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(37) L. J. Mittal, J. P. Mittal, and E. Hayon, J. Phys. Chem., 77, 1482 (1973).
(38) The reduction of ground state pyruvic acid by ·COOH is known to be an efficient process,[39] and a corresponding mechanism involving CO_2^{-}· has been postulated for photoinduced decarboxylation of the conjugate base of pyruvic acid in aqueous solution.[40]
(39) N. H. Anderson, A. J. Dobbs, D. J. Edge, R. O. C. Norman, and P. R. West, J. Chem. Soc. B, 1004 (1971).
(40) (a) S. Steenken and D. Schulte-Frohlinde, Angew. Chem., Int. Ed. Engl., 14, 254 (1975); (b) S. Steenken, E. D. Sprague, and D. Schulte-Frohlinde, Photochem. Photobiol., 22, 19 (1975).
(41) G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc., 92, 7227 (1970).
(42) R. G. Lawler, J. Am. Chem. Soc., 89, 5519 (1967); G. L. Closs and L. E. Closs, ibid., 91, 4549 (1969). A comprehensive discussion of the effects of relaxation upon CIDNP may be found in ref 7a, p 185 ff.
(43) This statement is no longer valid for specific cases in which chain propagating steps yield nuclear spin polarization. Of course, it is strictly not possible to describe the relaxation of a coupled spin system containing more than two levels by a single relaxation time. The time constant in eq 25 and 26 should therefore be interpreted as an experimental decay constant instead of T_1 in the precise sense of its definition.
(44) Time constants calculated for the light(t)–τ–$\pi/2$ experiments are inherently less accurate than those determined by inversion–recovery because of the diminished dynamic range of the requisite exponential functions.[8]
(45) The possibility exists that the discrepancy between the T_1 measured by the inversion–recovery method and that obtained from the CIDNP method is indeed real. Theoretical justifications exist for different effective decay constants depending on the initial population patterns in a coupled multilevel system. The population distributions among the levels of the methyl protons are indeed different after a π pulse and after polarization in a CIDNP experiment. Work is in progress to examine this interesting problem.
(46) R. O. C. Norman and P. R. West, J. Chem. Soc. B, 389 (1969).
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(48) It might be suggested that disproportionation of RP-1 (Scheme I) could also yield polarized pyruvic acid. Arguments identical with those just presented imply that RP-1 would generate pyruvic acid exhibiting only net effects.
(49) Spectra were calculated employing the following coupling constants: 8, $J_{\alpha\beta} = +42$ Hz, $J_{\alpha\gamma} = -11$ Hz, $J_{\alpha\epsilon} = 0$ Hz, $J_{\beta\gamma} = +38$ Hz, $J_{\beta\epsilon} = -20$ Hz, $J_{\gamma\epsilon} = +34$ Hz, $a_\alpha = +49$ G, $a_\beta = +129$ G, $a_\gamma = +10$ G, $a_\epsilon = 0$ G; 12, $J_{\alpha\beta} = +34$ Hz, $J_{\alpha\beta'} = -6$ Hz, $J_{\alpha\alpha'} = 0$ Hz, $J_{\beta\beta'} = +40$ Hz, $a_\alpha = 0$ G, $a_\beta = +10$ G.
(50) K. Y. Choo and J. K. S. Wan, J. Am. Chem. Soc., 97, 7127 (1975).
(51) The observation of proton emission (i.e., diminished absorption) from the methyl singlet of pyruvic acid during photolysis of pyruvic acid–lactic acid mixtures in benzene solution[50] clearly constituted one of the major stimuli for rationalization of the photo-CIDNP of pyruvic acid by the so-called triplet mechanism.[50,52] The argument was properly stated[50] that within high magnetic fields where S–T± mixing is negligible, no net effect polarization can be induced between identical radicals by the radical pair mechanism because of the vanishing Δg term.[7a] By default the reported nuclear spin polarization was attributed to the triplet mechanism despite the fact that abstraction would have to occur on the nanosecond time scale in order to compete successfully with thermalization of the triplet sublevels. Lactic acid would, by necessity, also be found in net emission (possibly superimposed upon a pure AE multiplet effect from radical pair polarization), but no such result was reported. Investigations in this laboratory do not, however, support the previous experimental observations. Preliminary studies employing distilled syrup dl-lactic acid in both benzene-d_6 and acetonitrile-d_3 solutions yielded pyruvic acid in enhanced absorption. Repeated purification by preparative GLC sharply decreased the polarization intensity indicating the intervention of an impurity reaction. L(+)-Lactic acid was therefore chosen for further tests because of the greater ease with which this crystalline material could be rendered rigorously pure. Photolysis of pyruvic acid (0.10 M) in benzene-d_6 saturated with L(+)-lactic acid (0.028 M) afforded no nuclear spin polarization. No products could be detected following prolonged irradiation; thus there exists no evidence for the occurrence of reaction. Abstraction from lactic acid becomes an efficient process in acetonitrile with meso- and dl-dimethyltartaric acids being readily formed. Photolysis of equimolar (0.10 M) mixtures of pyruvic and L(+)-lactic acids in acetonitrile-d_3 exhibited CIDNP attributable solely to the decarboxylation reaction of pyruvic acid previously described. Samples containing lactic acid were directly compared to pyruvic acid blanks. All signals from polarized and subsequent dark spectra were integrated, and normalized to the integral of residual CD_2HCN. The ratios of polarized 8a and 8b to polarized $CH_3COCOOH$ were identical under all circumstances. As well, the polarizations were totally insensitive to the presence of dissolved oxygen. The fact that decarboxylation competes with abstraction from lactic acid clearly indicates that the rate coefficient for the latter process cannot significantly exceed 1×10^7 M^{-1} s^{-1}. Under the experimental conditions of both the current and prior[50] investigations, generation of nuclear spin polarization via the triplet mechanism is neither observable nor theoretically tenable.
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The Role of Substituents in Controlling the Mode of Intramolecular Cycloaddition of Nitrile Ylides[1]

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Abstract: The intramolecular photocycloaddition reactions of a number of *o*-allyloxyphenyl substituted 2*H*-azirines have been examined in mechanistic detail. Upon irradiation with ultraviolet light, these systems undergo intramolecular 1,1- and/or 1,3-cycloaddition depending on the substituent groups attached to the 2 position of the azirine ring. The internal cycloaddition reactions have been shown to proceed through transient nitrile ylide intermediates. A kinetic investigation involving Stern–Volmer plots shows that the rate of internal 1,3-cycloaddition is three times faster than that of 1,1-cycloaddition. Inspection of molecular models of these *o*-allyloxyphenyl substituted nitrile ylides shows that two paths for cycloaddition are possible depending on the geometry of the nitrile ylide. The parallel plane approach of addends produces a 1,3 cycloadduct and occurs when the dipole possesses linear geometry. The alternate 1,1-cycloaddition process occurs when the dipole possesses bent geometry. Since the energy difference between the nonplanar bent and linear forms is very small, the preferred mode of cycloaddition will depend on the nature of the substituent groups attached to the nitrile ylide. According to recent MO calculations, methyl or other electron-releasing substituents on the 3 carbon of the ylide will increase the preference for the bent geometry and favor the 1,1-cycloaddition process. Placing electron-withdrawing groups at C-3 (i.e., CF_3, H, $C_6H_4NO_2$) favors linearization of the nitrile ylide, thereby promoting 1,3-cycloaddition. The results show that when the energy difference between the nonplanar bent and linear forms is small, substituent effects can play an extremely important role in determining the course of the intramolecular cycloaddition reactions of nitrile ylides.

The monumental work of Huisgen and co-workers in the early 1960s led to the general concept of 1,3-dipolar cycloaddition.[2-7] Few reactions rival this process in the number of bonds that undergo transformation during the reaction, producing products considerably more complex than the reactants. Over the years this reaction has developed into a generally useful method of five-membered heterocyclic ring synthesis, since many 1,3-dipolar species are readily available and react with a wide variety of dipolarophiles.[8] Perturbation theory[9-16] has recently been shown to provide a powerful but simple

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method of understanding the nature of substituent effects on chemical reactivity and on the stereo- and regioselectivity of the 1,3-dipolar cycloaddition process.[17,18] Interest in substituent effects has been stimulated in recent years by the development of frontier molecular orbital models for reactivity, according to which the energies and shapes of the highest occupied and lowest unoccupied molecular orbitals determine chemical reactivity.[19]

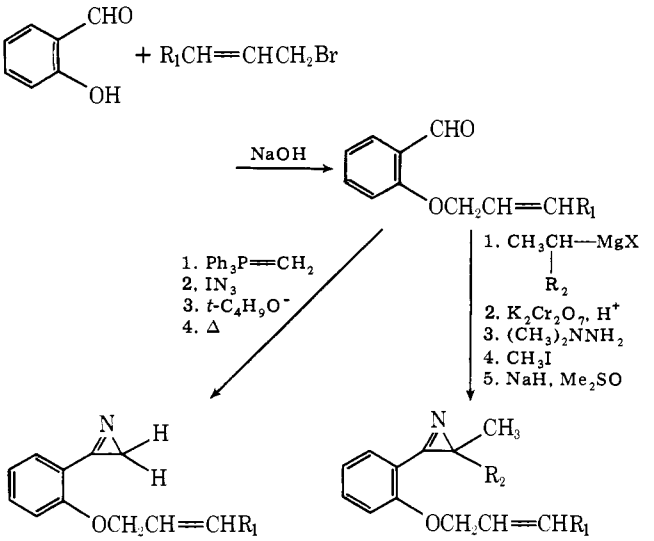
Our research group has recently been interested in the 1,3-dipolar cycloaddition reactions of nitrile ylides generated by photolysis of 2*H*-azirines.[20,21] When nitrile ylides are used as 1,3 dipoles, the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) interaction will be of greatest importance in stabilizing the transition state.[22] The favored cycloadduct will be that formed by union of the atoms with the largest coefficient in the dipole HOMO and dipolarophile LUMO.[23-26] Recent ab initio LCAO-MO-SCF calculations by Houk and co-workers have shown that nitrile ylides exist preferentially in the bent form with an HCN angle of 114-116°.[27,28] The nitrile ylide HOMO is heavily concentrated at C-1, but still resembles the normal three-orbital, four-electron system present in other 1,3 dipoles so that concerted cycloaddition can still occur. In earlier papers we have shown that there are two pathways by which nitrile ylides react with multiple π bonds.[29,30] 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.[31] With this path, the relative reactivity of the nitrile ylide toward a series of dipolarophiles will be determined primarily by the extent of stabilization afforded the transition state by interaction of the frontier orbitals of the two reactants. Substituents which lower the dipolarophile LUMO energy will accelerate the 1,3-dipolar cycloaddition reaction. The other path, designated as 1,1-cycloaddition, operates only in certain intramolecular cases.[29,32] It occurs when the p orbitals of the olefinic group have been deliberately constrained to attack perpendicular to the nitrile ylide plane. The effect of substituents upon the rate of the intramolecular carbene-like cycloaddition will be controlled by the interaction of the alkene HOMO and the second LUMO of the nitrile ylide. Placement of electron-releasing substituents on the π bond will raise both the HOMO and LUMO orbital energies of the olefin,[25] and consequently facilitate the rate of the 1,1-cycloaddition reaction.

