Spatial Requirements Associated with the Intramolecular 1,1-Cycloaddition Reactions of Nitrile Ylides[1]

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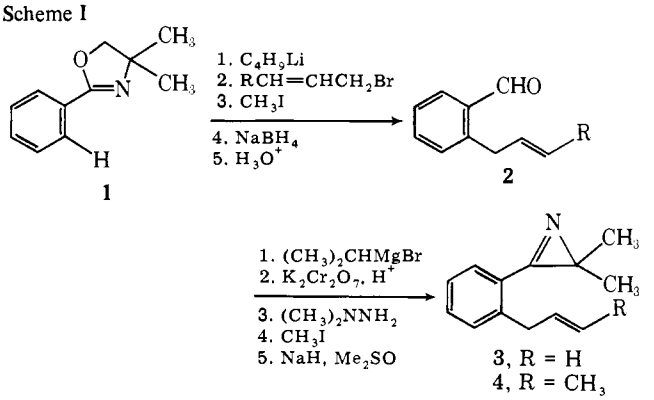
Abstract: The intramolecular photocycloaddition reactions of a number of *o*-vinyl, *o*-allyl, and *o*-butenylphenyl substituted 2*H*-azirines have been examined in mechanistic detail. Upon irradiation with ultraviolet light, the *o*-allylphenyl substituted systems undergo rearrangement to benzobicyclo[3.1.0]hexenes via transient nitrile ylides. Inspection of molecular models of these systems indicates that the normal "two-plane orientation approach" is difficult to achieve 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 represents 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. 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. A similar 1,1-cycloaddition reaction was observed with the related *o*-allylphenyl substituted imidoyl chloride. Irradiation of *o*-(3-carbomethoxy-2-propenylphenyl)-2,2-dimethyl-2*H*-azirine results in an intramolecular 1,3-dipolar cycloaddition. This result is consistent with the principles of frontier MO theory. Photolysis of the *o*-butenylphenyl substituted 2*H*-azirine system also results in 1,3-dipolar cycloaddition. With this system, the transition state for cycloaddition allows easy attainment of the parallel plane approach of the dipole and dipolarophile.

The fact that a double bond can participate in an intramolecular 1,3-dipolar cycloaddition reaction with a suitably placed 1,3-dipole has been known for a long time. The first example of such a process was reported by LeBel and Whang in 1959.[2] Since their initial report, many papers dealing with intramolecular 1,3-dipolar cycloadditions have been published and considerable use has been made of this reaction for organic synthesis.[3] Our research group has recently been concerned with the intramolecular 1,3-dipolar cycloaddition reactions of nitrile ylides[4] generated by photolysis of 2*H*-azirines.[5,6] The internal cycloadditions of this dipole are of interest for a number of reasons. First, the reaction represents a general scheme for the synthesis of novel fused ring heterocycles. Secondly, among the possible forms of a nitrile ylide, a carbene structure can be envisaged which makes conceivable an intramolecular 1,1-cycloaddition of this 1,3-dipole.[7] Thirdly, the spatial relationship of the dipole and dipolarophile moieties would be expected to play an important role in controlling the rate and regioselectivity of the intramolecular cycloaddition reaction. The primary spatial requirement for 1,3-dipolar cycloaddition is that the distance between the two reacting centers should be sufficiently short so that effective three-center overlap of the nitrile ylide with the dipolarophile can occur. Moreover, the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the nitrile ylide[8] for internal 1,3-dipolar addition to occur. The technique of attaching two potentially interacting groups to a chain of methylene units was previously shown to be of considerable value in delineating the geometric features associated with the intramolecular dipolar cycloaddition reactions of nitrile ylides.[9] In view of the stringent spatial requirements encountered with these systems, we thought it worthwhile to consider what effect a variation in the spatial proximity between the nitrile ylide and a dipolarophile would have on the course of the intramolecular photocycloaddition reactions of a series of *o*-alkenylphenyl substituted 2*H*-azirines. We report here the results of these studies.[10]

Results

Intramolecular 1,1-Cycloaddition Reactions of *o*-Allylphenyl Substituted 2*H*-Azirines. As our first model we chose to investigate the photochemistry of a series of *o*-allylphenyl substituted 2*H*-azirines. These compounds were conveniently prepared by the series of reactions outlined in Scheme I. *o*-

Scheme I



Allylbenzaldehyde (**2**) was synthesized from 2-phenyl-4,4-dimethyl-2-oxazoline (**1**) according to the general procedure of Meyers[11] and Gschwend.[12] This unsaturated aldehyde was converted to azirines **3** and **4** in high yield by treatment with isopropyl Grignard reagent, oxidation of the benzylic alcohol with potassium dichromate, and conversion of the resulting ketone to the 2*H*-azirine ring system by a modified Neber reaction.[13] A related series of reactions was used to prepare azirine **15.**

When a thoroughly deaerated solution of **3** was irradiated with light of wavelength > 280 nm, an extremely rapid and clean conversion to a single photoproduct occurred. Assignment of this product as 6,6a-dihydro-*N*-(isopropylidene)cycloprop[*a*]inden-1a(1H)amine (**5**) was made on the basis of its straightforward spectral properties. This material was readily hydrolyzed to acetone and the corresponding amine **6** on thick layer chromatography. The NMR of **6** showed a triplet at τ 9.64 (1 H, J = 5.0 Hz), a doublet of doublets at τ 8.63 (1 H, J = 8.0 and 5.0 Hz), a multiplet at τ 8.20 (1 H), a singlet for the amine protons at τ 7.80 (exchanged with D_2O), a doublet at τ 7.26 (1 H, J = 17.0 Hz), a doublet of doublets at τ 6.76 (1 H, J = 17.0 and 6.0 Hz), and a multiplet centered at τ 2.80 (4 H). In support of this assignment 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,[14-16] while

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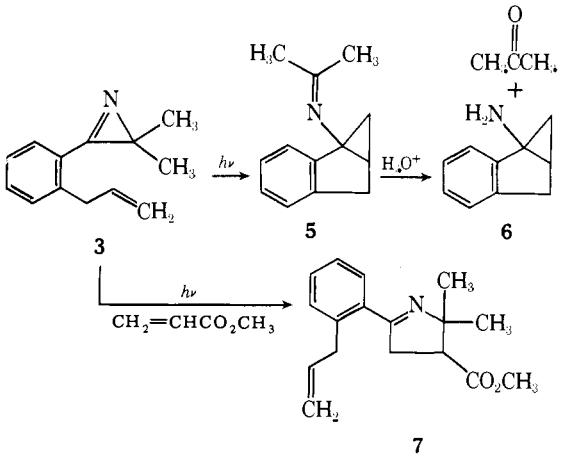
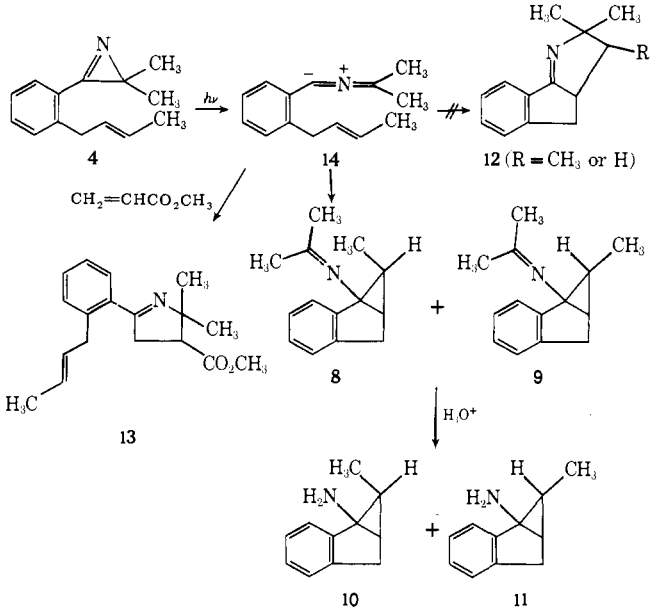


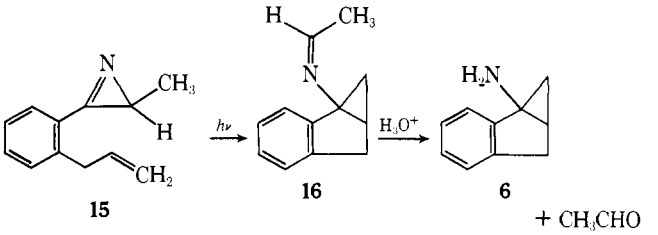
that for cis vicinal coupling is ca. 6 Hz.[17] This is to be expected since molecular models show that the dihedral angle for the trans C(4)-C(5) protons is about 110°, while that for the cis protons is approximately 0°. Photolysis of **3** is the presence of excess methyl acrylate afforded cycloadduct **7** in high yield. Under these conditions, the formation of **5**, which is produced in quantitative yield in the absence of a trapping reagent, is entirely suppressed.

Irradiation of the closely related *o*-2-butenylphenyl substituted 2*H*-azirine system **4** afforded a quantitative yield of a mixture of endo (20%) (**8**) and exo (80%) (**9**) bicyclohexene isomers. Chromatography of the mixture over silica gel resulted in the separation of the corresponding endo (**10**) and exo (**11**) bicyclohexylamines. It should be pointed out that no de-

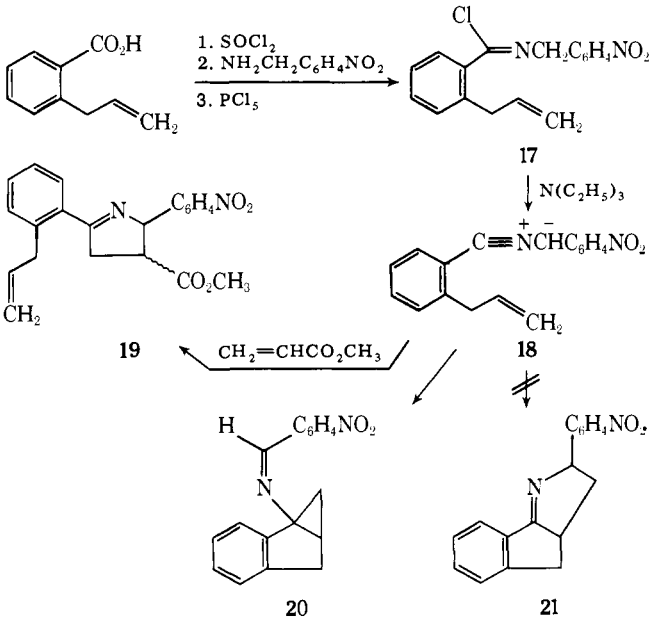


tectable quantities of an isomeric 1,3-dipolar adduct (**12**) could be observed in the crude photolysate of either **3** or **4**. The stereochemical assignments of the endo and exo isomers were made on the basis of their NMR spectra. The location of the endo methyl group at a higher field (τ 9.49) in compound **10** relative to **11** (τ 8.75) is consistent with the expected anisotropic shielding effect of the neighboring aromatic ring.[18] When the irradiation of **4** was carried out in the presence of methyl acrylate, the normal Δ^1-pyrroline **13** was obtained as the exclusive photoproduct.

