1:2 ether–cyclohexane) gave a white solid (325 mg), mp 58–60 °C, whose structure was identified as dimethyl 5-allyl-5-methyl-2-phenyl-2*H*-pyrrole-3,4-dicarboxylate (**15**) on the basis of its spectral data: IR (KBr) 3010, 2900, 1739, 1724, 1621, 1430, 1315, 1250, 1124, 1050, 1010, 917, 797, 692 cm^{-1}; *m/e* 313 (M^+) and 256 (base); NMR ($CDCl_3$, 100 MHz) τ 8.30 (s, 3 H), 7.04 (dd, 1 H, J = 14.0 and 8.0 Hz), 6.84 (dd, 1 H, J = 14.0 and 8.0 Hz), 5.98 (s, 3 H), 4.68–4.90 (m, 2 H), 4.0–4.6 (m, 1 H), 2.0–2.6 (m, 5 H).

Irradiation of 2-Allyl-2-phenyl-3-methyl-2*H*-azirine (8). A solution containing 200 mg of azirine **8** in 150 ml of cyclohexane was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. After

removal of the solvent the photolysate was found to consist of a single product whose structure was established as 3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**6**) on the basis of its spectral data which were identical in every detail with the product obtained from the photolysis of **5.** Irradiation of azirine **8** for short periods of time (<50% conversion) did not give rise to any detectable quantities of azabicyclohexene **7.** The only product present was 3-methyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**6**).[57] Isomerization of 3-methyl-2*H*-azirine **8** to the isomeric 3-phenyl-2*H*-azirine **5** did not occur.

The irradiation of 3-methyl-2*H*-azirine **8** was also carried out in the presence of a trapping agent. A solution containing 170 mg of **8** and 10 ml of methyl trifluoroacetate in 150 ml of cyclohexane was irradiated for 20 min. Removal of the solvent followed by thick-layer chromatography (5% acetone–hexane) gave (2*R*,5*S*)- and (2*S*,5*R*)-2-allyl-4-methyl-5-methoxy-5-trifluoromethyl-2-phenyl-2,5-dihydro-1,3-oxazine **9** (48%) as the major adduct: IR (neat) 3040, 2985, 2900, 2820, 1670, 1640, 1485, 1425, 1372, 1330, 1258, 1175, 1117, 1075, 1060, 966, 918, 876, 773, and 702 cm^{-1}; UV (cyclohexane) 257 nm (ϵ 290); *m/e* 299 (M^+), 268, 258 (base); NMR (CCl_4, 100 MHz) τ 7.90 (s, 3 H), 7.44 (s, 1 H), 7.36 (s, 1 H), 7.20 (s, 3 H), 4.95–5.28 (m, 2 H), 4.16–4.64 (m, 1 H), 2.44–2.86 (m, 5 H). The minor isomer obtained (28%) from the thick layer plate was assigned the structure of (2*R*,5*R*)- and (2*S*,5*S*)-2-allyl-4-methyl-5-methoxy-5-trifluoromethyl-2-phenyl-2,5-dihydro-1,3-oxazine; NMR (CCl_4, 100 MHz) τ 7.93 (s, 3 H), 7.40 (dd, 1 H, J = 13.0 and 7.0 Hz), 7.20 (dd, J = 13.0 and 7.0 Hz, 1 H), 6.58 (s, 3 H), 4.94–5.22 (m, 2 H), 4.20–4.64 (m, 1 H), 2.52–2.90 (m, 5 H); UV (cyclohexane) 257 nm (ϵ 300); IR (neat) 3030, 2900, 2820, 1665, 1640, 1485, 1440, 1420, 1370, 1315, 1261, 1178, 1130, 1074, 1060 cm^{-1}; *m/e* 299 (M^+), 258 (base) and 105.

The cycloadducts obtained with 3-methyl-2*H*-azirine **8** were substantially different from those obtained on irradiation of 3-phenyl-2*H*-azirine **5** with methyl trifluoroacetate. Thus, the irradiation of 200 mg of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**5**) and 5 ml of methyl trifluoroacetate in 150 ml of cyclohexane gave a 1:1 mixture of the isomeric 2-allyl-2-methyl-5-methoxy-5-trifluoromethyl-4-phenyl-2,5-dihydro-1,3-oxazines (**10**) in 65% isolated yield. One of the isomers showed signals in the NMR (CCl_4, 100 MHz) at τ 8.54 (s, 3 H), 7.56 (d, 2 H, J = 6.0 Hz), 6.68 (s, 3 H), 4.84–5.17 (m, 2 H), 3.90–4.56 (m, 1 H), 2.2–3.1 (m, 5 H) while the other isomer showed signals at τ 8.54 (s, 3 H), 7.42 (d, 2 H, J = 6.0 Hz), 6.64 (s, 3 H), 4.84–5.17 (m, 2 H), 3.90–4.56 (m, 1 H), 2.2–3.1 (m, 5 H); IR (neat) of mixture: 2920, 2840, 1624, 1444, 1372, 1320, 1180, 1135, 1075, 915, 772, and 692 cm^{-1}; UV (hexane) 248 nm; *m/e* 299 (M^+), 258 (base), 219, 189, and 105.