Although the preceding discussion gives a satisfactory accounting of the effects of substituents on the dipolarophile end, it does not address the question of how a substituent will affect the rate, regioselectivity, and mode of dipolar cycloaddition when it is directly attached to the nitrile ylide portion. Assuming the simple perturbation model traditionally used for substituent effects, the effect of a substituent on the dipole might be expected to be a function of the magnitude of the coefficient at the site of attachment. Substituents which raise the energy of the nitrile ylide's HOMO should accelerate the reaction. At the time that we started our studies, little experimental data were available to determine the precise effect of dipole substituents on frontier orbital energies and coefficients. In an attempt to rectify this deficiency, we initiated a study of the photochemistry of a series of *o*-allyloxyphenyl substituted 2*H*-azirines. During the course of our investigations, we uncovered a strikingly novel and unprecedented substituent effect.[33] The present publication describes our preliminary findings in detail and delineates the significant role played by alkyl substituents in controlling the mode of cycloaddition.

Results

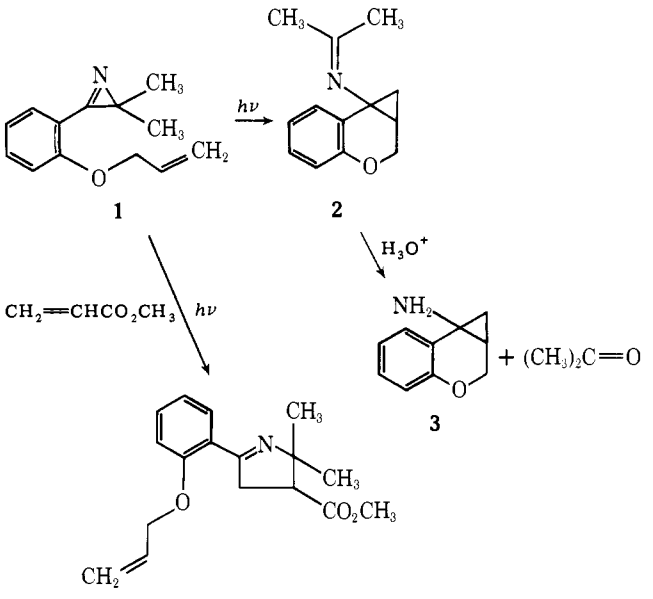
As our first model we chose to investigate the photochemistry of a series of *o*-allyloxyphenyl substituted 2*H*-azirines. Examination of molecular models of the nitrile ylides derived

Scheme I



from these 2*H*-azirines shows that the side chain is of sufficient length to allow the dipole and dipolarophile units to approach each other in parallel planes. One of our initial goals was to determine whether the intramolecular cycloaddition reaction of these systems would proceed in the 1,1 or 1,3 sense. We were also interested in determining whether different substituents on the azirine ring would affect the overall course of the cycloaddition process. The *o*-allyloxyphenyl substituted 2*H*-azirines were conveniently prepared by the series of reactions outlined in Scheme I.

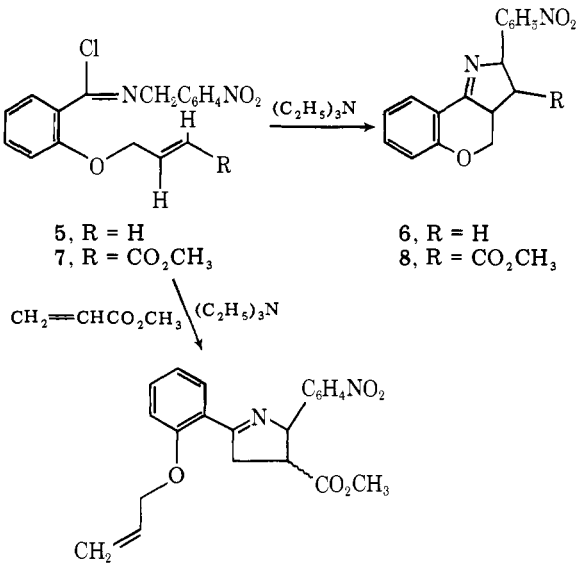
Irradiation of a solution of 3-(*o*-allyloxyphenyl)-2,2-dimethyl-2*H*-azirine (**1**) in benzene with light of wavelength >250 nm gave a single photoproduct (>95%) which showed all the properties expected for 1a,2-dihydro-*N*-isopropylidenebenzo[*b*]cyclopropa[*d*]pyran-7b(1*H*)-amine (**2**). This material was readily hydrolyzed to acetone and the corresponding amine **3** on thick layer chromatography. The NMR spectrum (100 MHz, $CDCl_3$) of structure **3** ($Eu(fod)_3$ added)



showed a triplet at τ 8.50 (1 H, J = 5.0 Hz), a doublet of doublets at 8.30 (1 H, J = 8.0 and 5.0 Hz), a multiplet at 7.70 (1 H), doublets at 5.96 (1 H, J = 10.0 Hz) and 5.65 (1 H, J = 10.0 Hz), a broad singlet at 4.90 (2 H, exchanged with D_2O), and the aromatic protons at 2.1-3.1 (m, 4 H). Photolysis of **1** in the presence of excess methyl acrylate afforded cycloadduct **4** in high yield. Under these conditions, the forma-

tion of **2**, which is produced in high yield in the absence of a trapping agent, is entirely suppressed.

We had previously reported that nitrile ylides generated by nonphotochemical techniques also undergo the intramolecular 1,1-cycloaddition reaction.[32] Thus we were rather surprised to find that treatment of *o*-oxyallylimidoyl chloride **5** with triethylamine gave 1,3-dipolar cycloadduct **6**, mp 137–138 °C,



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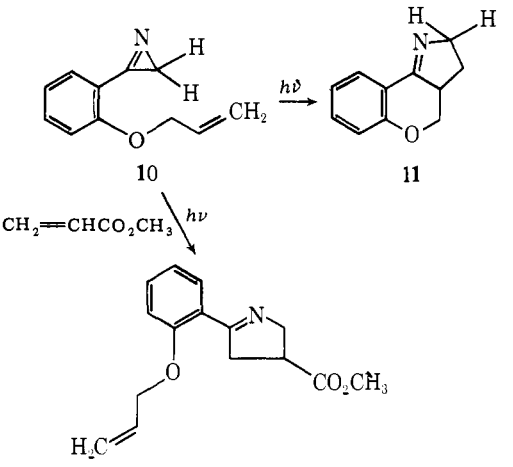
as the exclusive product. The identity of **6** was determined by its straightforward spectral properties (NMR, 100 MHz), τ 8.60 (td, 1 H, J = 12.0 and 10.0 Hz), 7.20 (td, 1 H, J = 12.0 and 6.0 Hz), 6.60 (m, 1 H), 5.28 (dd, 1 H, J = 10.0 and 6.0 Hz), 4.80 (ddd, 1 H, J = 10.0, 6.0, and 2.0 Hz), 1.68–3.00 (m, 8 H).

The formation of **6** could be completely suppressed when the base-induced reaction was carried out in the presence of methyl acrylate. The only product formed under these conditions was a mixture of diastereomeric Δ^1-pyrrolines (**9**). This result clearly establishes that a nitrile ylide is involved in this reaction and that **6** arises by intramolecular 1,3-dipolar cycloaddition of the transient ylide with the neighboring double bond. Huisgen's group had previously demonstrated that nitrile ylides can be readily generated by treating imidoyl chlorides with base.[34]

A similar reaction occurred when imidoyl chloride **7** (R = CO_2CH_3) was treated with base. The only product obtained here was 1,3-dipolar cycloadduct **8**, mp 156–157 °C. All attempts to trap the initially generated nitrile ylide with excess methyl acrylate failed. The 1,3-dipolar cycloadduct **8** was the only product formed in quantitative yield. With this system, the rate of internal cycloaddition is much faster than bimolecular trapping. This is undoubtedly due to the extremely favorable entropy effect which operates in the internal cycloaddition. Bimolecular cycloadditions exhibit large negative entropies of activation[3] since the reactants must be precisely aligned with respect to each other. The interplay of entropy and enthalpy will control the rate-determining activation process. The larger entropy term associated with the intramolecular cycloaddition of **7** is clearly dominant in this competitive situation. With imidoyl chloride **5**, the intramolecular process involves the reaction of a nitrile ylide with an unactivated olefin, a substrate which is generally unreactive toward this class of 1,3 dipoles.[31] Thus, the unfavorable enthalpy term sufficiently diminishes the rate of internal 1,3-addition to allow the nitrile ylide derived from **5** to be trapped with an added dipolarophile.

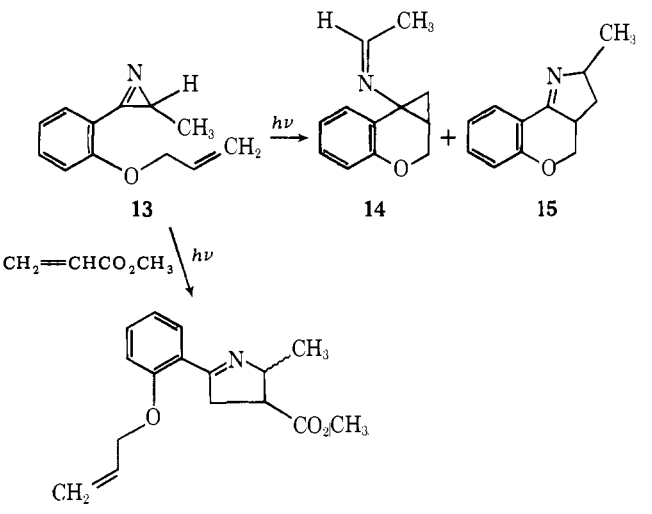
In order to determine whether the striking difference in the course of the intramolecular cycloaddition of azirine **1** and imidoyl chloride **5** was related to the manner in which the nitrile ylide was generated, we examined the photochemistry of 3-(*o*-allyloxyphenyl)-2*H*-azirine (**10**). Irradiation of **10** in benzene using a 450-W Hanovia immersion apparatus equipped with a Corex filter sleeve led to the complete consumption of reactant in 20 min. The only product obtained was 2,3,3a,4-tetrahydro[1]benzopyrano[4,3-*b*]pyrrole (**11**), mp



12

98–99 °C [NMR (100 MHz) τ 8.48 (dddd, 1 H, J = 12.0, 10.0, 10.0, and 9.0 Hz), 7.78 (ddd, 1 H, J = 12.0, 8.0, and 7.0 Hz), 6.52–7.04 (m, 1 H), 6.24 (dddd, 1 H, J = 16.0, 10.0, 8.0, and 2.0 Hz), 6.19 (dd, 1 H, J = 13.0 and 10.0 Hz), 5.80 (ddd, 1 H, J = 16.0, 9.0, and 2.0 Hz), 5.38 (dd, 1 H, J = 10.0 and 6.0 Hz), 2.08–3.16 (m, 4 H)]. When methyl acrylate was used as a trapping agent, the only product isolated was the usual Δ^1-pyrroline (i.e., **12**).