An additional system which was also studied involved the photochemistry of 3-(*o*-allylphenyl)-2-methyl-2*H*-azirine (**15**). Photolysis of this system produced bicyclohexene **16** in good yield. Hydrolysis of this material afforded acetaldehyde and 6,6a-dihydrocycloprop[*a*]inden-1a(1*H*)amine (**6**) in quantitative yield.



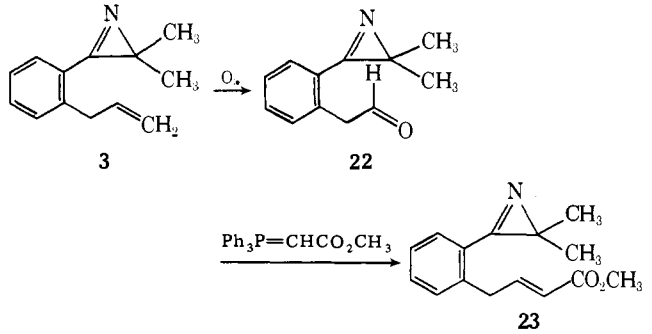
Recent results in the 1,3-dipolar cycloaddition reactions of pyridinium ylides have disclosed significant differences between the reactivity of the 1,3-dipole when it is generated in the ground state or in an excited state.[19,20] In order to determine whether electronically relaxed or excited nitrile ylide intermediates are involved in the 1,1-photocycloaddition reactions of these *o*-allyl substituted 2*H*-azirines, we decided to investigate the base-induced chemistry of imidoyl chloride **17**. Huisgen's group had previously demonstrated that nitrile ylides can be readily generated by treating imidoyl chlorides with base. *o*-Allyl substituted imidoyl chloride **17** was conveniently prepared by successive treatment of *o*-allylbenzoic acid with thionyl chloride, *p*-nitrobenylamine, and phosphorus pentachloride. Reaction of triethylamine with a benzene solution of **17** at room temperature produced triethylammonium chloride and an orange-red solution, which presumably contains the unstable nitrile ylide **18**. This reactive species undergoes facile 1,3-dipolar cycloaddition with methyl acrylate and affords a mixture of two diastereomeric Δ^1-pyrrolines (**19**) in high yield. In the absence of a dipolarophile, the only product



isolated was benzobicyclo[3.1.0]hex-2-ene (**20**). No detectable quantities of the 1,3-dipolar cycloadduct **21** could be observed in the crude reaction mixture. The identity of **20** was determined by its straightforward spectral properties and was further verified by an independent synthesis which involved treating bicyclohexene **6** with *p*-nitrobenzaldehyde and isolating structure **20** in quantitative yield. The successful 1,1 trapping of the nitrile ylide generated from the base treatment of imidoyl chloride **17** clearly establishes that the internal 1,1-cycloaddition reaction is independent of the precursor used to generate the 1,3-dipole. Taken with the formation of similar products from the irradiation of the related azirine system, this constitutes good evidence for the generality of 1,1-cycloadditions of nitrile ylides.

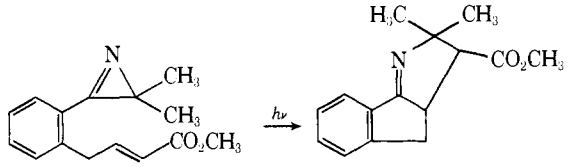
The intramolecular cycloadditions of the above systems are interesting not only because they proceed in the 1,1 sense but also because the cycloaddition occurs readily with an unacti-

vated olefin, a substrate which is generally unreactive toward nitrile ylides.[21] Conjugated and electron-deficient olefins are known to undergo ready bimolecular 1,3-dipolar cycloadditions with nitrile ylides[21,22] since such a pair of addends possesses a narrow dipole-HOMO dipolarophile-LUMO gap.[23] Bimolecular reactions of nitrile ylides with electron-rich olefins, however, have never been observed, thereby indicating that the dipole LU-dipolarophile HO interaction is never large. Because of their high nucelophilicities, nitrile ylides generally undergo bimolecular reactions with their precursors, dimerize, or isomerize faster than they undergo reactions with unactivated olefins.[7,24,25] As was pointed out in an earlier paper,[26] the dipole HO-dipolarophile LU orbitals control the rate and regioselectivity of 1,3-dipolar cycloadditions with nitrile ylides. Placement of an electron-withdrawing substituent on the π bond should lower the dipolarophile LU energy and thereby accelerate the rate of 1,3-dipolar cycloaddition. Thus, it became of interest to study the intramolecular photocycloaddition of an unsaturated 2*H*-azirine which possessed an electron-withdrawing substituent on the double bond in order to determine whether this electronic perturbation would change the course of the internal cycloaddition from the 1,1 to the 1,3 sense. To this end we synthesized 3-[*o*-(3-methoxycarbonyl)-2-propenyl)phenyl]-2,2-dimethyl-2*h*-azirine (**23**). This compound was prepared by subjecting azirine **3** to ozonolysis followed by treatment of the resulting aldehyde **22** with carbomethoxymethylenetriphenylphosphorane.



3 **22** **23**

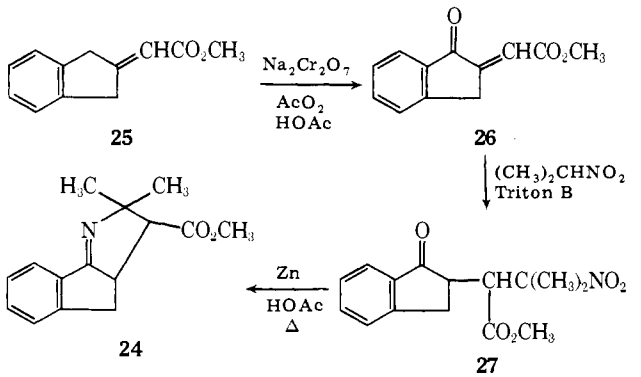
Irradiation of **23** in benzene using a 450-W Hanovia immersion apparatus equipped with a Vycor filter sleeve led to the complete consumption of reactant in 20 min. The only product obtained was methyl 2,3,3a,4-tetrahydro-2,2-dimethylindeno[1,2-*b*]pyrrole-3-carboxylate (**24**). The structure



23 **24**

of the photoproduct was further confirmed by its unequivocal synthesis as outlined in Scheme II. The above result clearly

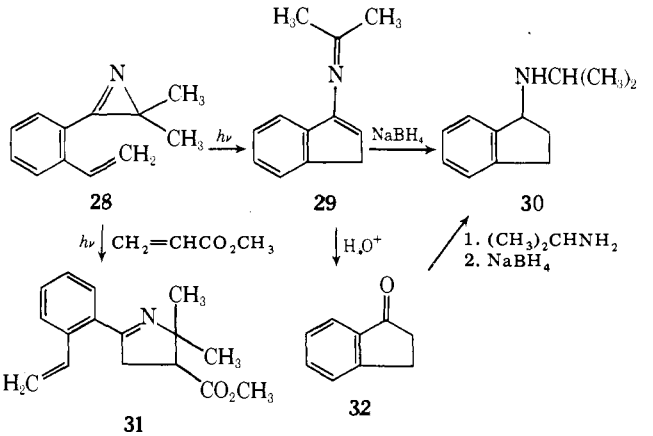
Scheme II



25 **26** **24** **27**

establishes that attachment of an electron-withdrawing substituent on the double bond has a pronounced effect on the manner by which the intramolecular cycloaddition proceeds.

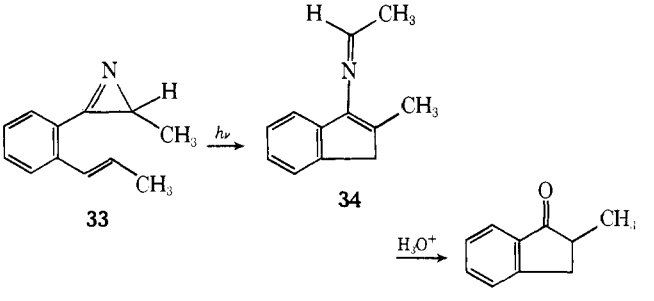
Internal Cyclization Reactions of *o*-Vinylphenyl Substituted 2*H*-Azirines. As part of our continuing program of exploration of the mechanistic nuances and synthetic scope of intramolecular dipolar cycloadditions of unsaturated 2*H*-azirines, we decided to investigate the photochemistry of the next lower homologous series. The several new azirines employed in these studies were synthesized from known starting materials using synthetic sequences similar to those outlined above. We initially examined the photochemistry of *o*-vinylphenyl substituted 2*H*-azirine **28.** Irradiation of a solution of **28** in benzene resulted in the formation of a single product (>90%) which showed all the properties expected for 1-*N*-isopropylideneindene-3-amine (**29**). The structure of **29** was confirmed by



28 **29** **30** **31** **32**

hydrolysis of 1-indanone and by sodium borohydride reduction to *N*-isopropylindan-3-amine (**30**) which, in turn, was independently synthesized from 1-indanone. Photolysis of **28** in the presence of methyl acrylate resulted in the trapping of a nitrile ylide and gave cycloadduct **31** in high yield. Under these conditions the formation of **29,** which is produced in near-quantitative yield in the absence of a trapping agent, is entirely suppressed.

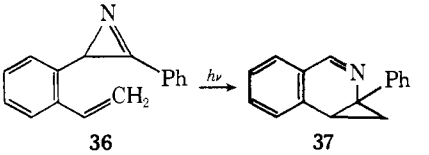
We also examined the photochemical behavior of the closely related *o*-(1-propenylphenyl)-2-methyl-2*H*-azirine (**33**) system. Irradiation of **33** in benzene afforded a quantitative yield of 1-*N*-ethylidene-2-methylidene-3-amine (**34**), which, in turn,



33 **34** **35**

was readily hydrolyzed to 2-methyl-1-indanone (**35**). The only product formed when methyl acrylate was used as the trapping agent was the usual Δ^1-pyrroline.