Irradiation of 2-Methyl-2-(2-methylallyl)-3-phenyl-2*H*-azirine (18). A solution containing 300 mg of **18** in 200 ml of cyclohexane was irradiated for 10 min using a Vycor filter sleeve. The photolysate obtained on removal of the solvent was identified as pure 3,5-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**20**) on the basis of its spectral properties:[57] NMR (CCl_4, 100 MHz) τ 9.38 and 8.59 (2 H, AB pattern, J_{AB} = 5.0 Hz), 8.95 (s, 3 H), 7.38 (AB pattern with small $\Delta\tau$, 2 H), 8.06 (s, 3 H), 3.0–3.5 (m, 5 H).

Irradiation of a solution containing 100 mg of **18** in 25 ml of cyclohexane using a low-pressure mercury lamp to 80% conversion produced a 2:1 mixture of 3,5-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**20**) and an isomeric compound which was assigned the structure[57] of 1,5-dimethyl-3-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**21**) on the basis of its NMR spectrum which showed peaks at τ 9.78 (1 H) and 9.35 (1 H) (AB pattern, J_{AB} = 5.0 Hz), 8.72 (s, 3 H), 8.47 (s, 3 H), 7.01 (s, 2 H), 2.0–3.0 (m, 5 H). On further irradiation, the mixture was exclusively converted to 3,5-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**20**). No detectable quantities of the isomeric 3-methyl-2*H*-azirine **19** could be found in the crude photolysate derived from 3-phenyl-2*H*-azirine **18.**

The irradiation of azirine **18** was also carried out in the presence of a trapping agent. A solution containing 350 mg of **18** and 8.5 g of methyl trifluoroacetate in 200 ml of cyclohexane was irradiated for 30 min using a Vycor filter. Removal of the solvent followed by thick-layer chromatography gave a mixture of 2-methyl-2-(2-methylallyl)-5-trifluoromethyl-5-methoxy-4-phenyl-2,5-dihydro-1,3-oxazines. The faster moving isomer was assigned the trans structure (CF_3 and allyl groups trans); NMR (CCl_4, 100 MHz) τ 8.46 (s, 3 H), 8.09 (s, 3 H), 7.41 (s, 2 H), 6.54 (s, 3 H), 5.02 (m, 2, H), 1.8–2.8 (m, 5 H); UV (cyclohexane) 250 nm (ϵ 15 700); *m/e* 313 (M^+) and 258 (base). The slower moving isomer showed signals at τ 8.39 (s, 3 H), 8.08 (s, 3 H), 7.52 (s, 1 H), 7.48 (s, 1 H), 6.58 (s, 3 H), 5.04 (s, 1 H), 4.98 (s, 1 H), 1.8–2.8 (m, 5 H); *m/e* 313 (M^+), 258 (base), and 105.

Irradiation of 2-(2-Methylallyl)-2-phenyl-3-methyl-2*H*-azirine (19). A solution containing 100 mg of **19** in 25 ml of cyclohexane was irradiated to 40% conversion using a low-pressure mercury lamp. Analysis of the photolysate by NMR spectroscopy indicated the presence of a 4:1 mixture of 3,5-dimethyl-1-phenyl (**20**) and 1,5-dimethyl-3-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**21**). These are the same products as those formed on irradiation of azirine **18.** Careful monitoring of the photoreaction showed that the azirines were not interconverted under the photolytic conditions.

Irradiation of 2-Methyl-2-(1-methylallyl-3-phenyl-2*H*-azirine (22). Photolysis of a sample (450 mg) of **22** in 300 ml of cyclohexane for 15 min using a Vycor filter sleeve afforded a quantitative yield of 3,4-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**24**)[57] as a mixture of endo (25%) and exo (75%) isomers. The exo isomer showed signals in the NMR (CCl_4, 100 MHz) at τ 9.62 (t, 1 H, J = 4.6 Hz), 8.92 (d, 3 H, J = 8.0 Hz), 8.66 (dd, 1 H, J = 8.0 and 4.6 Hz), 8.42 (dd, 1 H, J = 8.0 and 4.6 Hz), 8.12 (s, 3 H), 7.48 (q, 1 H, J = 8.0 Hz), 2.4–3.0 (m, 5 H). The minor endo isomer exhibited a doublet at τ 8.88 (3 H, J = 8.0 Hz), a singlet at 8.20 (3 H), and a pentuplet at τ 6.89 (1 H, J = 8.0 Hz). The remaining signals were not significantly separated from those of the exo isomer.