The exclusive formation of a 1,3-dipolar cycloadduct from azirine **10** strongly suggests that the mode of cycloaddition of these *o*-allyloxyphenyl substituted 2*H*-azirines is markedly dependent on the nature of the substituent groups attached to the 3 carbon of the nitrile ylide. Further support for this contention was obtained from a study of the photobehavior of 2*H*-azirine **13**. Irradiation of **13** in benzene produced a 1:1 mixture of the 1,1 and 1,3 cycloadducts **14** and **15** in quantitative yield. The identity of structure **14** rests on its spectroscopic properties and its facile hydrolysis to acetaldehyde and amine **3**. Structure **15** was assigned on the basis of its charac-



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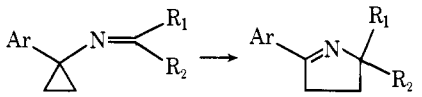
teristic spectral properties (see Experimental Section). Photolysis of **13** in the presence of excess methyl acrylate afforded cycloadduct **16** in high yield. Under these conditions, the formation of both **14** and **15**, which are produced in quantitative

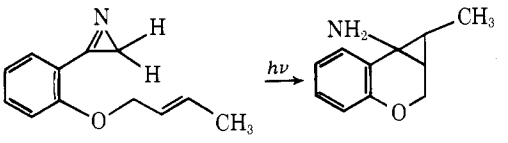
yield in the absence of a trapping agent, is completely suppressed. More importantly, when the irradiation of **13** was carried out in the presence of limited quantities of methyl acrylate, the ratio of cycloadducts **14/15** did not change. It should also be noted that the ratio of cycloadducts did not vary with changes in temperature or the wavelength of incident light used.

Since azirine **13** gave rise to both 1,1 and 1,3 cycloadducts, it was necessary to ascertain whether the 1,3 adduct arises from a subsequent rearrangement of the 1,1 adduct. Literature analogy[35-37] suggests that this transformation is a reasonable

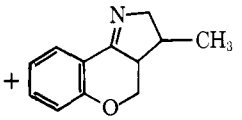


one, so it was important to determine the feasibility of this process with the above system. However, all attempts to induce the photochemical rearrangement of **14** to **15** failed. Moreover, the thermal and acid-catalyzed reactions of **14** also failed to produce any detectable quantities of **15.**[38] Similar experiments with **15** did not afford any detectable quantities of **14.** Thus, we can conclude that structures **14** and **15** are both primary products derived from a transient nitrile ylide intermediate.

Another case where an oxyallylphenyl substituted 2*H*-azirine was found to undergo both 1,1- and 1,3-dipolar cycloaddition was encountered in the photolysis of 3-(*o*-(2-butenyloxy)phenyl)-2*H*-azirine (**17**). Irradiation of **17** in benzene followed by column chromatography afforded a 3:4 mixture of cycloadducts **18** and **19.** Structure **18** is derived from the



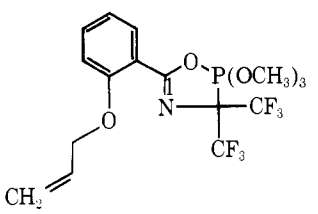
17 **18**



19

ready hydrolysis of the corresponding *N*-formylimine. The isolation of **18** in this experiment is especially noteworthy since photolysis of the closely related azirine system **10** produced only a 1,3-dipolar cycloadduct (i.e., **11**). When the irradiation of **17** was carried out in the presence of methyl acrylate, the normal Δ^1-pyrroline was obtained as the exclusive photoproduct. When limited quantities of methyl acrylate were used, the ratio of cycloadducts (**18/19**) remained the same as that observed in the direct irradiation experiment.

In an effort to gain further mechanistic insight into the nature of this novel substituent effect, we studied the photochemistry of oxaphosphole **20.** This material was prepared by a modification of the procedure developed by Burger and coworkers.[38] Thermolysis or photolysis of 4,5-dihydro-1,3,5-λ^5-oxazaphospholes are known to produce bis(trifluoromethyl)benzonitrile ylides in excellent yield,[39-43] In this case, the only product obtained from the photolysis or thermolysis of **20** was 1,3 cycloadduct **22,** mp 140–141 °C. The isolation of **22** strongly suggests that the substituent effect encountered in these nitrile ylide cycloadditions is electronic rather than steric in nature. A steric effect would have been expected to result in the formation of a 1,1 cycloadduct since the trifluoromethyl group is slightly larger than a methyl group.[44] This is clearly not the case.



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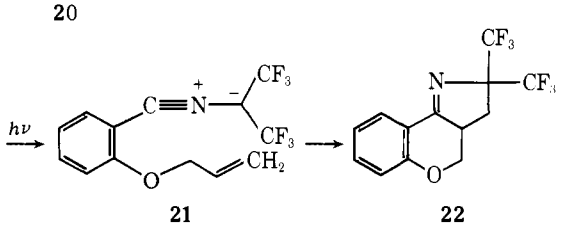
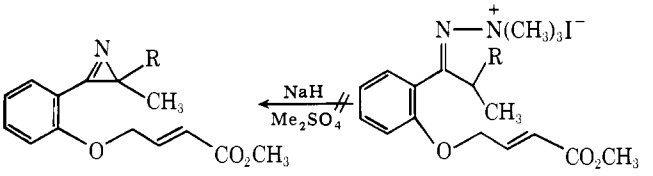
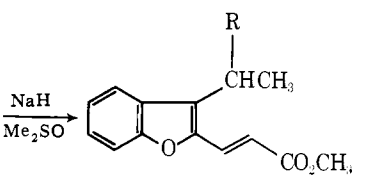


21 **22**

As was mentioned earlier, the dipole-HOMO dipolarophile-LUMO orbitals control the rate and regioselectivity of 1,3-dipolar cycloadditions with nitrile ylides. Placement of an electron-withdrawing substituent on the olefinic π bond should lower the dipolarophile's LUMO energy and thereby accelerate the rate of 1,3-dipolar cycloaddition. Thus, it became of interest to study the intramolecular photocycloaddition of an oxyallylphenylazirine which possessed an electron-withdrawing substituent on the double bond in order to determine whether this electronic perturbation would change the course of the cycloaddition of a disubstituted azirine from the 1,1 to the 1,3 sense. Trimethylhydrazonium iodide **23** was considered to be a reasonable precursor to the desired azirine system and was prepared in high yield by a series of reactions similar to that outlined in Scheme I. Unfortunately, the expected Neber reaction did not take place when **23** was treated with base. Instead, the reaction of **23** with sodium hydride in Me_2SO gave



24 **23**, R = CH_3; **26**, R = H



25, R = CH_3; **27**, R = H

rise to methyl 3-isopropyl-2-benzofuran acrylate (**25**). A similar reaction was also found to occur when the related hydrazonium iodide **26** was treated with base. Apparently, the incorporation of a carbomethoxy group on the double bond has increased the acidity of the allylic protons to such a degree that internal condensation across the C–N double bond now becomes the favored process.

In order to avoid the synthetic complications associated with this system, we decided to study the photochemistry of the closely related 3-[*o*-(4-carbomethoxy-3-butenyl)phenyl]-2,2-dimethyl-2*H*-azirine system (**29**). This compound was readily prepared by the ozonolysis of the terminal methylene group of azirine **28** followed by treatment of the resulting aldehyde with carbomethoxymethylenetriphenylphosphorane. Irradiation of a solution of **29** in benzene resulted in the formation of a single product which showed all the properties expected for methyl 3,3a,4,5-tetrahydro-2,2-dimethyl-2*H*-benz[*g*]indole-3-carboxylate (**30**). The isolation of a 1,3-dipolar cycloadduct with this system stands in marked contrast with the results encountered with 2*H*-azirine **1.** The above result clearly establishes that attachment of an electron-

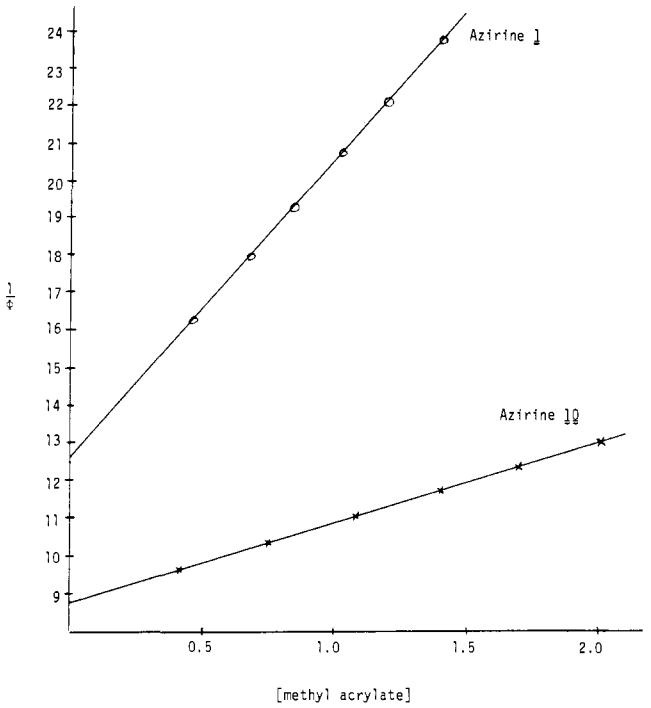
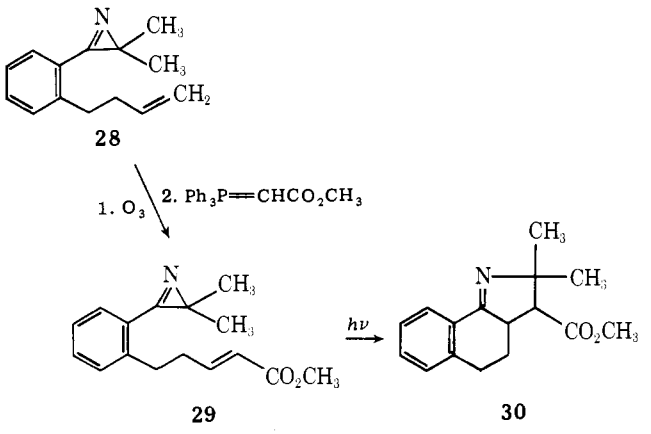


Figure 1. Plot of [quantum yield of cyclization]$^{-1}$ against [methyl acrylate] for 3-(*o*-allyloxyphenyl) substituted 2*H*-azirines **1** and **10**.



withdrawing substituent on the double bond has a pronounced effect on the mode of internal cycloaddition of a dimethyl substituted 2*H*-azirine.

In order to derive additional mechanistic information concerning the nature of the substituent effect, a more quantitative investigation of the cycloaddition reactions of azirines **1** and **10** was undertaken. These systems were of interest since the spatial proximity between the dipole and dipolarophile is very similar yet the mode of internal cycloaddition is significantly different. Quantum yields for product formation were determined using cyclopentanone as the chemical actinometer.[45] Degassed and sealed quartz tubes containing solutions of azirines **1** and **10** were irradiated along with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by GLC using internal standards. The quantum yield for produce formation as a function of the concentration of added methyl acrylate was also studied. The data are presented graphically in Figure 1 for the 3-(*o*-allyloxyphenyl)-(**10**) and 3-(*o*-allyloxyphenyl)-2,2-dimethyl-2*H*-azirine (**1**) systems.

Several features become apparent upon examination of the data shown in Figure 1. Good linear relationships are observed between the inverse of the quantum yield for product formation and the concentration of added methyl acrylate. The slopes and intercepts of the plots depend on the structure of the azirine used. At zero dipolarophile concentration, the quantum yield for cycloaddition is 0.08 for azirine **1** and 0.11 for azirine **10.** The results obtained using these unsaturated azirines as nitrile ylide precursors are consistent with the mechanism outlined in Scheme II.