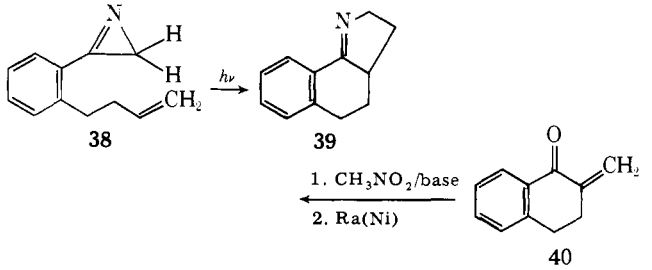
Attention was next turned to the photochemical behavior of 3-phenyl-2-(*o*-vinylphenyl)-2*H*-azirine (**36**). When a thoroughly deaerated solution of **36** was irradiated with light



36 **37**

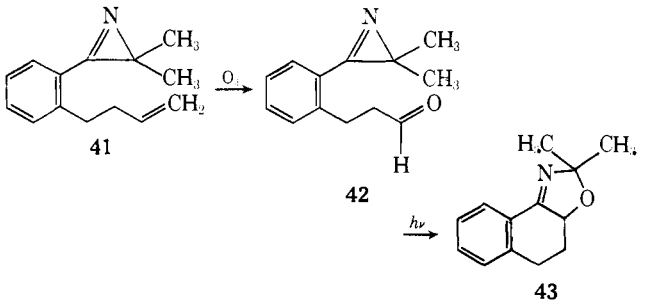
of wavelength >280 nm, an extremely rapid and clean conversion to a single photoproduct occurred. Assignment of this product as 2-aza-3-phenyl-6,7-benzobicyclo[4.1.0]heptene (**37**) was made on the basis of its straightforward spectral properties. The exclusive formation of a 1:1 cycloadduct with this system indicates that the nitrile ylide produced is capable of undergoing carbene type of addition to a vinyl group just as long as there are no considerable bond distortions involved in the transition state for the internal cycloaddition.

Intramolecular 1,3-Dipolar Cycloaddition Reactions of *o*-(3-Butenylphenyl) Substituted 2*H*-Azirines. In view of the stringent spatial requirements associated with the intramolecular 1,1-cycloadditions of nitrile ylides, we thought it worthwhile to examine the photochemistry of an ortho-substituted unsaturated azirine where the methylene chain would be of sufficient length to allow the dipole and dipolarophile to approach each other in parallel planes. To this end we synthesized *o*-(3-butenylphenyl)-2*H*-azirine (**38**) using a synthetic sequence similar to that outlined above. Irradiation of **38** in benzene gave 3,3a,4,5-tetrahydro-2*H*-benz[*g*]indole (**39**) as



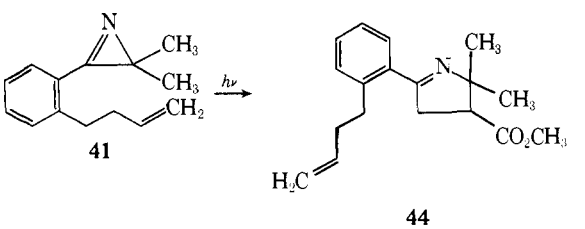
the exclusive photoproduct. The structure of this material was assigned on the basis of its spectral data and was further verified by comparison with an independently synthesized sample prepared by treating 2-methylene-1-tetralone (**40**) with the anion of nitromethane followed by Raney nickel reduction.

A related intramolecular 1,3-dipolar cycloaddition reaction was found to occur upon irradiation of azirinyl aldehyde **42.** This carbonyl compound was readily prepared by ozonolysis of azirine **41.** Photolysis of **42** in benzene gave 2,3a,4,5-tetrahydro-2,2-dimethylnaphth[1,2-*d*]oxazole (**43**) as the exclusive



photoproduct. The orientation encountered in this internal cycloaddition is the same as that normally observed in the bimolecular cycloaddition reactions of 2*H*-azirines with aldehydes.[27-29]

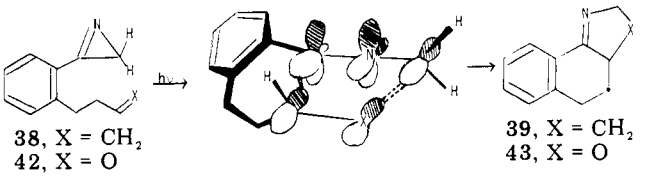
We also investigated the excited state behavior of azirine **41.** Whereas azirine **38** was smoothly converted to benz[*g*]indole **39** on irradiation, photolysis of the dimethyl substituted azirine **41** resulted in the formation of a complex mixture of



products. Examination of the NMR spectrum of the crude photolysate clearly showed that the olefinic protons of the butenyl side chain were still present. When the irradiation of **41** was carried out in the presence of methyl acrylate, however, the normal Δ^1-pyrroline cycloadduct (**44**) could be obtained in high yield. All attempts to detect an intramolecular cycloadduct from the photochemically generated nitrile ylide derived from **41** failed. This result suggests that the nature of the substituent groups on the azirine ring may play an important role in the intramolecular cycloaddition reactions of these unsaturated nitrile ylide systems.[30]

Discussion

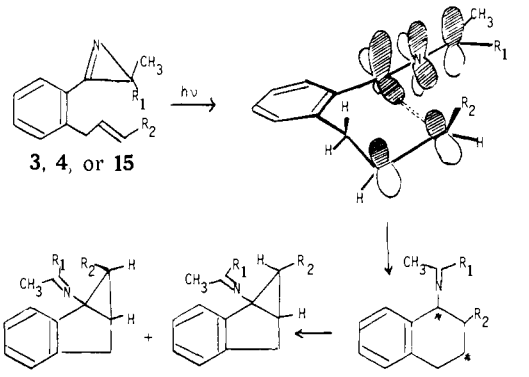
There exists a large body of compelling experimental evidence in the literature which indicates that the cycloaddition of 1,3-dipoles to alkenes are concerted processes.[31,32] The most popular model adopted for the geometry of approach of the dipole and dipolarophile assumes that the molecules are oriented in two parallel planes.[8] The transition state for cycloaddition with the nitrile ylides generated from the irradiation of azirines **38** and **42** allows easy attainment of the "par-



allel-plane approach" of the dipole and olefin and, consequently, intramolecular 1,3-dipolar cycloaddition readily occurs.

Inspection of molecular models of the nitrile ylides generated from the photolysis of *o*-allyl substituted 2*H*-azirines **3, 4,** and **15** shows that the methylene chain is not of sufficient length to readily allow the bent nitrile ylide[34-36] and double bond to approach each other in parallel planes. Since the "parallel plane orientation approach" cannot be easily attained here, an alternate nonconcerted mechanism for dipolar cycloaddition occurs. This pathway is outlined below (Scheme III).

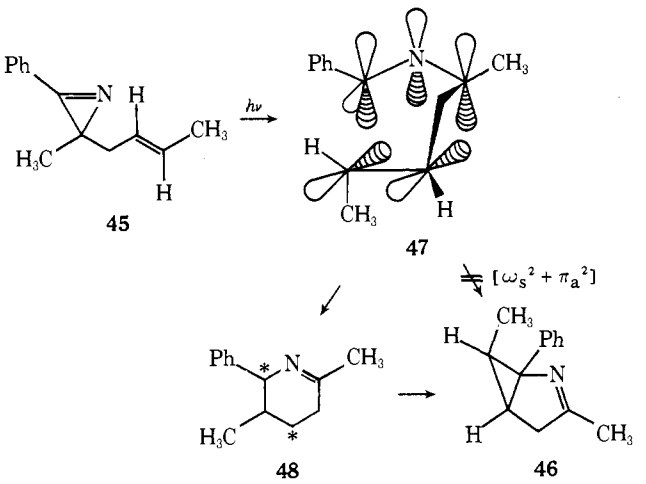
Scheme III



The 1,1-cycloaddition reaction is initiated by interaction of the terminal carbon of the olefin with the second LUMO of the nitrile ylide. The second LUMO of the dipole is perpendicular to the ylide plane, and presents a large vacancy of C_1 of the dipole for attack by the terminus of the neighboring double bond, without the possibility of simultaneous bonding at the C_3 carbon. In fact, the HOMO and second LUMO of the bent nitrile ylide bear a strong resemblance to the HOMO and LUMO of a singlet carbene. Carbenes, of course, are known to react rapidly with alkyl substituted double bonds.[37]

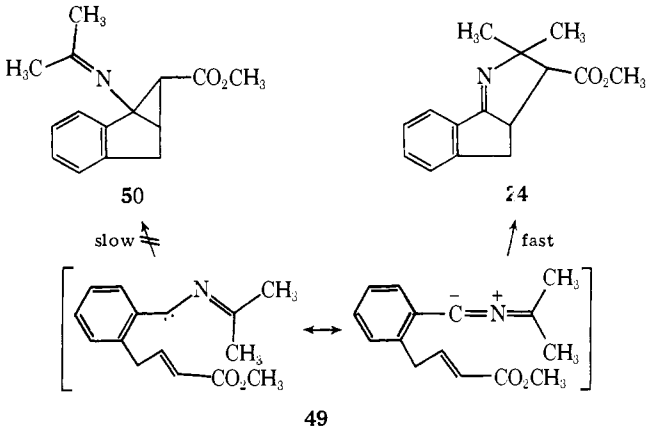
In an earlier report,[38] we suggested that the most favorable transition state for the 1,1-cycloaddition reaction is one in which the π orbitals of the nitrile ylide and olefinic double bond are orthogonal. This orthogonality could permit, in principle, the occurrence of an orbital symmetry allowed $[\omega_s^2 + \pi_a^2]$

cycloaddition. This unusual mode of addition was originally considered by us in order to account for the stereochemical results encountered with (*E*)-2-(2-butenyl)-2-methyl-3-phenyl-2*H*-azirine (**45**). Photolysis of this azirine produced the thermodynamically less favored endo azabicyclohexene isomer (**46**) as the exclusive photoproduct. Thus, the overall cycloaddition reaction with this system (i.e., **45** + $h\nu$ → **46**) corresponds to a complete inversion of stereochemistry about the double bond. We have now found that irradiation of azirine **4** gives rise to a mixture of stereoisomers. With this system, the structure of the major product obtained (80%) corresponds to retention of stereochemistry about the double bond. From this work it is clear that the stereochemical outcome is not that predicted by a concerted [$\omega_s^2 + \pi_a^2$] carbene addition. The stereochemical results previously encountered with **45** can now be rationalized by assuming that the trimethylene derivative **48**, obtained from **47** by stepwise bond closure, simply collapses to the kinetic product. This closure moves the phenyl and methyl groups increasingly farther apart and accounts for the formation of the thermodynamically less stable product. Collapse of **48** to the exo isomer would have resulted in a severe torsional barrier on ring closure.