Further proof for the structure of 3,4-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**24**) was obtained by its smooth oxidation to 2,3-dimethyl-6-phenylpyridine (**25**). This was accomplished by allowing a 300-mg sample of **24** in 5 ml of carbon tetrachloride to stand at room temperature for 4 days. Removal of the solvent followed by thick-layer chromatography gave 150 mg of pyridine **25,** whose spectral properties were identical with those of an authentic sample.[24] A picrate derivative was prepared in the normal fashion, mp 194–195 °C (lit.[24] 192–193 °C).

The photolysis of **22** was also carried out in the presence of methyl acrylate. A solution containing 300 mg of **22** and 25 ml of methyl acrylate in 200 ml of cyclohexane was irradiated for 15 min using a Vycor filter sleeve. Removal of the solvent followed by thick-layer chromatography afforded a mixture of two isomeric cycloadducts which could not be separated. The NMR spectrum of the mixture (CCl_4, 100 MHz) showed a singlet at τ 8.88 and two doublets at τ 8.83 and 8.94 both with J = 7.0 Hz (6 H); τ 7.46 (p, 1 H, J = 7.0 Hz), 7.0–7.7 (m, 3 H), 6.32 (s, 3 H), 4.9 (m, 2 H), 3.8–4.8 (m, 1 H), 2.0–2.8 (m, 5 H).

Irradiation of (*E*)-2-(2-Butenyl)-2-phenyl-3-methyl-2*H*-azirine (23). A solution containing 300 mg of **23** in 150 ml of cyclohexane was irradiated for 16 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a clear oil which was identified as a mixture of *endo*- (25%) and *exo*- (75%) 3,4-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**24**). The product distribution was identical with that obtained from the photolysis of 2-methyl-2-(1-methylallyl)-3-phenyl-2*H*-azirine (**22**). Careful monitoring of the reaction mixture showed that the two azirines were not interconverted under the photolytic conditions.

Irradiation of (*E*)- (26) and (*Z*)-2-(2-Butenyl)-2-methyl-3-phenyl-2*H*-azirines (29). A solution containing 200 mg of (*E*)-3-phenyl-2*H*-azirine **26** in 200 ml of cyclohexane was irradiated under a nitrogen atmosphere for 16 min using a Vycor filter. Concentration of the solution under reduced pressure left an oil which was shown by NMR analysis to contain only a single compound whose structure was assigned as *endo*-3,6-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**27**);[57] NMR (CCl_4, 100 MHz) τ 9.24 (d, 3 H, J = 6.0 Hz), 8.42 (dq, 1 H, J = 8.0 and 6.0 Hz), 8.13 (t, 1 H, J = 8.0 Hz), 8.00 (s, 3 H), 7.80 (d, 1 H, J = 18.0 Hz), 7.26 (dq, 1 H, J = 18.0 and 8.0 Hz), 2.4–3.0 (m, 5 H). When the NMR sample was allowed to stand in the dark, new peaks at τ 8.08 (s) and 9.15 (d, J = 6.0 Hz) appeared while those at 8.00 and 9.24 disappeared. These new signals were assigned to the isomeric *exo*-bicyclohexene **28.** Identical results were obtained on irradiation of the corresponding *Z*-azirine **29.**

The structures of azabicyclohexenes **27** and **28** were further verified by oxidation to 2,5-dimethyl-6-phenylpyridine (**31**). This was accomplished by heating a solution of the photoadduct(s) in cyclohexane for 12 h. Removal of the solvent followed by thick-layer chromatography gave a 79% yield of 3,6-dimethyl-2-phenylpyridine (**31**). This structure was unequivocably established by comparison with an authentic sample,[24] picrate derivative, mp 139–140 °C (lit.[24] 134–135 °C).