Scheme II

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

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

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

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

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

In this scheme, Ao = unsaturated azirine (**1** or **10**), NY = nitrile ylide, P = product, and O = dipolarophile (methyl acrylate). By making the usual steady-state assumption, we can write

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

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

From the slope and intercept of the Stern–Volmer analysis for product formation with a given dipolarophile, we find that the slope/intercept = k_2/k_1. For the case of azirine **1**, k_2/k_1 = 0.75, while, with azirine **10**, k_2/k_1 = 0.22. These values indicate that the nitrile ylide intermediate obtained from azirine **1** is more easily trapped with added methyl acrylate than the 1,3 dipole derived from azirine **10.** If we assume that the rate of cycloaddition (i.e., k_2) of both nitrile ylides with methyl acrylate is the same,[46] we can obtain the relative rate differences for internal cycloaddition of these azirines:

$$[k_2/k_1 \text{ (azirine } \mathbf{1})/k_2/k_1 \text{ (azirine } \mathbf{10})] = k_{10}/k_1 = k_{rel} = 3.4$$

Thus, 1,3-dipolar cycloaddition of the nitrile ylide derived from **10** proceeds at a slightly faster rate (3.4 times) than 1,1-cycloaddition of the dipole derived from dimethyl substituted 2*H*-azirine **1**.

Discussion

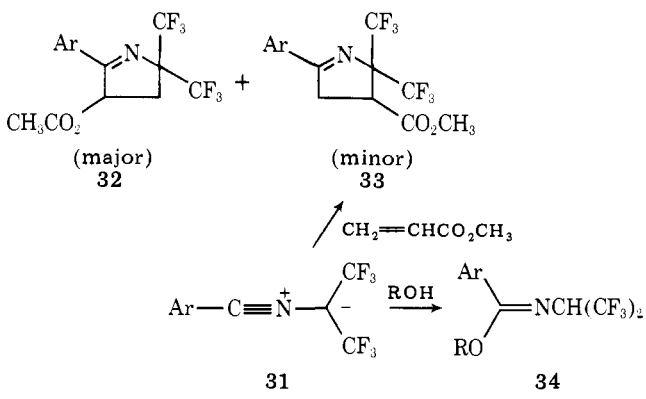
A striking feature of the present results is the finding that the mode of intramolecular cycloaddition of these *o*-allyloxyphenyl substituted nitrile ylides is markedly dependent on the nature of the substituent groups attached to the C-3 carbon atom of the dipole. In order to rationalize this novel substituent effect it will be necessary to discuss the geometric features associated with the nitrile ylide. Huisgen originally suggested that the bent geometric form of a nitrile ylide would be less stable than the linear form, since allyl resonance would be at a maximum with the linear arrangement.[3] Recently, Salem has carried out some ab initio computations on the ground- and excited-state energy surfaces of the 2*H*-azirine molecule.[47] 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

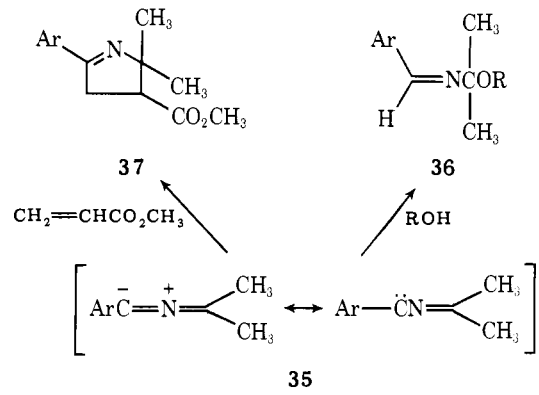
opened to give an intermediate with bent geometry, a diradical state with partial dipolar character will be obtained which may undergo reactions different from the linear species. According to Salem's calculations, the lowest energy ground-state geometry of the nitrile ylide has a CNC angle of 156.7° and is ca. 18 kcal/mol more stable than the linear form.

A similar conclusion was reached by Houk and Caramella.[27,28] These authors have carried out optimizations of the geometries of the parent nitrilium betaines by both ab initio LCAO-MO-SCF and MINDO calculations and find that the geometry of the nitrile ylide is appreciably different from that suggested by Huisgen.[3] Their calculations show that the parent nitrile ylide is definitely bent with an HCN angle of 114-116°. The stabilization over the optimized linear form was calculated to be 11.1 (4-31G), 22.4 (STO-3G), 12.9 (MINDO/2), and 16.4 kcal/mol (MINDO/3). These findings indicate that the most stable form of a nitrile ylide resembles a bent allenyl anion rather than a planar propargyl anion. More recent calculations by Houk and Gandour show that introduction of a phenyl or vinyl group at C_1 drastically flattens the dipole.[48] Both the MINDO/3 and STO-3G calculations reveal that attachment of a phenyl group at C_1 significantly lowers the energy separation between the linear and bent forms by about 10-15 kcal/mol. These results clearly indicate that the *o*-allyloxyphenyl substituted nitrile ylide system will be less bent and easier to linearize than the corresponding parent system (i.e., $HCNCH_2$). As the dipole becomes less bent, the C_1N bond length will shorten and NC_3 will lengthen, as expected for going toward a propargyl-type structure.

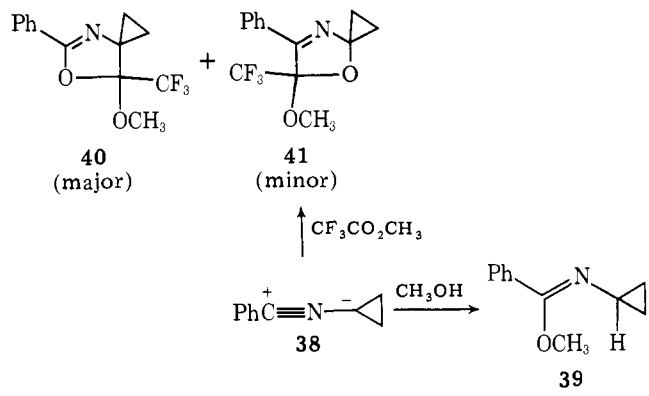
Another noteworthy feature of Houk's calculations is that a trend of increasing linearization is observed as one proceeds along the isoelectronic series $RC{\equiv}N^+CH_2^-$, $RC{\equiv}N^+N^-H$, $RC{\equiv}N^+{-}O^-$. The optimized nitrile imine system with a linear $HC{\equiv}N^+N^-H$ group was found to be about 2 kcal/mol higher in energy than the bent form while the linear form of the nitrile oxide was found to be significantly more stable than the bent form. The increasing stability of the linear geometry relative to the bent form, as the electronegativity of the X terminus increases ($RC{\equiv}N^+{-}X^-$), can be attributed to the fact that the linear structure places more negative charge on the X atom and possesses less N-X double bond character. The valence bond structure, $RC{\equiv}N^+{-}X^-$, is a good representation of the electronic structure of the dipole when X is an electronegative atom. When the X atom is of comparable electronegativity to the C_1 carbon atom, the $R\ddot{C}N{=}X$ (carbene-like) structure increases in stability relative to the other structure. Bending of the C_1 carbon atom will result in an overall stabilization because of the increase of s character in the orbital bearing negative charge.

Placement of an electron-withdrawing group at C-3, like substitution of O for CH_2, will favor linearization of the nitrile ylide. For example, bis(trifluoromethyl)benzonitrile ylide (**31**) adds alcohols and electron-deficient alkenes with regioselectivity which indicates that the $C(CF_3)_2$ terminus is most nucleophilic,[49] as expected from considerations of the frontier molecular orbitals of a linear nitrile ylide.[23-26] On the other hand, bis(methyl)benzonitrile ylide **35** exists in the bent form and reacts with alcohols to give alkoxyimines (**36**) as the exclusive product.[50] The regioselectivity of cycloaddition of this ylide with electron-deficient alkenes[51] further establishes C_1 as the nucleophile terminus[22] rather than C-3 as was found for the linear nitrile ylide **31**.

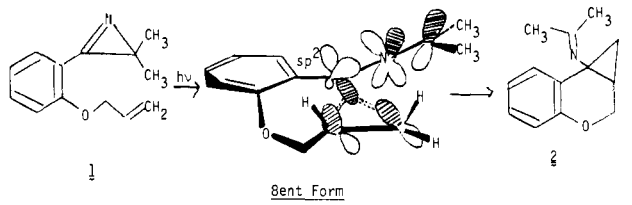




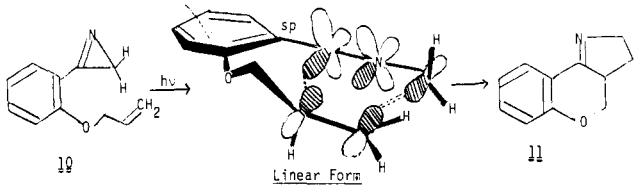
It is also worthy to note that the trapping of benzonitrile cyclopropylide **38** with methanol and methyl trifluoroacetate occurs in a different sense from that observed with other alkyl-substituted nitrile ylides.[22,52] This would imply that the largest HOMO coefficient of **38** rests on the cyclopropyl carbon atom and is compatible with the notion that the effective electronegativity and resistance to planarization of the cyclopropyl anion terminus cause this ylide to be linear.



As discussed in the introductory section, there are two pathways by which nitrile ylides react with multiple π bonds. For concerted 1,3-dipolar cycloaddition to take place, the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the nitrile ylide. The 1,1-cycloaddition path, on the other hand, will occur when the p orbitals of the olefin are constrained to attack perpendicular to the nitrile ylide plane.[29] Inspection of molecular models of these *o*-oxyallylphenyls shows that both approaches are possible depending on the geometry of the nitrile ylide. The energy difference between the nonplanar bent and linear forms is small and the preferred mode of approach depends on the substituent groups present on the nitrile ylide. According to Houk's calculations,[27,28] methyl or other electron-releasing substituents on the 3 carbon of the ylide will increase the preference for the bent geometry. In other words, the nitrile ylide species becomes more carbene-like as methyl groups are added and is more prone to undergo the 1,1-cycloaddition reaction. This is exactly what is observed. Thus, 3-(*o*-allyloxyphenyl)-2,2-dimethyl-2*H*-azirine (**1**) undergoes 1,1-cycloaddition to give *N*-isopropylidenebenzo[*b*]cyclopropa[*d*]pyranamine (**2**) as the exclusive photoproduct. Placing electron-withdrawing groups at C-3



(i.e., H, CF_3, $C_6H_4NO_2$) will favor linearization of the nitrile ylide. As the dipole becomes less bent, the C_1N bond shortens and the NC_3 lengthens and the system prefers to undergo 1,3-dipolar cycloaddition. The incorporation of the *o*-oxyallylphenyl group has sufficiently flattened the dipole so that it is now much more sensitive to C-3 substitution than the unsubstituted case.



The formation of a mixture of 1,1 (**14**) and 1,3 cycloadducts (**15**) from the irradiation of the monomethyl-substituted 2*H*-azirine (**13**) is an intriguing result and deserves some comment. We assume that the energy barrier for interconversion of the two geometric forms of the ylide is lower than the activation energies for formation of the cycloadducts. This assumption seems reasonable since the interconversion process requires only a change in hybridization about the C_1 carbon atom. The energy requirement for the rehybridization should be very similar to the measured inversion barrier of vinyl radicals. ESR studies indicate that the barrier to inversion in the simple vinyl radical is about 2 kcal/mol.[53,54] Hence, the ratio of cycloadducts obtained from azirine **13** should depend only on the difference in energy for the transition states leading to the products (Curtin-Hammett principle[55]). The Stern-Volmer studies with azirines **1** and **10** show that the rate constant for internal 1,3-dipolar cycloaddition is only three times faster than that for 1,1-cycloaddition. Consequently, the difference in activation energies for intramolecular 1,3- vs. 1,1-cycloaddition must be less than 1 kcal/mol. Since equal quantities of the 1,1 and 1,3 cycloadducts are obtained from the irradiation of **13**, it follows that the energy levels of the bent and linear forms must lie very close (ca. 1 kcal/mol) to each other.