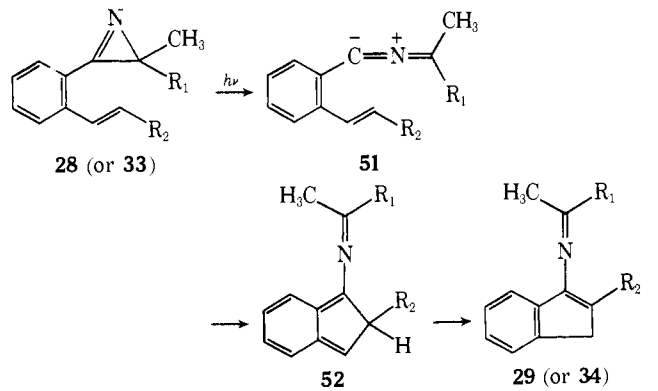
It is worthwhile to note that the cycloaddition sequence shown in Scheme III proceeds in a nonconcerted manner and bears a strong resemblance to the stepwise diradical mechanism suggested by Firestone to account for bimolecular 1,3-dipolar cycloadditions.[32] The fact that the nitrile ylide generated from the base treatment of imidoyl chloride **17** also undergoes 1,1-cycloaddition provides additional support for the generality of this type of internal cycloaddition reaction. Since our original report of this phenomenon appeared,[38] a related intramolecular carbene type of 1,1-cycloaddition of a nitrile imine has been reported by Garanti and co-workers.[39]

The photocycloaddition reaction of azirine **23** represents an interesting case which warrants some discussion. In contrast to the related *o*-allylphenyl substituted 2*H*-azirines which undergo 1,1-cycloaddition, this azirine cycloadds exclusively in the 1,3 sense. The formation of a 1,3-dipolar cycloadduct with this system is perfectly consistent with the principles of frontier MO theory.[23,40-42] According to the frontier orbital treatment of 1,3-dipolar cycloadditions, 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 of 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 most rapidly with electron-deficient alkenes,[21] since such a pair of addends possesses a narrow dipole-HOMO dipolarophile-LUMO gap.[43] Thus, the rate of internal 1,3-dipolar cycloaddition of the nitrile ylide (**49**) derived from azirine **23**



should proceed much more rapidly than that of the ylides derived from azirines **3**, **4**, and **15**. On the other hand, the effect of substitutents upon the rate of the intramolecular carbenelike cycloaddition should be controlled by the interaction of the alkene HOMO and the second LUMO of the nitrile ylide. Placement of an electron-withdrawing substituent on the double bond will lower both the HOMO and LUMO orbital energies and thereby diminish the rate of the carbenelike addition of the nitrile ylide. As a result of this unfavorable electronic factor, nitrile ylide **49** will be less likely to add in the 1,1 sense. In order for the 1,3-dipolar cycloaddition of **49** to occur, a slight distortion away from the strictly parallel plane approach of the dipole and dipolarophile will be necessary. The interplay of entropy and enthalpy factors will control the rate-determining activation process. With the above system, the enthalpy term is the dominant factor and the internal 1,3-dipolar cycloaddition process wins out.

Remaining for discussion are the internal cyclization reactions of the *o*-vinylphenyl substituted 2*H*-azirines. The formation of *N*-alkylideneindene-3-amines **29** and **34** from the irradiation of azirines **28** and **33** can be interpreted in terms of a mechanism which involves a nitrile ylide (**51**) intermediate.



Intramolecular reorganization of this species followed by a 1,5-sigmatropic hydrogen shift of the initially formed isoindene ring (**52**) readily rationalizes the formation of the final product. This mechanism is supported by the observation that the nitrile ylide intermediate can be trapped by the addition of an added dipolarophile (i.e., **28** → **31**). Several examples are also available in the literature which provide good analogy for the above cyclization.[4a] An alternate pathway would involve internal 1,1-cycloaddition followed by a rapid ring opening of a transient benzobicyclo[2.1.0]pentane to give isoindene **52**. The available data do not distinguish between these two possibilities. Finally, *o*-vinylphenyl substituted azirine **36** was found to undergo smooth internal 1,1-cycloaddition to give azabicyclo[4.1.0]heptene **37**. With this system, the dipole and

dipolarophile groups are properly aligned to allow ready attack of the vinyl group onto the vacant p orbital of the bent nitrile ylide.

In conclusion, it is noteworthy that the intramolecular photocycloaddition reaction of unsaturated 2*H*-azirines is proving to be a general, synthetically useful, and mechanistically intriguing process. It is evident from our data that a distortion from the normal "parallel plane approach of addends" can have a major effect on the course of the cycloaddition process. We are continuing to examine the effects of geometry and substituents on the reaction and will report additional findings at a later date.

Experimental Section[44]

General Procedure for the Preparation of *o*-Allylphenyl Substituted 2*H*-Azirines. The desired *o*-allylphenyl substituted 2*H*-azirines were prepared by a modified Neber reaction in which variously substituted 1-(*o*-allylphenyl)propan-1-ones were treated with *N,N*-dimethylhydrazine according to the method of Leonard and Zwanenburg.[13] The general procedure used for the synthesis of the *o*-allylphenyl substituted propan-1-ones involved the ortho lithiation of 2-aryl-4,1-dimethyl-Δ^2-oxazoline[45] with *n*-butyllithium followed by the addition of the appropriate allyl-substituted bromide according to the general procedure of Meyers[11] and Gschwend.[12] A typical procedure involves the addition of a 2.3 M *n*-butyllithium solution to a tetrahydrofuran solution of 2-phenyl-4,4-dimethyl-Δ^2-oxazoline[45] at −45 °C. The solution was kept at −45 °C for 1.5 h and was then transferred to a solution containing the appropriate allyl bromide in tetrahydrofuran at −45 °C. The mixture was allowed to warm to ambient temperature, stirred for 2 h, and poured into ether. After washing, drying, and removing the solvent, the resulting Δ^2-oxazoline was quaternarized with methyl iodide, reduced with sodium borohydride, and hydrolyzed with oxalic acid according to the general procedure of Meyers and coworkers.[46] The *o*-allyl substituted benzaldehyde was then treated with an appropriate Grignard reagent and the resulting alcohol was subjected to Jones oxidation.

The unsaturated ketone was then 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 mixture 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. Using these procedures the following 2*H*-azirines were synthesized.

3-(*o*-Allylphenyl)-2,2-dimethyl-2*H*-azirine (3) was prepared in 65% yield from 1-(*o*-allylphenyl)-2-methylpropan-1-one (bp 58–60 °C (0.1 mm); NMR (60 MHz) τ 8.85 (d, 6 H, J = 7.0 Hz), 6.62 (sept, 1 H, J = 7.0 Hz), 6.50 (d, 2 H, J = 6.0 Hz), 4.87–5.24 (m, 2 H), 3.84–4.40 (m, 1 H), 2.54–2.87 (m, 4 H)) by procedure B: bp 43–45 °C (0.3 mm); IR (neat) 3.35, 6.00, 7.22, 8.20, 10.25, 11.30, and 12.95 μ; NMR (60 MHz) τ 8.61 (s, 6 H), 6.27 (d, 2 H, J = 7.0 Hz), 4.85–5.15 (m, 2 H), 3.75–4.31 (m, 1 H), and 2.29–2.60 (m, 4 H); *m/e* 185 (M^+), 170 (base), 145, 130, 116, and 77; UV (methanol) 248 nm (ϵ 35 000).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.13; H, 8.22; N, 7.54.

(*E*)-3-(*o*-2-Butenylphenyl)-2,2-dimethyl-2*H*-azirine (4) was prepared in 56% yield from 1-(*o*-2-butenylphenyl)-2-methylpropan-1-one (bp 67–70 °C (0.02 mm); NMR (60 MHz) τ 8.85 (d, 6 H, J = 7.0 Hz), 8.37 (m, 3 H), 6.63 (sept, 1 H, J = 7.0 Hz), 6.59 (d, 2 H, J = 4.0 Hz), 4.50–4.80 (m, 2 H), 2.17–2.75 (m, 4 H)) by procedure A: bp 62–63 °C (0.2 mm); IR (neat) 3.40, 5.90, 7.00, 8.35, 10.30, and 13.05 μ; NMR ($CDCl_3$, 60 MHz) τ 8.62 (s, 6 H), 8.20–8.40 (m, 3 H), 6.30–6.50 (m, 2 H), 4.30–4.50 (m, 2 H), 2.10–2.80 (m, 4 H); *m/e* 199 (M^+), 184 (base), 170, 143, 115, 77; UV (methanol) 248 nm (ϵ 16 000).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.30; H, 8.75; N, 6.97.

3-(*o*-Allylphenyl)-2-methyl-2*H*-azirine (15) was prepared in 64% yield from 1-(*o*-allylphenyl)propan-1-one (bp 57–58 °C (0.1 mm); NMR (100 MHz) τ 8.92 (t, 3 H, J = 7.0 Hz), 7.20 (q, 2 H, J = 7.0 Hz), 6.52 (d, 2 H, J = 6.0 Hz), 5.0–5.2 (m, 2 H), 4.0–4.40 (m, 1 H), 2.52–3.00 (m, 4 H) by procedure B: bp 55–56 °C (0.2 mm); IR (neat) 3.40, 5.85, 6.90, 10.00, 10.85, and 13.00 μ; NMR (60 MHz) τ 8.67 (d, 3 H, J = 5.0 Hz), 7.80 (q, 2 H, J = 5.0 Hz), 6.17 (d, 2 H, J = 6.0 Hz), 4.83–5.13 (m, 2 H), 3.67–4.30 (m, 1 H), 2.40–2.77 (m, 3 H), 2.10–2.33 (m, 1 H); *m/e* 171 (M^+), 170, 156, 145 (base), 129, 115, and 77; UV (methanol) 247 nm (ϵ 36 000).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.25; H, 7.71; N, 7.99.