When the irradiation of 150 mg of **26** was carried out in the presence of 20 ml of methyl acrylate and 200 ml of cyclohexane, a 2:3 mixture of cycloadducts was obtained. The mixture of isomeric 4-carbomethoxy-4-((*E*)-2-butenyl)-5-methyl-2-phenyl-Δ^1-pyrrolines could not be separated into its component parts by chromatography but was characterized by NMR spectroscopy (CCl_4, 100 MHz). The major component (59%) showed a singlet at τ 8.93 (3 H) while the minor component (41%) showed a singlet at τ 8.04 (3 H). Both isomers exhibited multiplets at τ 7.40–8.0 (2 H), 6.5–7.2 (m, 3 H), a singlet at 6.32 (3 H), and multiplets at 4.4–4.8 (2 H) and 2.0–2.8 (5 H).

Thermal Addition of Methyl Acrylate to 3,6-Dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene. A solution containing 150 mg of azabicyclohexene **27** and 5 ml of methyl acrylate in 50 ml of toluene was heated at reflux for 12 h. Removal of the solvent followed by thick-layer chromatography using chloroform as the eluent gave methyl 1,4-dimethyl-5-phenyl-8-azabicyclo[3.2.1]oct-2-ene-6- (or 7-) carboxylate (**32**) as a clear oil; IR (neat) 3020, 2960, 2865, 1722, 1600, 1492, 1445, 1433, 1375, 1362, 1357, 1270, 1195, 1164, 862, 750, and 700 cm^{-1}; *m/e* 271 (M^+), 214, 212, 174, and 105 (base); NMR (CCl_4, 100 MHz) τ 9.40 (d, 3 H, J = 7.0 Hz), 8.75 (s, 3 H), 7.80 (ddq, 1 H, J = 7.0, 4.0, and 1.0 Hz), 7.78 (dd, 1 H, J = 13.0 and 2.5 Hz), 7.56 (1 H, exchanged with D_2O), 7.55 (dd, 1 H, J = 13.0 and 8.0 Hz), 4.60 (dd, 1 H, J = 9.5 and 4.0 Hz), 4.42 (dd, 1 H, J = 9.5 and 1.0 Hz), 2.8 (m, 5 H).

Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.24; H, 7.80; N, 5.16. Found: C, 75.32; H, 7.85; N, 4.96.

Irradiation of 2-(1-Methylallyl)-2-phenyl-3-methyl-2*H*-azirine (30). A 200-mg sample of the above azirine **30** in 150 ml of cyclohexane was irradiated for 17 min with a 450-W Hanovia mercury lamp equipped with a Vycor filter sleeve. Removal of the solvent left a pale-yellow oil whose NMR spectrum was identical with that of *endo*-3,6-dimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**27**) prepared from the irradiation of (*E*)-2-(2-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**26**); IR (neat) 3050, 3020, 2910, 1625, 1595, 1490, 1440, 1420, 1370, 1315, 1260, 1125, 830, 740, and 695 cm^{-1}; *m/e* 185 (M^+), 183 (base), 142, 141, 115, 104, 91, and 77.

Irradiation of 2-Methyl-2-(3-methyl-2-butenyl)-3-phenyl-2*H*-azirine (33). A solution containing 180 mg of **33** in 200 ml of cyclohexane was irradiated for 5 min with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Evaporation of the solvent left a pale-yellow oil whose structure[57] was assigned as 3,6,6-trimethyl-1-phenyl-2-azabicyclo[3.1.0]hex-2-ene (**34**) on the basis of its NMR spectrum: (CCl_4, 100 MHz) τ 9.18 (s, 3 H), 8.38 (dd, 1 H, J = 7.0 and 1.0 Hz), 8.05 (s, 3 H), 7.22 (dd, 1 H, J = 18.0 and 1.0 Hz), 7.24 (dd, 1 H, J = 18.0 and 7.0 Hz), 2.4–3.0 (m, 5 H); IR (neat) 2960, 2860, 1630, 1597, 1490, 1437, 1366, 1312, 1274, 1205, 1106, 1065, 1020, 798, 735, 694 cm^{-1}; UV (cyclohexane) 220 nm (ϵ 7200); *m/e* 199 (M^+), 184, 104, 96 (base), 91, 81, and 77.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly at room temperature using a Rayonet reactor equipped with eight 2537 Å lamps. Samples were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. A 10-ml solution approximately 2×10^{-2} M in azirine in a 1.5×15 cm quartz tube was placed in a merry-go-round apparatus at a distance of approximately 1 cm from the lamps. Cyclopentanone solutions were used as the chemical actinometer for which a quantum yield of 0.38 was used[58] giving a reproducible lamp output of 1.63×10^{17} quanta s^{-1}. After irradiation, the degree of reaction was determined by quantitative NMR spectroscopy. The conversions were run to 20% or less. *p*-Dimethoxybenzene was used as the internal standard.

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