Our results strongly suggest that the energy gap between the two geometric forms is the major factor responsible for the novel substituent effect that we have encountered with these systems. Unfortunately, it is impossible to accurately determine the ΔE values and these can only be approximated by MO calculations. We can only assume that the energy difference between the nonplanar bent and linear forms is extremely dependent on the nature of the substituent groups.

One final point of importance which warrants discussion relates to the photochemistry of azirines **17** and **28**. The isolation of both 1,1 and 1,3 cycloadducts from the irradiation of **17** is especially noteworthy since photolysis of the closely related azirine **10** produced only a 1,3 cycloadduct. According to the arguments outlined above, one might have expected the nitrile ylide derived from **17** to possess linear geometry and therefore undergo exclusive 1,3-cycloaddition. As was pointed out earlier, the dipole HOMO dipolarophile-LUMO orbitals control the rate of 1,3-dipolar cycloaddition with nitrile ylides. Placement of an electron-donating substituent on the π bond, however, should raise both the HOMO and LUMO orbital energies of the olefin and thereby diminish the rate of 1,3-dipolar cycloaddition. On the other hand, the effect of substituents upon the rate of intramolecular carbene-like 1,1-cycloaddition should be controlled by the interaction of the alkene HOMO with the second LUMO of the nitrile ylide. Consequently, attachment of a methyl group on the double bond should accelerate the rate of 1,1-cycloaddition. The combination of both of these factors is undoubtedly responsible for the formation of the 1,1 cycloadduct (i.e., **18**) with this system. The exclusive formation of a 1,3-dipolar cycloadduct (i.e., **30**) from the irradiation of azirine **28** can, in turn, be attributed to a significant lowering of the activation energy associated with the 1,3-cycloaddition reaction and to a substantial increase in the activation energy for the 1,1-cycloaddition process.

In summary, the above results show that when the energy difference between the nonplanar bent and linear forms is small, substituent effects can play an extremely important role in determining the course of intramolecular cycloaddition reactions of nitrile ylides.

Experimental Section[56]

General Procedure for the Preparation of *o*-Allyloxyphenyl Substituted 2*H*-Azirines. The desired *o*-allyloxyphenyl substituted 2*H*-azirines were prepared by a modified Neber reaction in which variously substituted 1-(*o*-allyloxyphenyl)propan-1-ones were treated with *N,N*-dimethylhydrazine according to the method of Leonard and Zwanenburg.[57] The general procedure used for the synthesis of the *o*-allyloxyphenyl-substituted propan-1-ones involved treating salicylaldehyde with an appropriately substituted allyl halide in the presence of sodium hydroxide. The resulting *o*-allyloxybenzaldehyde was then treated with the appropriate Grignard reagent and the resultant alcohol was oxidized with Jones reagent.

The *o*-allyloxyphenyl-substituted 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 used for the preparation of the 2*H*-azirine ring system 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 high purity. The azirines were distilled under reduced pressure before use. Using these procedures the following 2*H*-azirines were synthesized.

3-(*o*-Allyloxyphenyl)-2,2-dimethyl-2*H*-azirine (1) was prepared in 95% yield from the corresponding hydrazonium iodide (mp 91-92 °C) and was a pale yellow oil: mp 75-77 °C (0.2 mm); IR (neat) 3.35, 6.15, 6.65, 7.70, 8.00, 9.95, 10.60, and 13.15 μ; NMR (100 MHz) τ 8.65 (s, 6 H), 5.35 (d, 2 H, J = 4.0 Hz), 4.45-4.75 (m, 2 H), 3.75-4.15 (m,

1 H), 2.25–3.10 (m, 4 H); UV (methanol) 310 nm (ε 5100) and 250 (10 400); *m/e* 201 (M^+), 186, 145, 120, 117, 91, and 77.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.89; H, 7.56; N, 6.66.

3-(*o*-Allyloxyphenyl)-2-methyl-2*H*-azirine (13) was prepared in quantitative yield from the corresponding hydrazonium iodide and was a clear oil: bp 70–72 °C (0.01 mm); IR (heat) 3.30, 5.90, 6.80, 7.70, 8.50, 9.70, 10.60, 11.80, and 13.10 μ; NMR (60 MHz) τ 8.76 (d, 3 H, *J* = 4.5 Hz), 7.96 (q, 2 H, *J* = 4.5 Hz), 5.42 (dt, 2 H, *J* = 4.5 and 1.2 Hz), 4.40–5.00 (m, 2 H), 3.70–4.35 (m, 1 H), 2.30–3.20 (m, 4 H); UV (cyclohexane) 302 nm (ε 5400) and 247 (11 300); *m/e* 187 (M^+), 186, 172 (base), 145, 120, 117, 105, and 77.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.82; H, 6.94; N, 7.44.

Preparation of *o*-Allyloxy-*N*-(*p*-nitrobenzyl)benzimidoyl Chloride (5). A solution containing 3.04 g of *p*-nitrobenzylamine was prepared by shaking 3.76 g of the *p*-nitrobenzylamine hydrochloride salt in 20 mL of water with 30 mL of a 1 N sodium hydroxide solution and extracting the aqueous layer with ether. The ethereal layer was dried over anhydrous magnesium sulfate and this solution was added dropwise at 0 °C to a solution containing 1.56 g of salicyclic acid chloride in 30 mL of ether. The mixture was allowed to warm to room temperature and then 18 mL of a 1 N sodium hydroxide solution was added, followed by 18 mL of water. The mixture was extracted with ether and the extracts were washed with a 5% hydrochloric acid solution. The organic layer was dried and concentrated under reduced pressure to give 1.36 g (50%) of *N*-(*p*-nitrobenzyl)-*o*-hydroxybenzamide: mp 159–160 °C; NMR (100 MHz) τ 5.40 (d, 2 H, *J* = 6.0 Hz), 2.50–3.40 (m, 8 H), 1.88 (d, 1 H, *J* = 8.0 Hz), and −1.79 (s, 1 H). To a stirred solution containing 383 mg of sodium hydroxide in 50 mL of a 75% aqueous ethanol solution were added 2.60 g of the above amide and 1.16 g of allyl bromide. The reaction mixture was heated at 75 °C for 20 h. The solvent was partially removed and the residue was extracted with ether, washed with water, dried, and concentrated to give 2.2 g (74%) of *N*-(*p*-nitrobenzyl)-*o*-allyloxybenzamide: mp 99–100 °C; IR (KBr) 6.00, 6.50, 7.35, 8.00, 12.10 μ; NMR (100 MHz) τ 5.20–5.40 (m, 4 H), 4.56–4.80 (m, 2 H), 3.80–4.20 (m, 1 H), 1.80–3.12 (m, 9 H); UV (methanol) 275 nm (ε 22 000); *m/e* 312 (M^+), 133, 121 (base), 115, and 77.

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.28; H, 5.19; N, 8.95.

In a dried 50-mL flask were placed 312 mg of the above heide, 25 mL of freshly distilled benzene, and 228 mg of phosphorus pentachloride. The reaction mixture was heated at 65 °C for 45 min and the solvent was removed under reduced pressure to give *N*-(*p*-nitrobenzyl)-*o*-allyloxybenzimidoyl chloride (**5**) as a relatively hygroscopic material which was immediately reacted with triethylamine. The NMR spectrum of **5** (100 MHz) contained signals at τ 5.48 (d, 2 H, *J* = 6.0 Hz), 5.12 (s, 2 H), 4.56–4.84 (m, 2 H), 3.80–4.20 (m, 1 H), and 1.8–3.20 (m, 8 H).

Preparation of *N*-(*p*-Nitrobenzyl)-*o*-(3-carbomethoxy-2-propenyloxy)benzimidoyl Chloride (7). To a stirred solution containing 383 mg of sodium hydroxide in 50 mL of a 75% aqueous ethanol were added 2.6 g of *N*-(*p*-nitrobenzyl)-*o*-hydroxybenzamide and 1.71 g of methyl 4-bromocrotonate.[58] The reaction mixture was heated at 75 °C for 20 h and the solvent was then evaporated to give 2.3 g (65%) of *N*-(*p*-nitrobenzyl)-*o*-(3-carbomethoxy-2-propenyloxy)benzamide: mp 128–129 °C; IR (KBr) 5.75, 6.55, 7.60, 8.45, 9.80, 11.65, 12.10, and 13.10 μ; NMR (100 MHz) τ 6.24 (s, 3 H), 5.10–5.30 (m, 4 H), 3.92 (d, 1 H, *J* = 16.0 Hz), 1.72–3.12 (m, 9 H); UV (methanol) 275 nm (ε 38 000); *m/e* 370 (M^+), 121 (base), 161, 77.

Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.61; H, 4.90; N, 7.56. Found: C, 61.91; H, 4.94; N, 7.49.

In a dried 50-mL flask containing 370 mg of the above amide in 25 mL of freshly distilled benzene was added 228 mg of phosphorus pentachloride. The reaction mixture was heated at 65 °C for 45 min and the solvent was removed under reduced pressure to give *N*-(*p*-nitrobenzyl)-*o*-(3-carbomethoxy-2-propenyloxy)benzimidoyl chloride (**7**) as a relatively hygroscopic material which was immediately used in the next step. The NMR spectrum of **7** showed signals at τ 6.30 (s, 3 H), 5.28 (m, 2 H), 5.04 (s, 2 H), 3.84 (d, 1 H, *J* = 15.0 Hz), 1.80–3.16 (m, 8 H).

Preparation of 3-(*o*-Allyloxyphenyl)-2*H*-azirine (10). To a mixture containing 14.2 g of methyltriphenylphosphonium bromide in 250 mL of anhydrous ether was added 20 mL of a 2.4 M *n*-butyllithium solution in hexane at 20 °C. After stirring for 30 min at 20 °, 6.4 g of *o*-allyloxybenzaldehyde in 20 mL of ether was added dropwise and the reaction mixture stirred for an additional 12 h at room temperature. The solution was filtered and concentrated to give a yellow oil which was chromatographed on a silica gel column with ether as the eluent to give 4.8 g (75%) of *o*-allyloxystyrene: NMR (100 MHz) τ 5.54 (d, 2 H, *J* = 6.0 Hz), 4.80 (d, 2 H, *J* = 10.0 Hz), 4.72 (dd, 1 H, *J* = 18.0 and 2.0 Hz), 4.36 (dd, 1 H, *J* = 18.0 and 2.0 Hz), 3.88–4.24 (m, 1 H), 2.60–3.40 (m, 5 H).

To a mixture containing 1.3 g of sodium azide and 1.83 g of iodine monochloride in 30 mL of acetonitrile was added 1.6 g of *o*-allyoxystyrene in 5 mL of acetonitrile. The mixture was stirred for 30 min and was then added to water and extracted with ether. The ether extracts were washed with a 5% sodium thiosulfate solution and water, dried, and evaporated to give 3.3 g of 1-azido-2-iodo-1-(*o*-allyoxyphenyl)ethane: NMR (100 MHz) τ 6.40–6.80 (m, 2 H), 5.46 (d, 2 H, *J* = 6.0 Hz), 4.48–4.96 (m, 3 H), 3.80–4.20 (m, 1 H), 2.60–3.20 (m, 4 H).

To a stirred and cooled solution containing 3.3 g of the above iodine azide adduct in 40 mL of ether was added 1.34 g of potassium *tert*-butoxide and the resulting mixture was allowed to stir at 5 °C for 8 h. The slurry was washed with water and the ether layer dried over magnesium sulfate. Removal of the solvent under reduced pressure left 1.46 g (72%) of allyl *o*-(1-azidovinyl)phenyl ether: NMR (100 MHz) τ 5.50 (d, 2 H, *J* = 6.0 Hz), 5.16 (s, 1 H), 5.08 (s, 1 H), 4.56–4.92 (m, 2 H), 3.88–4.20 (m, 1 H), 2.68–3.24 (m, 4 H).