3-[*o*-(3-Methoxycarbonyl)-2-propenyl)phenyl]-2,2-dimethyl-2*H*-azirine (23) was prepared by ozonization of 3-(*o*-allylphenyl)-2,2-dimethyl-2*H*-azirine (**3**) followed by a Wittig reaction of the resulting aldehyde with carbomethoxymethylenetriphenylphosphorane.[47] A solution containing 1.0 g of **3** in 50 mL of methylene chloride was treated with ozone at −78 °C until the solution turned blue. To this cold solution was added 10 mL of dimethyl sulfide and the resulting mixture was allowed to stand at room temperature for 5 h. At the end of this time, 1.8 g of carbomethoxymethylenetriphenylphosphorane[47] was added and the reaction mixture was stirred for 14 h. The solvent was removed under reduced pressure and the residue was extracted with ether–hexane. The extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. Concentration of the solution left a yellow oil which was subjected to liquid–liquid partition chromatography.[48] The major component isolated (400 mg) was a clear oil whose structure was assigned as 3-[*o*-((3-methoxycarbonyl)-2-propenyl)phenyl]-2,2-dimethyl-2*H*-azirine (**23**): IR (neat) 3.35, 5.70, 6.90, 7.75, 8.50, 10.05, 11.25, and 12.95 μ; NMR (60 MHz) τ 8.60 (s, 6 H), 6.30 (s, 3 H), 6.10 (dd, 2 H, J = 6.0 and 2.0 Hz), 4.25 (td, 1 H, J = 16.0 and 2.0 Hz), 2.00–3.00 (m, 5 H); *m/e* 243 (M^+), 185, 184 (base), 170, 128, 78; UV (methanol) 243 nm (ϵ 12 600).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.24; H, 6.92; N, 5.70.

Preparation of *N*-(*p*-Nitrobenzyl)-*o*-allylbenzocarboximidoyl Chloride (17). *o*-Allylbenzoic acid was synthesized from 2-phenyl-4,4-dimethyl-2-oxazoline according to the general method of Meyers[11] and Gschwend:[12] mp 82–83 °C; NMR (60 MHz) τ 6.17 (d, 2 H, J = 6.0 Hz), 4.72–5.20 (m, 2 H), 3.60–4.38 (m, 1 H), 2.38–2.92 (m, 3 H), 1.88–2.10 (m, 1 H), and −2.10 (s, 1 H). To a solution containing 4.7 g of *o*-allylbenzoic acid, 0.3 mL of dimethylformamide, and 180 mL of ether at 0 °C was added 5.85 g of oxalyl chloride in 75 mL of

ether. The mixture was stirred at 5 °C for 15 h under a nitrogen atmosphere. The solvent and excess oxalyl chloride were removed under reduced pressure to give 5.12 g (94%) of *o*-allylbenzoic acid chloride. To a solution containing 5.1 g of the above acid chloride in 100 mL of ether at 0 °C was added 5.32 g of *p*-nitrobenzylamine in 50 mL of ether. After the addition was complete, the mixture was allowed to warm to room temperature and then 50 mL of a 1 M sodium hydroxide solution was added. The ether layer was separated from the basic aqueous layer, neutralized, dried over magnesium sulfate, and concentrated under reduced pressure to give 6.9 g (87%) of *p*-nitrobenzyl-*o*-allylbenzamide: mp 106–107 °C; IR (KBr) 3.08, 6.10, 6.21, 6.62 μ; UV (methanol) 270 nm (ϵ 11 100); NMR (60 MHz) τ 6.49 (d, 2 H, J = 7.0 Hz), 5.48 (d, 2 H, J = 6.0 Hz), 4.90–5.29 (m, 2 H), 3.77–3.43 (m, 1 H), 2.48–3.11 (m, 6 H), and 1.98 (d, 2 H, J = 8.0 Hz); *m/e* 296 (M^+), 106 (base).

Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44; N, 9.45. Found: C, 68.78; H, 5.48; N, 9.54.

To a solution containing 310 mg of the above amide in 5 mL of benzene under a nitrogen atmosphere was added 250 mg of phosphorus pentachloride in 5 mL of benzene. The mixture was heated at 60 °C until the evolution of hydrogen chloride gas had ceased. The solvent and phosphoryl chloride were removed under reduced pressure leaving behind a pale yellow oil which was identified as *N*-(*p*-nitrobenzyl)-*o*-allylbenzocarboximidoyl chloride (**17**) on the basis of its spectral properties: IR (neat) 6.06, 6.21, 6.62, 7.41, 9.01, 9.83, 10.00, 11.60, and 13.55 μ; NMR (60 MHz) τ 6.42 (d, 2 H, J = 6.0 Hz), 5.08 (s, 2 H), 4.90–5.06 (m, 2 H), 3.81–4.46 (m, 1 H), 2.59–2.88 (m, 4 H), 2.50 (d, 2 H, J = 8.0 Hz), and 1.91 (d, 2 H, J = 8.0 Hz). The imidoyl chloride was quite hygroscopic and was used immediately in the next step.

Preparation of 3-(*o*-Vinylphenyl)-2,2-dimethyl-2*H*-azirine (28). A sample of 1-(*o*-vinylphenyl)-2-methylpropan-1-one (bp 46–50 °C (0.1 mm); NMR (60 MHz) τ 8.87 (d, 6 H, J = 7.0 Hz), 6.73 (sept, 1 H, J = 7.0 Hz), 4.70 (d, 1 H, J = 10.0 Hz), 4.40 (d, 1 H, J = 16 Hz), 3.10 (dd, 1 H, J = 16.0 and 10.0 Hz), 2.44–2.77 (m, 4 H)) was prepared by treating *o*-formylstyrene with isopropylmagnesium bromide followed by Jones oxidation of the resulting alcohol. 3-(*o*-Vinylphenyl)-2,2-dimethyl-2*H*-azirine (**28**) was prepared in 50% yield from the hydrazonium iodide of the above ketone using procedure B: bp 43–45 °C (0.1 mm); IR (neat) 3.30, 5.75, 6.70, 7.25, 8.25, 10.00, 10.80, 11.25, 12.85, and 13.05 μ; NMR (60 MHz) τ 8.60 (s, 6 H), 4.54 (d, 1 H, J = 10.0 Hz), 4.17 (d, 1 H, J = 18.0 Hz), 2.17–2.79 (m, 5 H); UV (methanol) 232 nm (ϵ 41 000), 261 (31 000); *m/e* 171 (M^+), 156, 131, 115 (base), 103, and 77.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.06; H, 7.62; N, 8.14.

Preparation of 3-(*o*-1-Propenylphenyl)-2-methyl-2*H*-azirine (33). The hydrazonium iodide salt derived from 1-(*o*-allylphenyl)propan-1-one was heated at reflux in ethyl acetate which contained a trace of acid. These conditions were sufficient to cause isomerization of the double bond into conjugation with the phenyl group. Removal of the solvent gave the hydrazonium salt of 3-(*o*-1-propenylphenyl)propan-1-one, mp 120–121 °C. This material was converted to 3-(*o*-1-propenylphenyl)-2-methyl-2*H*-azirine (**33**) by procedure B in 81% yield, bp 57–60 °C (0.2 mm): IR (neat) 3.30, 5.70, 6.70, 6.85, 10.20, and 13.00 μ; NMR (100 MHz) τ 8.66 (d, 3 H, J = 6.0 Hz), 7.96 (dd, 3 H, J = 8.0 and 2.0 Hz), 7.72 (q, 1 H, J = 6.0 Hz), 3.42 (dd, 1 H, J = 16.0 and 8.0 Hz), 2.0–2.6 (m, 5 H); UV (methanol) 262 nm (ϵ 36 000) and 236 (6000).

Anal. Calcd for $C_{12}H_3N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.40; H, 7.59; N, 8.25.

Preparation of 3-Phenyl-2-(*o*-vinylphenyl)-2*H*-azirine (36). A solution containing 3 g of 2-phenylindene[50] in 30 mL of methylene chloride was treated with ozone at −78 °C. The ozonization was continued until the solution turned blue. To this cold solution was added 20 mL of methyl sulfide and the resulting mixture was allowed to stand at room temperature for 5 h. At the end of this time the solvent and excess methyl sulfide was removed under reduced pressure and the residue was taken up in ether, washed with water, dried, and concentrated under reduced pressure to give 2.1 g (62%) of *o*-formyldeoxybenzoin: mp 90–91 °C; IR (KBr) 5.80, 6.30, 7.40, 8.10, 9.90, 13.00, 13.20, and 14.40 μ; NMR (100 MHz) τ 5.40 (s, 2 H), 2.1–2.9 (m, 9 H), and 0.16 (s, 1 H).

To a solution containing 5.1 g of methyltriphenylphosphonium bromide in 50 mL of ether was added 6.5 mL of a 2.2 M *n*-butyllithium solution at 0 °C. The mixture was stirred at 25 °C for 1 h and was then added to a solution containing 2.0 g of *o*-formyldeoxybenzoin in 100 mL of ether at 0 °C. The solution was allowed to stir at 25 °C for 14 h and was then diluted with ether. The triphenylphosphine oxide which precipitated was filtered and the solution was concentrated under reduced pressure to give a pale yellow oil which was chromatographed over silica using ether as the eluent. The major component isolated (200 mg) was a colorless oil whose spectral properties indicated it to be *o*-vinyldeoxybenzoin: IR (neat) 3.30, 5.90, 6.80, 7.40, 8.15, 9.25, 10.80, 12.90, and 14.40 μ; NMR (100 MHz) τ 5.80 (s, 2 H), 4.84 (dd, 1 H, J = 8.0 and 1.5 Hz), 4.48 (dd, 1 H, J = 16.0 and 1.5 Hz), 3.28 (dd, 1 H, J = 16.0 and 8.0 Hz), and 1.8–2.9 (m, 9 H).

This unsaturated ketone was converted to 3-phenyl-2-(*o*-vinylphenyl)-2*H*-azirine (**36**) using the general method B: bp 120–122 °C (0.01 mm); IR (neat) 5.60, 6.02, 6.80, 10.00, 10.80, 13.00, and 14.40 μ; NMR (100 MHz) τ 6.50 (s, 1 H), 4.60 (dd, 1 H, J = 10.0 and 2.0 Hz), 4.24 (dd, 1 H, J = 16.0 and 2.0 Hz), 1.90–3.00 (m, 10 H); UV (methanol) 245 nm (ϵ 15 000); *m/e* 219 (M^+), 218, 115, 105 (base), and 77.

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C 87.48, H, 6.14; N, 6.46.

Preparation of 3-(*o*-(3-Butenylphenyl)-2*H*-azirine (38). A sample of *o*-(3-butenyl)styrene (bp 41–42 °C (0.05 mm); NMR τ 7.56–7.80 (m, 2 H), 7.30 (t, 2 H, J = 8.0 Hz), 4.96–5.12 (m, 2 H), 4.80 (d, 1 H, J = 10.0 Hz), 4.46 (d, 1 H, J = 18.0 Hz), 4.0–4.4 (m, 1 H), 3.12 (dd, 1 H, J = 18.0 and 10.0 Hz), 2.92 (m, 3 H), 2.50–2.68 (m, 1 H)) was prepared by a Wittig reaction of methyltriphenylphosphonium bromide and *o*-(3-butenyl)benzaldehyde.

To an ice-cooled solution containing 1.04 g of sodium azide in 25 mL of acetonitrile was added a solution containing 1.65 g of iodine monochloride in 5 mL of acetonitrile. The resulting mixture was allowed to stir for an additional 30 min at 0 °C and then a solution containing 1.5 g of *o*-(3-butenyl)styrene in 5 mL of acetonitrile was added dropwise. The solution was allowed to stir for 3 h at 0 °C and was then extracted with ether. The ether layer was washed with a 5% sodium thiosulfate solution and water, dried over anhydrous magnesium sulfate, and concentrated to give 1-azido-2-iodo-1-(*o*-(3-butenyl)phenyl)ethane: NMR (60 MHz) τ 7.4–7.7 (m, 2 H), 7.0–7.3 (m, 2 H), 6.67 (d, 2 H, J = 7.4 Hz), 4.84–5.17 (m, 3 H), 3.99–4.63 (m, 1 H), 2.80 (m, 4 H).

The above iodine azide adduct was taken up in 40 mL of ether, 1.3 g of potassium *tert*-butoxide was added, and the mixture was allowed to stir at 0 °C for 9 h. The ether layer was then washed with water, dried, and concentrated to give 1.8 g (96%) of 1-azido-1-(*o*(3-butenyl)phenyl)ethylene: IR (neat) 4.65 μ; NMR (60 MHz) τ 7.4–7.8 (m, 2 H), 7.0–7.38 (m, 2 H), 5.18–5.40 (m, 2 H), 4.8–5.0 (m, 2 H), 3.8–4.6 (m, 1 H), 2.60 (m, 4 H).

A 100-mg sample of the above vinyl azide was heated at reflux in 5 mL of toluene for 1 h. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate using a 15% ethyl acetate–hexane mixture as the eluent to give 30 mg (35%) of 3-(*o*-butenyl)phenyl)-2*H*-azirine (**38**): IR (neat) 3.30, 5.98, 6.25, 6.80, 7.80, 10.00, and 13.00 μ; NMR (60 MHz) τ 8.33 (s, 2 H), 7.53 (q, 2 H, J = 8.0 Hz), 6.80 (t, 2 H, J = 8.0 Hz), 4.8–5.2 (m, 2 H), 3.9–4.47 (m, 1 H), 2.20–2.60 (m, 4 H); *m/e* 171 (M^+), 170 (base), 156, 143, 130, 117, 77.

3-(*o*-3-Butenylphenyl)-2,2-dimethyl-2*H*-azirine (41) was prepared in 62% yield from 1-(*o*-3-butenylphenyl)-2-methylpropan-1-one (bp 72–73 °C (0.5 mm); NMR (100 MHz) τ 8.80 (d, 6 H, J = 8.0 Hz), 7.48–7.76 (m, 2 H), 7.16 (t, 2 H, J = 8.0 Hz), 6.68 (sept, 1 H, J = 8.0 Hz), 4.88–5.12 (m, 2 H), 3.93–4.36 (m, 1 H), 2.40–2.88 (m, 4 H)) by procedure B: bp 45–46 °C (0.2 mm); IR (neat) 3.35, 5.70, 6.00, 6.70, 7.25, 8.20, 9.95, 10.85, 11.25, and 13.05 μ; NMR (100 MHz) τ 8.60 (s, 6 H), 7.40–7.82 (m, 2 H), 6.96 (t, 2 H, J = 8.0 Hz), 4.88–5.08 (m, 2 H), 4.00–4.32 (m, 1 H), 2.60–2.80 (m, 3 H), and 2.20–2.26 (m, 1 H); *m/e* 199 (M^+), 157 (base), 131, 117, and 77; UV (methanol) 250 nm (ϵ 46 900).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.30; H, 8.75; N, 6.97.

Preparation of 2-(2,2-Dimethyl-2*H*-azirin-3-yl)benzenepropanal (42). A solution containing 1.0 g of 3-(*o*-3-butenyl)phenyl)-2,2-dimethyl-2*H*-azirine (**41**) in 50 mL of methanol was treated with a stream of ozone at −78 °C until the solution turned blue. To this cold solution was added 10 mL of dimethyl sulfide and the resulting solution was allowed to stand at room temperature for 5 h. The solvent and excess dimethyl sulifide were removed under reduced pressure and

the residue was taken up in ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.0 g of 2-(2,2-dimethyl-2*H*-azirine-3-yl)benzenepropanal (**42**) as a colorless oil: IR (neat) 3.30, 5.60, 6.75, 7.15, 8.80, 9.30, 10.20, and 12.90 μ; NMR (100 MHz) τ 8.60 (s, 6 H), 7.16 (t, 2 H, J = 8.0 Hz), 6.64 (t, 2 H, J = 8.0 Hz), 2.30–2.60 (m, 4 H), 0.24 (s, 1 H); *m/e* 201 (M^+), 184, 159, 144, 131, 117 (base), and 77; UV (methanol) 275 (nm (ϵ 16 100) and 245 (39 000).

Irradiation of 3-(*o*-Allylphenyl)-2,2-dimethyl-2*H*-azirine (3). Photolysis of a sample (100 mg) of **3** in 150 mL of benzene for 20 min using a Vycor filter sleeve afforded a quantitative yield of 6,6a-dihydro-*N*-(isopropylidene)cycloprop[*a*]inden-1a(1*H*)-amine (**5**): IR (neat) 3.45, 6.10, 6.80, 7.40, 13.15 μ; NMR (60 MHz) τ 9.39 (t, 1 H, J = 4.5 Hz), 8.60 (dd, 1 H, J = 8.0 and 4.5 Hz), 7.90–8.30 (m, 1 H), 8.11 (s, 3 H), 7.90 (s, 3 H), 7.20 (d, 1 H, J = 17.0 Hz), 6.65 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.91 (m, 4 H). Chromatography of this material on a thick layer plate using a 15% ethyl acetate–hexane mixture gave 6,6a-dihydrocycloprop[*a*]inden-1a(1*H*)-amine (**6**) as the only identifiable product: IR (neat) 3.00, 3.40, 6.20, 13.10, 13.80 μ; NMR (60 MHz) τ 9.64 (t, 1 H, J = 4.5 Hz), 8.63 (dd, 1 H, J = 9.0 and 4.5 Hz), 8.0–8.30 (m, 1 H), 7.80 (s, 2 H, exchanged with D_2O), 7.26 (d, 1 H, J = 17.0 Hz), 6.76 (dd, 1 H, J = 17.0 and 6.0 Hz), and 2.65–2.91 (m, 4 H); UV (methanol) 247 nm (ϵ 550); *m/e* 145 (M^+), 144 (base), 143, 129, 116, 115, 114, and 77.

A benzenesulfonamide derivative of the amine was prepared by treating a mixture of 80 mg of **6**, 4 mL of water, and 1 mL of a 10% sodium hydroxide solution with 4 drops of benzenesulfonyl chloride. The precipitate that formed was cooled and recrystallized from ethanol to give 60 mg of 6,6a-dihydro-*N*-(benzenesulfonyl)cycloprop[*a*]-inden-1a(1*H*)-amine: mp 138–139 °C; IR (KBr) 3.10, 6.20, 7.10, 7.60, 8.60, 9.20, and 13.15 μ; NMR (60 MHz) τ 9.58 (t, 1 H, J = 5.0 Hz), 8.53 (dd, 1 H, J = 8.0 and 5.0 Hz), 7.70–7.90 (m, 1 H), 7.33 (d, 1 H, J = 16.0 Hz), 6.80 (dd, 1 H, J = 16.0 and 8.0 Hz), 4.33 (s, 1 H), and 2.25–3.20 (m, 9 H); UV (methanol) 275 nm (ϵ 3300) and 265 (5000); *m/e* 285 (M^+), 220, 144 (base), 129, 116, and 77.

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.33; H, 5.31; N, 4.91; S, 11.24. Found: c, 67.07; H, 5.35; N, 4.87; S, 11.13.

The photolysis of **3** was also carried out in the presence of methyl acrylate. A solution containing 160 mg of **3** and 20 mL of methyl acrylate in 120 mL of benzene was irradiated for 20 min using a Vycor filter sleeve. Removal of the solvent followed by thick layer chromatography afforded 90 mg of 2-(*o*-allylphenyl)-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**7**): IR (neat) 3.45, 5.80, 7.00, 8.25, 8.65, and 13.20 μ; NMR (60 MHz) τ 8.80 (s, 3 H), 8.43 (s, 3 H), 6.50–7.07 (m, 3 H), 6.27 (s, 3 H), 4.80–5.20 (m, 2 H), 3.67–4.33 (m, 1 H), and 2.73 (m, 4 H); UV (methanol) 240 nm (ϵ 7050); *m/e* 271 (M^+), 256, 224, 212 (base).

Irradiation of (*E*)-3-(*o*-2-Butenylphenyl)-2,2-dimethyl-2*H*-azirine (4). A solution containing 500 mg of **4** in 1 L of benzene was irradiated for 20 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a clear oil which was identified as a mixture of *endo*- (20%) (**8**) and *exo*- (80%) 1-methyl-6,6a-dihydro-*N*-(isopropylidene)cycloprop[*a*]inden-1a(1*H*)-amine (**9**). Thick layer chromatography of the oil resulted in the separation of the endo (**10**) and exo (**11**) isomers of 1-methyl-6,6a-dihydrocycloprop[*a*]inden-1a(1*H*)-amine. The endo isomer (**10**) showed the following spectral properties: IR (neat) 3.50, 6.00, 7.10, 9.20, 13.15 μ; NMR (60 MHz) τ 9.49 (d, 3 H, J = 6.0 Hz), 8.15–8.89 (m, 2 H), 7.79 (s, 2 H, exchanged with D_2O), 7.39 (d, 1 H, J = 18.0 Hz), 6.83 (dd, 1 H, J = 18.0 and 6.0 Hz), 2.70–3.00 (m, 4 H); UV (methanol) 270 nm (ϵ 1800) and 265 (1800); *m/e* 159 (M^+), 148, 144 (base), 130, 118, 78. The spectral properties of the exo isomer (**11**) showed the following peaks: IR (neat) 3.50, 6.00, 6.85, 7.60, 8.50, 9.85, 10.35, 13.30, and 13.85 μ; NMR (60 MHz) τ 9.30–9.60 (m, 1 H), 8.75 (d, 3 H, J = 6.0 Hz), 8.50–8.93 (m, 1 H), 7.93 (s, 2 H, exchanged with D_2O), 7.27 (d, 1 H, J = 17.0 Hz), 6.77 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.80–2.95 (m, 4 H); *m/e* 159 (M^+), 158, 144 (base), 130, 118, 90, and 77; UV (methanol) 277 nm (ϵ 2200) and 270 (2500).