A 300-mg sample of the above vinyl azide in 5 mL of toluene was heated at reflux for 1 h. Removal of the solvent followed by distillation of the residue at 75 °C (0.08 mm) gave 200 mg (80%) of 3-(*o*-allyloxyphenyl)-2*H*-azirine (**10**): IR (neat) 3.35, 6.15, 6.60, 6.80, 7.70, 8.05, 9.50, 10.50, and 13.10 μ; NMR (100 MHz) τ 8.38 (s, 2 H), 5.40 (m, 2 H), 4.80 (d, 1 H, *J* = 10.0 Hz), 4.56 (d, 1 H, *J* = 16.0 Hz), 3.82–4.20 (m, 1 H), 2.30–3.34 (m, 4 H); *m/e* 173 (M^+), 172, 134, 119, 104, 91, and 77; UV (methanol) 380 nm (ε 26 200) and 248 (5400).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.55; H, 6.53; N, 8.16.

Preparation of (*E*)-3-(*o*-2-Butenyloxyphenyl)-2*H*-azirine (17). The general procedure of Hassner and Levy was used to prepare this azirine.[59] A sample of *o*-(2-butenyloxy)benzaldehyde was prepared by treating salicylaldehyde with crotyl bromide followed by distillation of the product at 112–115 °C (1.5 nm): NMR (100 MHz) τ 8.24 (d, 3 H, *J* = 7.5 Hz), 5.50 (d, 2 H, *J* = 5.0 Hz), 4.26 (m, 2 H), 3.0–3.2 (m, 2 H), 2.20–2.72 (m, 2 H), and −0.40 (s, 1 H). Treatment of this aldehyde with triphenylmethylenephosphorane gave a 92% yield of (*E*)-(*o*-2-butenyloxy)styrene: NMR (100 MHz) τ 8.24 (d, 3 H, *J* = 8.0 Hz), 5.44 (d, 2 H, *J* = 7.5 Hz). 4.22 (dd, 1 H, *J* = 11.0 and 2.0 Hz), 3.96–4.20 (m, 3 H), 2.26–3.04 (m, 5 H). Treatment of this material with iodine azide in the normal fashion afforded 1-azido-2-iodo-(*E*)-(*o*-2-butenyloxyphenyl)ethane in quantitative yield: NMR (100 MHz) τ 8.20 (d, 3 H, *J* = 4.0 Hz), 6.78 (dd, 1 H, *J* = 12.0 and 8.0 Hz), 6.56 (dd, 1 H, *J* = 12.0 and 4.5 Hz), 5.54 (m, 2 H), 4.99 (dd, 1 H, *J* = 8.0 and 4.5 Hz), 4.28 (m, 2 H), 2.28–2.72 (m, 4 H). Treatment of this material with potassium *tert*-butoxide gave 1-azido-1-((*E*)-(*o*-2-butenyloxyphenyl))ethylene in 80% yield: NMR (100 MHz) τ 8.22 (d, 3 H, *J* = 4.5 Hz), 5.54 (m, 2 H), 5.02 (s, 2 H), 4.24 (m, 2 H), 2.60–3.20 (m, 4 H). Thermolysis of this vinyl azide in refluxing toluene for 3.5 h gave (*E*)-3-(*o*-2-butenyloxyphenyl)-2*H*-azirine (**17**) in 91% yield: IR (neat) 3.44, 5.75, 6.27, 6.33, 6.73, 6.92, 7.30, 7.81, 8.60, 9.10, 9.20, 9.34, 10.20, 11.90, and 13.20 μ; NMR (100 MHz, CCl_4) τ 8.48 (s, 2 H), 8.23 (d, 3 H, *J* = 7.5 Hz), 5.43 (d, 2 H, *J* = 5.0 Hz), 4.34 (dt, 1 H, *J* = 16.0 and 5.0 Hz), 4.12 (dq, 1 H, *J* = 16.0 and 7.5 Hz), 2.92–3.12 (m, 2 H), 2.50–2.68 (m, 1 H), and 2.28–2.40 (m, 1 H); UV (cyclohexane) 303 nm (ε 4450) and 246 (9100); *m/e* 187 (M^+), 120 (base), 91, and 77.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.00; H, 7.14; N, 7.52.

Preparation of 5,5,5-Trimethoxy-2-(*o*-allyloxyphenyl)-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,5-oxazaphosph(V)ol (20). A sample of *o*-(allyloxy)benzoic acid, mp 64–65 °C, was prepared by the silver oxide oxidation of *o*-(allyloxy)benzaldehyde: NMR (60 MHz) τ 5.23 (d, 2 H, *J* = 5.0 Hz), 4.40–4.77 (m, 2 H), 3.53–4.22 (m, 1 H), 2.33–3.10 (m, 3 H), 1.80–2.00 (m, 1 H), and −0.01 (s, 1 H, exchanged with D_2O).

Anal. Calcd for $C_{10}H_{11}D_3$: C, 67.40; H, 5.66. Found: C, 67.51; H, 5.64.

This material was converted to the corresponding acid chloride by

stirring with excess thionyl chloride at room temperature for 24 h. A solution containing 5.0 g of the acid chloride in 10 mL of dioxane was added to 30 mL of a concentrated ammonium hydroxide solution. The mixture was stirred at room temperature for 30 min and was then diluted with water. The resulting precipitate was recrystallized from ethanol–water to give a 79% yield of *o*-(allyloxy)benzamide: mp 93–94 °C; NMR (100 MHz) τ 5.38 (d, 2 H, J = 8.0 Hz), 4.44–4.88 (m, 2 H), 3.40–4.30 (m, 1 H), 2.48–3.22 (m, 3 H), 1.73–2.00 (m, 1 H), and 2.20 (broad s, 2 H, exchanged with D_2O).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.45; H, 6.20; N, 7.95.

To a solution containing 1.77 g of *o*-(allyloxy)benzamide in 20 mL of methylene chloride was added an excess of anhydrous hexafluoroacetone. The mixture was allowed to reflux for 4 h and the excess hexafluoroacetone was removed under reduced pressure. The resulting residue was taken up in ether, washed with water, dried, and concentrated under reduced pressure to give a crystalline solid, mp 93–94 °C, corresponding to the addition across the C–O double bond of hexafluoroacetone: IR (KBr) 3.05, 5.99, 6.29, 6.50, 6.78, 6.90, 7.27, 8.10, 8.64, 8.82, 9.52, 9.78, 10.50, 10.63, 13.23, and 13.97 μ; NMR (100 MHz, benzene-d_6) τ 6.33 (d, 2 H, J = 6.5 Hz), 4.98–5.20 (m, 2 H), 4.20–4.66 (m, 1 H), 3.87 (dd, 1 H, J = 8.0 and 1.5 Hz), 3.34 (dt, 1 H, J = 8.0 and 1.5 Hz), 3.05 (dt, 1 H, J = 8.0 and 2.0 Hz), 1.78 (dd, J = 8.0 and 2.0 Hz, 1 H), 0.70 (broad s, 1 H, exchanged with D_2O), 0.60 (broad s, 1 H, exchanged with D_2O); *m/e* 343 (M^+), 165, 149, 148, and 135.

Anal. Calcd for $C_{13}H_{11}F_6NO_3$: C, 45.49; H, 3.23; N, 4.07. Found: C, 45.88; H, 3.47; N, 4.04.

To a cooled and stirred solution containing 3.43 g of the above compound in 40 mL of ether were simultaneously added 1.72 g of pyridine and 4.22 g of trifluoroacetic anhydride over a period of 30 min. The resulting mixture was stirred at 0 °C for 1 h followed by filtration and concentration under reduced pressure. The viscous oil obtained was used in the next step without purification. A solution containing the above oil in 20 mL of hexane was cooled to 0 °C and 2.0 g of trimethyl phosphite was added dropwise. The mixture was allowed to stir for 7 h at 0 °C and was then cooled to −50 °C. The crystalline mass obtained was filtered, washed with hexane, and dried to give 3.35 g (75%) of 5,5,5-trimethoxy-2-(*o*-allyloxyphenyl)-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,5-oxazaphosph(V)ol (**20**) as a crystalline solid: mp 60–62 °C; IR (KBr) 3.45, 6.27, 6.76, 6.92, 7.41, 7.91, 8.13, 8.40, 9.34, 9.66, 10.05, 10.55, 11.33, 12.25, 13.40, and 13.80 μ; NMR (100 MHz, benzene-d_6) τ 6.62 (d, 9 H, J = 12.5 Hz), 6.01 (d, 2 H, J = 4.5 Hz), 4.74–5.14 (m, 2 H), 4.20–4.60 (m, 1 H), 2.80–3.60 (m, 3 H) and 1.86 (m, 1 H); ^{19}F NMR (94.1 MHz, benzene-d_6) τ 8.90 and 9.95 (ratio 1:3) upfield from hexafluorobenzene; UV (cyclohexane) λ 239 nm (ϵ 810) and 293 (375); *m/e* 308, 239, 170, 139, 109 (base), 108, 97, 96, 80, and 79.

Anal. Calcd for $C_{16}H_{18}NO_5F_6P$: C, 42.77; H, 4.04; N, 3.11. Found: C, 42.72; H, 4.05; N, 3.11.

Treatment of 1-*o*-((3-Carbomethoxy-2-propenyloxy)phenyl)-2-methylpropan-1-one *N,N,N*-Trimethylhydrazonium Iodide (23) with Base. To a cooled solution containing 20.2 g of diisopropylamine in 40 mL of tetrahydrofuran was added 87.3 mL of a 2.29 M *n*-butyllithium solution. After stirring at 0 °C for 20 min, 19.2 g of 1-hydroxypropiophenone *N,N*-dimethylhydrazone was added. The solution was stirred at 20 °C for 2 h and then 14.8 g of methyl iodide was added. A normal workup procedure afforded 7.2 g (35%) of 1-(*o*-hydroxyphenyl)-2-methylpropan-1-one. A 5-g sample of this material in 20 mL of methyl iodide was refluxed for 2 days. Removal of the methyl iodide left 5.2 g (60%) of the hydrazonium salt, mp 134–136 °C. To a stirred solution containing 440 mg of sodium hydroxide in 50 mL of a 75% aqueous methanol solution was added 2 g of the above salt followed by 2.0 g of methyl 4-bromocrotonate. The mixture was heated at 75 °C for 8 h and was then extracted with ether. The ether layer was washed with water, dried, and concentrated under reduced pressure to give 1.2 g (50%) of *o*-((3-carbomethoxy-2-propenyloxy)-phenyl)-2-methylpropan-1-one hydrazonium iodide (**23**): mp 148–150 °C; NMR (60 MHz) τ 8.83 (m, 6 H), 7.20 (septet, 1 H, J = 6.0 Hz), 6.45 (s, 9 H), 6.23 (s, 3 H), 5.27 (m, 2 H), 4.10 (d, 1 H, J = 16.0 Hz), and 2.67–3.10 (m, 5 H).

A 700-mg sample of the above salt was dissolved in 10 mL of dimethyl sulfoxide and then 40 mg of sodium hydride was added. The reaction mixture was allowed to stir at 25 °C for 4 h and was quenched with water, extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a white solid which was recrystallized from hexane to give 230 mg of methyl 3-isopropyl-2-benzofuranacrylate (**25**): mp 60–61 °C; IR (KBr) 3.35, 5.80, 6.10, 6.90, 7.80, 8.50, 9.50, 10.25, 10.65, 11.00, and 13.30 μ; NMR (60 MHz) τ 8.57 (d, 6 H, J = 7.0 Hz), 6.70 (septet, 1 H, J = 7.0 Hz), 6.23 (s, 3 H), 3.50 (d, 1 H, J = 16.0 Hz), 2.30–3.00 (m, 4 H), 2.33 (d, 1 H; J = 16.0 Hz); *m/e* 244 (M^+, base), 229, 186, 159, 115, and 77.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.42; H, 6.47.

Treatment of 1-*o*-((3-Carbomethoxy-2-propenyloxy)phenyl)propan-1-one *N,N,N*-Trimethylhydrazonium Iodide (26) with Base. A mixture containing 3.84 g of 1-(*o*-hydroxyphenyl)propan-1-one *N,N*-dimethylhydrazone and 10 mL of methyl iodide was heated at reflux for 25 h. Removal of the excess methyl iodide left 4 g (60%) of the corresponding trimethylhydrazonium salt, mp 120–121 °C. To a stirred solution containing 400 mg of sodium hydroxide in 50 mL of a 75% aqueous methanol solution was added 1.7 g of the above salt followed by 1.7 g of methyl 4-bromocrotonate. The mixture was heated at 74 °C for 8 h and extracted with ether. The ethereal layer was washed with water, dried, and evaporated to give 1.2 g (50%) of 1-(*o*-(3-carbomethoxy-2-propenyloxy)phenyl)propan-1-one *N,N,N*-trimethylhydrazonium iodide (**26**), mp 144–145 °C.

A 1.0-g sample of **26** was dissolved in 10 mL of dry dimethyl sulfoxide and 55 mg of sodium hydride was added. The mixture was stirred at 25 °C for 4 h and then water was added. The solution was extracted with ether and the extracts were washed with water, dried, and concentrated to give 250 mg (50%) of methyl 3-ethyl-2-benzofuranacrylate (**27**) as a white solid: mp 56–57 °C; IR (KBr) 3.35, 5.80, 6.10, 6.85, 7.60, 8.50, 10.25, 11.50, and 13.30 μ; NMR (60 MHz) τ 8.73 (t, 3 H, J = 8.0 Hz), 7.20 (q, 2 H, J = 8.0 Hz), 6.23 (s, 3 H), 2.57 (d, 1 H, J = 15.0 Hz), 2.43 (d, 1 H, J = 15.0 Hz), 2.46–3.00 (m, 4 H); *m/e* 230 (M^+), 215, 171, 147, 121, 119 (base), 91, and 77.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.81; H, 6.03.

Preparation of (*E*)-3-[*o*-(4-Carbomethoxy-3-butenyl)phenyl]-2,2-dimethyl-2*H*-azirine (29). A solution containing 100 mg of 2-(2,2-dimethyl-2*H*-azirin-3-yl)benzenepropanal[60] (prepared from the ozonization of 3-(*o*-(3-butenyl)phenyl)-2,2-dimethyl-2*H*-azirine) (**28**) and 1.8 g of carbomethoxymethylenetriphenylphosphorane[61] in 25 mL of methylene chloride was stirred at room temperature for 14 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using ether as the eluent to give 1.2 g (94%) of a pale yellow oil whose structure was assigned as (*E*)-3-(*o*-(4-carbomethoxy-3-butenyl)phenyl)-2,2-dimethyl-2*H*-azirine (**29**): IR (neat) 3.30, 5.70, 5.90, 6.90, 7.80, 8.25, 9.50, 13.80, and 14.30 μ; NMR (100 MHz) τ 8.86 (s, 6 H), 7.50–7.70 (m, 2 H), 6.90–7.10 (m, 2 H), 6.48 (s, 3 H), 4.30 (d, 1 H, J = 16.0 Hz), 2.4–3.4 (m, 5 H); *m/e* 257 (M^+), 242, 198, 116 (base), 77; UV (methanol) 275 nm (ϵ 4100) and 245 (38 000).

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.45; H, 7.33; N, 5.21.

Irradiation of 3-(*o*-Allyloxyphenyl)-2,2-dimethyl-2*H*-azirine (1). A solution containing 100 mg of **1** in 150 mL of benzene was irradiated under a nitrogen atmosphere for 15 min using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent left 100 mg of a pale yellow oil whose spectral properties were consistent with 1a,2-dihydro-*N*-isopropylidenebenzo[*b*]cyclopropa[*d*]pyran-7b-(1*H*)-amine (**2**); IR (neat) 3.35, 5.95, 6.18, 6.85, 7.70, 8.44, 9.60, 10.70, and 13.15 μ; NMR (100 MHz) τ 8.76–8.80 (m, 2 H), 8.60 (t, 1 H, J = 5.0 Hz), 8.14 (s, 3 H), 7.88 (s, 3 H), 6.12 (d, 1 H, J = 10.0 Hz), 5.72 (d, 1 H, J = 10.0 Hz), 2.70–3.20 (m, 4 H). Chromatography of this material on a thick layer plate using a 15% ethyl acetate–hexane mixture as the eluent gave 55 mg (56%) of 1a,2-dihydrobenzo[*b*]-cyclopropa[*d*]pyran-7b(1*H*)-amine (**3**) as the only identifiable material: IR (neat) 6.17, 6.85, 7.65, 8.55, 9.60, 10.75, and 13.15 μ; NMR (100 MHz) τ 8.88 (m, 2 H), 8.28 (dd, 1 H, J = 7.5 and 5.5 Hz), 7.82 (s, 2 H, exchanged with D_2O), 6.20 (d, 1 H, J = 10.0 Hz), 5.78 (d, 1 H, J = 10.0 Hz), 2.50–3.22 (m, 4 H). Addition of Eu(fod)$_3$ to the sample gave a spectrum which showed a triplet at τ 8.50 (1 H, J = 5.0 Hz), a doublet of doublets at 8.30 (1 H, J = 8.0 and 5.0 Hz), a multiplet at 7.70 (1 H), a doublet at 5.96 (1 H, J = 10.0 Hz), a doublet at 5.65 (1 H, J = 10.0 Hz), a broad singlet at 4.90 (2 H, exchanged with D_2O), and the aromatic protons at 2.1—3.1 (m, 4 H); UV (methanol) 280 nm (ϵ 4250) and 273 (4600); *m/e* 161, 160, 119, 96, and 91.

A mixture containing 100 mg of the above amine **3**, 115 mg of *p*-

nitrobenzaldehyde, and a trace of *p*-toluenesulfonic acid in 10 mL of toluene was heated at reflux for 1 h. Removal of the solvent left a residue which was recrystallized from hexane to give 62 mg of 1a,2-dihydro-*N*-(*p*-nitrobenzylidene)benzo[*b*]cyclopropa[*d*]-pyran-7b(1*H*)amine: mp 112–113 °C; IR (KBr) 6.00, 6.55, 7.70, 8.95, 9.58, 10.50, 11.78, 12.70, and 13.35 μ; NMR (100 MHz) τ 8.16–8.48 (m, 1 H), 7.94 (t, 1 H, *J* = 6.0 Hz), 5.96 (d, 1 H, *J* = 10.0 Hz), 5.68 (d, 1 H, *J* = 10.0 Hz), 1.64–3.20 (m, 8 H); *m/e* 294 (M^+, base), 279, 264, 248, 158, 144, 117, 107, and 77; UV (methanol) 280 nm (ε 23 500).

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.37; H, 4.80; N, 9.52. Found: C, 69.08; H, 4.82; N, 9.47.

The photolysis of **1** was also carried out in the presence of methyl acrylate. A solution containing 105 mg of **1** and 15 mL of methyl acrylate in 125 mL of benzene was irradiated under a nitrogen atmosphere for 20 min using a Vycor filter sleeve. Removal of the solvent followed by thick layer chromatography gave 90 mg (62%) of a 2-(*o*-allyloxyphenyl)-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**4**): IR (neat) 3.30, 5.65, 6.60, 7.25, 8.50, 9.35, 10.65, 11.65, 12.10, and 13.10 μ; NMR (100 MHz, benzene-d_6) τ 8.70 (s, 3 H), 8.36 (s, 3 H), 7.04 (d, 1 H, *J* = 10.0 Hz), 6.80 (d, 1 H, *J* = 18.0 Hz), 6.60 (s, 3 H), 6.18 (dd, 1 H, *J* = 18.0 and 10.0 Hz), 5.88 (d, 2 H, *J* = 4.0 Hz), 4.90 (d, 1 H, *J* = 10.0 Hz), 4.80 (d, 1 H, *J* = 17.0 Hz), 3.80–4.14 (m, 1 H), 3.06–3.20 (m, 2 H), 2.64–2.80 (m, 1 H), 2.28 (d, 1 H, *J* = 8.0 Hz); *m/e* 287 (M^+), 271, 256, 228, 200, 186, 172 (base), 144, 117, and 77; UV (methanol) 285 nm (ε 6000) and 255 (15 000).

Treatment of *o*-Allyloxy-*N*-(*p*-nitrobenzyl)benzimidoyl Chloride 5 with Triethylamine. A 350-mg sample of imidoyl chloride **5** in 15 mL of freshly distilled benzene was cooled to 0 °C and 0.3 mL of triethylamine was added. The mixture was allowed to stir for 14 h at room temperature and then the solvent was removed under reduced pressure. Chromatography of the residue on a thick layer plate using a 15% ethyl acetate–hexane mixture as the eluent gave 200 mg of 2,3,3a,4-tetrahydro-2-(*p*-nitrophenyl)[1]benzopyrano[4,3-*b*]pyrrole (**6**): mp 137–138 °C; IR (KBr) 6.05, 6.50, 7.30, 11.60, 12.75, 13.30, and 14.15 μ; *m/e* 294 (M^+, base), 279, 263, 158, 145, 115, 107, and 77; UV (methanol) 260 nm (ε 35 200); NMR (100 MHz) τ 8.60 (ddd, 1 H, *J* = 12.0, 10.0, and 10.0 Hz), 7.20 (ddd, 1 H, *J* = 12.0, 6.0, and 6.0 Hz), 6.40–6.80 (m, 1 H), 6.04 (dd, 1 H, *J* = 12.0 and 10.5 Hz), 5.28 (dd, 1 H, *J* = 10.5 and 6.0 Hz), 4.80 (ddd, 1 H, *J* = 10.0, 6.0, and 2.0 Hz), 1.68–3.00 (m, 8 H). Spin decoupling of the multiplet at τ 6.60 caused the signal at τ 4.80 to collapse to a doublet of doublets. External irradiation at τ 6.60 caused the signal at τ 8.60 to collapse to a triplet, the doublet of doublets at τ 5.28 to collapse to a doublet, and the signal at τ 4.80 to collapse to a doublet of doublets. External irradiation of the signal at τ 6.04 collapsed the doublet of doublets at τ 5.28 to a doublet. Similarly, decoupling at τ 5.28 collapsed the doublet of doublets at τ 6.04 to a doublet while irradiation of the signal at τ 4.80 collapsed the signal at τ 8.60 to a triplet.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.37; H, 4.80; N, 9.52. Found: C, 69.20; H, 4.82; N, 9.72.