Both the endo and exo isomers were converted to the corresponding benzenesulfonamide derivatives. Endo isomer: mp 116–118 °C; IR (KBr) 3.00, 7.60, 8.50, 9.05, 10.80, 11.65, 12.95, 13.10, and 14.45 μ; NMR (60 MHz) τ 9.50 (d, 3 H, J = 6.0 Hz), 7.80–8.80 (m, 2 H), 7.50 (d, 1 H, J = 18.0 Hz), 6.83 (dd, 1 H, J = 18.0 and 8.0 Hz), 3.30 (s, 1 H), 2.17–3.00 (m, 9 H); UV (methanol) 277 nm (ϵ 1400) and 268 (1800); *m/e* 299 (M^+), 158 (base), 144, 131, 117, 77. The exo benzenesulfonamide derivative (mp 165–166 °C) showed the following spectral properties: IR (KBr) 3.00, 7.50, 8.45, 9.05, 13.25 μ; NMR (60 MHz) τ 9.43 (pent, 1 H, J = 6.0 Hz), 8.83 (d, 3 H, J = 6.0 Hz), 7.95–8.20 (m, 1 H), 7.29 (d, 1 H, J = 18.0 Hz), 6.79 (dd, 1 H, J = 18.0 and 6.0 Hz), 4.13 (s, 1 H), 2.60–3.24 (m, 9 H); UV (methanol) 275 nm (ϵ 1000) and 265 (1300).

Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.19; H, 5.73; N, 4.68; S, 10.69. Found: C, 68.17; H, 5.72; N, 4.73; S, 10.76.

The photolysis of **4** was also carried out in the presence of methyl acrylate. A solution containing 400 mg of **4** and 20 mL of methyl acrylate in 120 mL of benzene was irradiated under a nitrogen atmosphere for 20 min using a Vycor filter. Removal of the solvent followed by thick layer chromatography gave 460 mg (80%) of 2-(*o*-2-butenylphenyl)-4-carbomethoxy-5,5-dimethyl-Δ'-pyrroline (**13**): IR (neat) 3.40, 5.75, 6.95, 8.60, and 13.15 μ; NMR (60 MHz) τ 8.83 (s, 3 H), 8.47 (s, 3 H), 8.30–8.50 (m, 3 H), 6.68–7.10 (m, 3 H), 6.30–6.60 (m, 2 H), 6.27 (s, 3 H), 4.45–4.60 (m, 2 H), and 2.73 (m, 4 H); *m/e* 285 (M^+), 256, 220 (base), 196, 171, 131, 115, 91, and 77; UV (methanol) 240 nm (ϵ 7000) and 230 (7500).

Irradiation of 3-(*o*-Allylphenyl)-2-methyl-2*H*-azirine (15). A solution containing 100 mg of **15** in 150 mL of benzene was irradiated for 20 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick layer chromatography using a 15% ethyl acetate–hexane mixture as the eluent. The only identifiable band isolated from the thick layer plate was 6,6a-dihydrocycloprop[*a*]-inden-1a(1*H*)-amine (**6**). This amine was identical in every detail with that obtained from the photolysis of 3-(*o*-allylphenyl)-2,2-dimethyl-2*H*-azirine (**3**). Analysis of the crude photolysate clearly showed the presence of 6,6a-dihydro-*N*-(ethylidene)cycloprop[*a*]-indene-1a(1*H*)-amine (**16**): NMR (60 MHz) τ 9.43 (t, 1 H, J = 4.0 Hz), 8.33–8.70 (m, 1 H), 8.50 (dd, 1 H, J = 8.0 and 4.0 Hz), 8.00 (d, 3 H, J = 5.0 Hz), 7.27 (d, 1 H, J = 16.0 Hz), 6.67 (dd, 1 H, J = 16.0 and 6.0 Hz), 2.58–3.00 (m, 4 H), 2.10 (q, 1 H, J = 5.0 Hz). This material could not be purified since it readily hydrolyzed to amine **6** upon standing.

Treatment of *N*-(*p*-Nitrobenzyl)-*o*-allylbenzocarboximidoyl Chloride (17) with Triethylamine. To a solution containing imidoyl chloride **17** in 5 mL of anhydrous benzene at 5 °C under a nitrogen atmosphere was added 210 mg of freshly distilled triethylamine. After stirring for 20 h at room temperature the solvent was removed under reduced pressure and the crude residue was chromatographed on a Florisil column. The major component isolated contained 67 mg (25%) of a pale yellow oil whose structure was assigned to 6,6a-dihydro-*N*-(*p*-nitrobenzylidine)cycloprop[*a*]inden-1a(1*H*)-amine (**20**): IR (neat) 6.70, 7.40, 9.01, and 10.90 μ; UV (cyclohexane) 306 nm (ϵ 9700); NMR (60 MHz) τ 9.08 (t, 1 H, J = 5.0 Hz), 8.12 (dd, 1 H, J = 8.0 and 5.0 Hz), 7.62 (m, 1 H), 7.12 (d, 1 H, J = 17.0 Hz), 6.60 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.2–2.9 (m, 4 H), 2.10 (d, 2 H, J = 8.0 Hz), 1.80 (d, 2 H, J = 8.0 Hz), and 1.42 (s, 1 H); *m/e* 278 (M^+ and base), 231, 129, 128, 115, and 77.

The structure of this material was further verified by treating 36 mg of **6** obtained from the photolysis of azirine **3** with 41 mg of *p*-nitrobenzaldehyde and 2 mg of *p*-toluenesulfonic acid in 12 mL of toluene at 120 °C for 45 min. Removal of the solvent and purification of the residue by thick layer chromatography afforded **20** which was identical with that obtained from the base treatment of imidoyl chloride **17**.

When imidoyl chloride **17** was treated with triethylamine in the presence of excess methylacrylate (4-mol excess), a mixture of *cis*- (31%) and *trans*- (38%) methyl 2-(*o*-allylphenyl)-5-(*p*-nitrophenyl)-1-pyrroline-4-carboxylate (**19**) was obtained. The cis isomer showed signals in the NMR at τ 6.43–7.04 (m, 3 H), 6.25 (s, 3 H), 6.12–6.28 (m, 2 H), 4.88–5.31 (m, 2 H), 3.67–4.50 (m, 2 H), 2.60–2.86 (m, 4 H), 2.68 (d, 2 H, J = 8.0 Hz), and 1.92 (d, 2 H, J = 8.0 Hz); *m/e* 245, 244, 216 (base), 186, 170, 122, and 94; UV (cyclohexane) 255 nm (ϵ 13 400). The trans isomer showed signals in the NMR at τ 6.85 (s, 3 H), 6.06–6.67 (m, 5 H), 4.83–5.23 (m, 2 H), 3.77–4.40 (m, 2 H), 2.42–2.85 (m, 6 H), and 1.90 (d, 2 H, J = 8.0 Hz); *m/e* 248, 246, 129, 115, 85, and 83 (base); UV (cyclohexane) 225 nm (ϵ 13 200).

Irradiation of 3-[*o*-(3-Methoxycarbonyl)-2-propenyl)phenyl]-2,2-dimethyl-2*H*-azirine (23). A 100-mg sample of azirine **23** in 150 mL of benzene was irradiated for 20 min with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Evaporation of the solvent left a yellow oil which was subjected to liquid–liquid partition chromatography.[48] The major product isolated (85%) was a clear oil whose

structure was identified as methyl 2,3,3a,4-tetrahydro-2,2-dimethylindeno[1,2-*b*]pyrrole-3-carboxylate (**24**) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (neat) 3.30, 5.75, 6.00, 6.95, 8.70, 11.50, and 13.10 μ; NMR (60 MHz) τ 8.80 (s, 3 H), 8.37 (s, 3 H), 7.43 (dd, 1 H, J = 16.0 and 8.0 Hz), 7.27 (d, 1 H, J = 10.0 Hz), 6.75 (dd, 1 H, J = 16.0 and 8.0 Hz), 6.23 (s, 3 H), 5.75–6.33 (m, 1 H), 2.17–2.90 (m, 4 H): *m/e* 243 (M^+), 185, 184 (base); UV (methanol) 245 nm (ϵ 9160).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.32; H, 7.18; N, 5.84.

An authentic sample of **24** was prepared in the following fashion. A mixture containing 6.6 g of 2-indanone and 17 g of carbomethoxymethylenetriphenylphosphorane was heated at 150 °C for 3 h. The resulting oil was passed through a silica gel column using ether as the solvent. The major component obtained (5.5 g, 58%) was identifed as 2-(carbomethoxymethylene)indane (**25**): bp 105–106 °C (0.1 mm); IR (neat) 3.35, 5.68, 6.15, 13.10, and 13.80 μ; NMR (60 MHz) τ 6.6 (broad s, 2 H), 6.5 (broad s, 2 H), 6.30 (s, 3 H), 3.40 (broad s, 1 H), 2.50–3.00 (m, 4 H). To a 0.94-g sample of the above compound was added 10 mL of a sodium dichromate solution prepared by dissolving 39.5 g of sodium dichromate in 5.5 mL of acetic anhydride and 100 mL of acetic acid. The reaction mixture was stirred for 15 h at room temperature and was then diluted with water and extracted with ether. The ether extracts were washed with a 5% sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure. Chromatography of the residue through silica gel using a 20% acetone–hexane mixture gave 400 mg (3) of 2-(carbomethoxymethylene)-1-indanone (**26**): mp 94–95 °C; IR (KBr) 5.65, 6.10, 9.70, and 13.80 μ; NMR (60 MHz) 6.20 (s, 3 H), 5.90 (d, 2 H, J = 2.5 Hz), 3.20 (t, 1 H, J = 25. Hz), 2.0–2.8 (m, 4 H).

To a mixture containing 300 mg of indanone **26** in 4 mL of 2-nitropropane and 5 mL of ether was added several drops of Triton B. The mixture was heated at reflux for 4 h and then stirred at home temperature for an additional 15 h. The solution was taken up in ether, washed with a saturated ammonium chloride solution, dried, and evaporated under reduced pressure to give 200 mg of 2-(1-carbomethoxy-2-methyl-2-nitropropyl)-1-indanone (**27**): mp 126–128 °C; IR (KBr) 5.80, 6.40, 7.20, and 13.10 μ; NMR (60 MHz) τ 8.20 (s, 6 H), 6.70–7.60 (m, 3 H), 6.60 (s, 3 H), 5.70 (d, 1 H, J = 2.0 Hz), 2.20–2.80 (m, 4 H). A solution containing 150 mg of indanone **27** in 5 mL of acetic acid was heated at 50–60 °C and then 350 mg of powdered zinc was added. After stirring at 60 °C for 3 h, the reaction mixture was cooled and taken up in ether. The ethereal layer was washed with a 5% sodium bicarbonate solution, dried, concentrated, and chromatographed through a Florisil column. The major component isolated (60 mg) was identical in every detail with a sample of **24** obtained from the photolysis of azirine **23**.

Irradiation of 3-(*o*-Vinylphenyl)-2,2-dimethyl-2*H*-azirine (28). A solution containing 100 mg of **28** in 150 mL of benzene was irradiated for 20 min through a Vycor filter sleeve. Removal of the solvent left a pale yellow oil whose structure was assigned a 1-*N*-isopropylideneindene-3-amine (**29**): NMR (60 MHz) τ 8.17 (s, 3 H), 7.70 (s, 3 H), 6.64 (d, 2 H, J = 2.5 Hz), 4.50 (t, 1 H, J = 2.5 Hz), 2.85–2.94 (m, 4 H).

The structure of this material was verified by the chemical reactions outlined below. Subjection of the photolysate to thick layer chromatography gave 1-indanone in 90% yield. To a solution containing 190 mg of the crude photolysate in 10 mL of methanol was added excess sodium borohydride. The mixture was stirred for 30 min at room temperature and the excess sodium borohydride destroyed by the addition of a 10% hydrochloric acid solution. The solution was then extracted with ether, dried over magnesium sulfate, and evaporated to give 170 mg of light yellow oil whose structure was identified as *N*-isopropylindane-3-amine (**30**) on the basis of its spectral properties and by comparison with an authentic sample: IR (neat)3.35, 6.80, 7.25, 8.50, and 13.40 μ; NMR (60 MHz) τ 8.86 (d, 6 H, J = 6.5 Hz), 8.55 (s, 1 H), exchanged from D_2O), 6.67–8.34 (m, 4 H), 5.72 (t, 1 H, J = 7.0 Hz), 2.57–3.00 (m, 4 H).

An authentic sample of **30** was prepared by heating a mixture of 2 g of 1-indanone, 3 mL of isopropylamine, 1 g of anhydrous magnesium sulfate, 1 g of sodium acetate, and 5 drops of acetic acid at 125 °C for 8 h. The mixture was taken up in ether, filtered, evaporated, and distilled at 60–62 °C (0.1 mm) to give 2.4 g (95%) of 1-*N*-isopropylindanimine: NMR (60 MHz) τ 8.79 (d, 6 H, J = 6.5 Hz), 6.79–7.44 (m, 4 H), 6.30 (sept, 1 H, J = 6.5 Hz), 2.60–2.80 (m, 3 H), and 2.10–2.30 (m, 1 H). A 500-mg sample of the above imine was reduced with sodium borohydride in methanol to give a sample of *N*-isopropyindanamine (**30**) which was identical with the material obtained from the reduction of the photolysate derived from azirine **28.**

Irradiation of 3-(*o*-1-Propenylphenyl)-2-methyl-2*H*-azirine (33). A solution containing 100 mg of **33** in 150 mL of benzene was irradiated for 20 min with a Vycor filter sleeve. Removal of the solvent left a pale oil whose spectral properties indicated it to be *N*-ethylidene-2-methylindene-3-amine (**34**): NMR (100 MHz) τ 8.00 (s, 3 H), 7.80 (d, 3 H, J = 6 Hz), 6.72 (s, 2 H), 2.40–3.00 (m, 4 H), and 2.00 (q, 1 H, J = 6.0 Hz). Chromatography of the oil on a thick layer plate gave a single component which was identified as 2-methyl-1-indanone (**35**) on the basis of its spectral properties and comparison with an authentic sample:[51] NMR (60 MHz) τ 8.73 (d, 3 H, J = 8.0 Hz), 7.20–7.67 (m, 2 H), 6.67 (dd, 1 H, J = 17.0 and 9.0 Hz), 2.27–2.99 (m, 4 H).

Irradiation of 3-Phenyl-2-(*o*-vinylphenyl)-2*H*-azirine (36). A solution containing 100 mg of **36** in 150 mL of benzene was irradiated under an argon atmosphere for 10 min using a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate using a 15% ethyl acetate–hexane mixture as the eluent. The only product that could be isolated was a colorless oil whose structure was assigned as 2-aza-3-phenyl-6,7-benzobicyclo[4.1.0]heptene (**37**) on the basis of the following data: IR (neat) 3.20, 6.10, 11.05, 13.00, 14.30 μ; NMR (100 MHz) τ 9.80 (t, 1 H, J = 5.0 Hz), 7.48 (dd, 1 H, J = 8.0 and 5.0 Hz), 7.28 (dd, 1 H, J = 8.0 and 5.0 Hz), 2.3–2.8 (m, 9 H), and 1.70 (s, 1 H). Spin decoupling of the signal at τ 9.80 caused the doublet of doublets at τ 7.48 and 7.28 to collapse to a doublet (J = 8.0 Hz): UV (methanol) 260 nm (ϵ 480), 250 (670), and 220 (1800); *m/e* 219 (M^+), 218 (base), 115, 105, and 77.

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.92; H, 6.14; N, 6.08.

Irradiation of 3-[*o*-(3-Butenylphenyl)]-2*H*-azirine (38). A 100-mg sample of **38** in 150 mL of benzene was irradiated for 20 min under a nitrogen atmosphere using a Vycor filter sleeve. Removal of the solvent left a yellow oil which was distilled at 85 °C (0.01 mm) to give 40 mg of a colorless oil whose structure is assigned as 3,3a,4,5-tetrahydro-2*H*-benz[*g*]indole (**39**) on the basis of its spectral properties and by an independent synthesis: IR (neat) 2.90, 6.10, 7.40, 9.80, 10.80, 11.60, 12.70, and 13.60 μ; NMR (100 MHz) τ 8.20–8.60 (m, 2 H), 7.60–7.88 (m, 2 H), 7.0–7.2 (m, 3 H), 6.02–6.40 (m, 1 H), 5.88 (dd, 1 H, J = 16.0 and 8.0 Hz), 2.60–2.80 (m, 3 H), 1.76 (d, 1 H, J = 8.0 Hz).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 83.95; H, 7.99; N, 7.83.

An authentic sample of **39** was prepared in the following fashion. To a solution containing 5 mL of diisopropylamine in 10 mL of tetrahydrofuran was added 16 mL of a 2.4 M *n*-butyllithium solution in hexane at −78 °C. To this solution was added 4.38 g of α-tetralone in 15 mL of tetrahydrofuran. The mixture was stirred at −78 °C for 1 h and then a 16.65-g sample of methyl(methylene)ammonium iodide[52,53] was added. After stirring for 10 min at −78 °C, the system was allowed to warm to −40 °C and was kept at this temperature for 30 min. The reaction mixture was then diluted with aqueous sodium bicarbonate and extracted with ether. The ethereal extracts were dried and the solvent was removed to give a light yellow oil. This oil was dissolved in 5 mL of methyl iodide and the mixture was stirred at 25 °C for 16 h. Removal of the excess methyl iodide followed by recrystallization gave 3.5 g (69%) of 2-(trimethylaminomethyl)-1-tetralonehydrazonium iodide. The above salt was transferred to a separatory funnel which contained 150 mL of a 5% sodium bicarbonate solution and 100 mL of methylene chloride. The mixture was shaken for 20 min, the organic layer was separated, dried, and concentrated, and the resulting residue was distilled at 78–80 °C (0.02 mm) to give 1.4 g of 2-methylene-1-tetralone (**40**).

The above oil was taken up in methanol and to this solution was added 0.2 g of sodium hydroxide in 5 mL of methanol, 1 mL of water, and 3 mL of nitromethane. The mixture was stirred at room temperature for 30 min, extracted with ether, dried over magnesium sulfate, and concentrated under reduced pressure. Chromatography of the residue on a thick layer plate gave 300 mg of 2-)2-nitroethyl)-1-tetralone: NMR (100 MHz) τ 6.80–8.20 (m, 7 H), 5.34 (t, 2 H, J = 6.0 Hz), 2.60 (m, 3 H), 1.94 (d, 1 H, J = 8.0 Hz). The above material was taken up in 10 mL of ethanol and to this solution was added an excess of W-2 Raney nickel. The mixture was stirred under a hydrogen

atmosphere for 10 h and then the Raney nickel was filtered. Removal of the solvent left a clear oil which was identical with the photoproduct obtained from the irradiation of azirine **38**.

Irradiation of 2-(2,2-Dimethyl-2*H*-azirin-3-yl)benzenepropanol (42). A solution containing 100 mg of **42** in 150 mL of benzene was irradiated under an argon atmosphere for 15 min using a Vycor filter sleeve. Removal of the solvent left a yellow oil which was distilled at 95–97 °C (0.01 mm) to give 60 mg (60%) of a colorless oil whose structure was assigned as 2,3a,4,5-tetrahydro-2,2-dimethylnaphth[1,2-*d*]oxazole (**43**): IR (neat) 3.30, 6.00, 6.75, 7.20, 8.20, 9.40, 10.30, 11.75, 12.35, 13.15, and 14.35 μ; NMR (100 MHz) τ 8.52 (s, 3 H), 8.40 (s, 3 H), 7.96–8.24 (m, 1 H), 7.44–7.76 (m, 1 H), 7.0–7.16 (m, 2 H), 5.26 (dd, 1 H, J = 14.0 and 6.0 Hz), 2.06–2.88 (m, 3 H), 2.00–2.10 (m, 1 H); UV (methanol) 285 nm (ϵ 4160) and 240 (12 500); *m/e* 201 (M^+), 186 (base), 145, 117, 115, and 77.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.69; H, 7.32; N, 6.59.

Irradiation of 3-(*o*-3-Butenylphenyl)-2,2-dimethyl-2*H*-azirine (41) in the Presence of Methyl Acrylate. A solution containing 150 mg of azirine **41** and 20 mL of methyl acrylate in 120 mL of benzene was irradiated under a nitrogen atmosphere for 15 min using a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick layer chromatography using a 15% ethyl acetate–hexane mixture as the eluent. The major band contained 170 mg (80%) of a light yellow oil which was assigned as 2-(*o*-3-butenylphenyl)-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**44**) on the basis of its spectral properties: IR (neat) 3.30, 5.70, 6.05, 6.90, 8.20, 8.55, 10.90, and 13.10 μ; NMR ($CDCl_3$, 100 MHz) τ 8.84 (s, 3 H), 8.48 (s, 3 H), 7.54–7.84 (m, 2 H), 6.36–7.14 (m, 5 H), 6.33 (s, 3 H), 4.96–5.13 (m, 2 H), 4.0–4.40 (m, 1 H), 2.60–2.92 (m, 4 H); *m/e* 285 (M^+), 270, 256, 186, 171, 164, 116 (base), 105, 91, and 77.

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