The nitrile ylide derived from **5** could be trapped with added methyl acrylate. To 330 mg of imidoyl chloride **5** in 20 mL of freshly distilled benzene was added 0.7 mL of methyl acrylate followed by 0.3 mL of triethylamine. After stirring overnight at room temperature, the solvent was evaporated and the residue was subjected to thick layer chromatography. The major products isolated corresponded to a set of isomeric 2-(*o*-allyloxyphenyl)-4-carbomethoxy-5-*p*-nitrobenzyl-Δ^1-pyrrolines (**9**): isomer A, NMR (100 MHz) τ 6.86 (t, 1 H, *J* = 8.0 Hz), 6.40 (d, 2 H, *J* = 8.0 Hz), 6.20 (s, 3 H), 5.38 (d, 2 H, *J* = 6.0 Hz), 4.48–4.76 (m, 2 H), 4.44 (d, 1 H, *J* = 8.0 Hz), 3.72–4.08 (m, 1 H), 1.72–3.08 (m, 8 H); *m/e* (M^+), 350, 321, 309, 150, 130, 115, 106, and 77; UV (methanol) 270 nm (ε 11 000); isomer B, NMR (100 MHz) τ 6.80 (s, 3 H), 6.13–6.68 (m, 3 H), 5.36 (d, 2 H, *J* = 6.0 Hz), 4.48–4.76 (m, 2 H), 4.28 (d, 1 H, *J* = 8.0 Hz), 3.76–4.12 (m, 1 H), 1.80–3.08 (m, 8 H); *m/e* 380 (M^+), 351, 321 (base), 293, 280, 265, 145, 130, 115, and 77; UV (methanol) 270 nm (ε 11 700).

Treatment of *N*-(*p*-Nitrobenzyl)-*o*-(3-carbomethoxy-2-propenyloxy)benzimidoyl Chloride (7) with Triethylamine. A 400-mg sample of imidoyl chloride **7** in 15 mL of freshly distilled benzene was cooled to 0 °C and 0.3 mL of triethylamine was added. The mixture was allowed to stir at room temperature for 14 h and then the solvent was removed under reduced pressure to leave behind a solid which was crystallized from ethanol to give 150 mg (42%) of methyl 2,3,3a,4-tetrahydro-2-(*p*-nitrophenyl)[1]benzopyrano[4,3-*b*]pyrrole-3-carboxylate (**8**): mp 156–157 °C; IR (KBr) 5.70, 6.60, 7.40, 11.60, and 13.10 μ; NMR (100 MHz, benzene-d_6) τ 7.26 (t, 1 H, *J* = 10.0 Hz), 7.12 (s, 3 H), 6.88 (dd, 1 H, *J* = 14.0 and 10.0 Hz), 6.20–6.40 (m, 1 H), 5.82 (dd, 1 H, *J* = 10.0 and 6.0 Hz), 4.56 (d, 1 H, *J* = 10.0 Hz), 1.80–3.32 (m, 8 H); *m/e* 352 (M^+), 294, 293, (base), 246, 171, 115, 77; UV (methanol) 270 nm (ε 34 500).

Anal. Calcd for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.64; H, 4.63; N, 7.94.

All attempts to trap a nitrile ylide by carrying out the base-induced reaction of imidoyl chloride **7** in the presence of methyl acrylate failed. The only product obtained under these conditions was the intramolecular dipolar cycloadduct **8**.

Irradiation of 3-(*o*-Allyloxyphenyl)-2*H*-azirine (10). A solution containing 80 mg of **10** in 150 mL of benzene was irradiated for 20 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent followed by thick layer chromatography gave 62 mg (75%) of a white solid, mp 98–99 °C, whose structure was assigned as 2,3,3a,4-tetrahydro[1]benzopyrano[4,3-*b*]pyrrole (**11**) on the basis of its characteristic spectra: IR (KBr) 3.45, 6.05, 6.15, 6.75, 7.40, 8.20, 9.60, 9.95, 12.10, and 13.80 μ; *m/e* 173 (M^+), 172, 145, 119, 91, 77, 55 (base); UV (methanol) 310 nm (ε 20 000) and 253; NMR (100 MHz) τ 8.48 (dddd, 1 H, *J* = 12.0, 10.0, 10.0, and 9.0 Hz), 7.78 (ddd, 1 H, *J* = 12.0, 8.0, and 7.0 Hz), 6.52–7.04 (m, 1 H), 6.24 (dddd, 1 H, *J* = 16.0, 10.0, 8.0, and 2.0 Hz), 6.19 (dd, 1 H, *J* = 13.0 and 10.0 Hz), 5.80 (ddd, 1 H, *J* = 16.0, 9.0, and 2.0 Hz), 5.38 (dd, 1 H, *J* = 10.0 and 6.0 Hz), 2.08–3.16 (m, 4 H). External irradiation of the signal at τ 7.78 collapsed the signal at τ 5.80 to a doublet while irradiation of the signal at τ 6.80 caused the doublet of doublets at τ 6.19 and 5.38 to collapse to a doublet. Irradiation at τ 6.19 caused the signal at τ 5.38 to collapse to a triplet while irradiation at τ 5.38 caused the doublet of doublets at τ 6.19 to collapse to a triplet.

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.13; H, 6.36; N, 8.24.

The photolysis of **10** was also carried out in the presence of methyl acrylate. A solution containing 150 mg of **10** in 150 mL of benzene and 20 mL of methyl acrylate was irradiated for 20 min under a nitrogen atmosphere using a Corex filter sleeve. Removal of the solvent followed by thick layer chromatography of the residue gave 77 mg of 2-(*o*-allyloxyphenyl)-4-carbomethoxy-Δ^1-pyrroline (**12**): IR (neat) 3.35, 5.60, 6.05, 6.70, 8.00, 9.60, 10.50, and 13.00 μ; NMR (100 MHz) τ 6.44–6.67 (m, 3 H), 6.27 (s, 3 H), 5.67–6.10 (m, 2 H), 5.40 (d, 2 H, *J* = 5.0 Hz), 4.60–4.89 (m, 2 H), 3.67–4.10 (m, 1 H), 2.90–3.20 (m, 2 H), 2.54–2.87 (m, 1 H), 2.20 (d, 1 H, *J* = 8.0 Hz); *m/e* 259 (M^+), 228, 200 (base), 172, 159, 144, 124, and 77.

Irradiation of 3-(*o*-Allyloxyphenyl)-2-methyl-2*H*-azirine (13). A solution containing 200 mg of **13** in 150 mL of benzene was irradiated for 20 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent followed by thick layer chromatography using a 30% acetone–hexane mixture as the eluent resulted in the separation of two bands. The band with the higher R_f value contained 60 mg (30%) of a crystalline solid, mp 60–61 °C, whose structure was assigned as 2-methyl-2,3,3a,4-tetrahydro[1]benzopyrano[4,3-*b*]-pyrrole (**15**) on the basis of its characteristic spectra: IR (KBr) 3.42, 3.49, 6.15, 6.21, 6.39, 6.80, 6.89, 7.25, 7.60, 8.16, 8.90, 9.17, 10.00, 12.19, and 13.25 μ; *m/e* 187, 186, 172 (base), 146, 145, 144, 131, 119, 117, 115, and 105; NMR (CCl_4, 60 MHz) τ 8.55 (d, 3 H, *J* = 7.0 Hz), 8.2 (m, 1 H), 7.68 (ddd, 1 H, *J* = 13.0, 8.0, and 5.0 Hz), 6.20 (m, 1 H), 6.17 (dd, 1 H, *J* = 13.0 and 10.0 Hz), 6.00 (m, 1 H), 5.40 (dd, 1 H, *J* = 10.0 and 6.0 Hz), 2.8–3.2 (m, 3 H), and 2.5–2.6 (m, 2 H).

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.77; H, 7.18; N, 7.41.

The second band isolated from the thick layer plate contained 66 mg (33%) of an oil whose structure was identified as 1a,2-dihydrobenzo[*b*]cyclopropa[*d*]pyran-7b(1*H*)-amine (**3**). This material was identical with that isolated from the irradiation of the related dimethylazirine **1**. The corresponding imine **14** from which **3** was obtained by hydrolysis on the thick layer plate could not be isolated but could be detected in the crude photolysate: NMR (60 MHz) τ 8.01 (d, 3 H, *J* = 7.0 Hz).

A 200-mg sample of the crude photolysate was stirred in 6 mL of a 5:1 mixture of ether–water for 1 h and was then added to 10 mL of a 0.2% 2,4-dinitrophenylhydrazine in a 2 M hydrochloric acid solution. The yellow solid which precipitated was filtered and recrystallized from ethanol to give the 2,4-dinitrophenylhydrazone of acetaldehyde, mp 145–146 °C (lit. 147 °C). This material was identical with an authentic sample which was independently synthesized.

The photolysis of **13** was also carried out in the presence of methyl

acrylate. A solution containing 150 mg of **13** and 0.5 mL of methyl acrylate in 15 mL of hexane was irradiated in a quartz tube for 35 min using a low-pressure mercury lamp. Removal of the solvent followed by thick layer chromatography using a 10% acetone–hexane mixture gave 185 mg (83%) of a light yellow oil which contained a mixture of the cis and trans isomers of 2-(*o*-allyloxyphenyl)-4-carbomethoxy-5-methyl-Δ^1-pyrroline (**16**) which could not be separated by thick layer chromatography: NMR (60 MHz, CCl_4) τ 8.90 (d, J = 7.0 Hz) and 8.62 (d, J = 7.0 Hz, 3 H total), 6.53–7.60 (m, 2 H), 5.80 (pentet, 1 H, J = 8.0 Hz), 5.50 (d, 2 H, J = 5.0 Hz), 4.50–4.93 (m, 2 H), 3.67–4.27 (m, 1 H), 2.67–3.33 (m, 3 H), and 2.07–2.23 (m, 1 H); *m/e* 273 (M^+), 158 (base), 91, and 77.

Irradiation of 3-(*o*-(2-Butenyloxy)phenyl)-2*H*-azirine (17). A solution containing 40 mg of **17** in 200 mL of benzene was irradiated for 20 min with a 450-W Hanovia medium pressure lamp equipped with a Vycor filter sleeve. Removal of the solvent left a yellow oil which was subjected to preparative thick layer chromatography using a 20% acetone–hexane mixture as the eluent. The faster moving band contained 13.1 mg (34%) of a crystalline solid, mp 54–55 °C, whose structure was assigned as 1-methyl-1a,2-dihydrobenzo[*b*]cyclopropa[*d*]pyran-7b-amine (**18**) on the basis of its spectral data: IR (neat) 2.94, 3.40, 3.49, 6.27, 6.33, 6.73, 6.89, 7.25, 7.69, 7.98, 8.19, 8.80, 9.30, 9.70, 10.02, 10.29, 10.95, 12.35, and 13.20 μ; UV (cyclohexane) 283, 277, and 227 nm (ϵ 1800, 1900, and 7200); NMR ($CDCl_3$, 100 MHz) τ 8.66 (broad s, 5 H), 8.14 (broad singlet, 2 H, exchanged with D_2O), 5.72 and 6.15 (AB pattern, 2 H, J = 10.5 Hz), 2.8–3.32 (m, 3 H), and 2.48–2.60 (m, 1 H). Addition of Eu(fod)$_3$ shift reagent caused the singlet at τ 8.66 to separate into three discrete signals, a doublet (3 H, J = 6.0 Hz), a pentuplet (1 H, J = 6.0 Hz), and a doublet (1 H, J = 6.0 Hz); *m/e* 175 (M^+), 160, 158, 135, 120, 91, and 84.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.61; H, 7.85; N, 7.93.

The second band obtained from the thick layer plate contained 16.3 mg (41%) of a colorless oil whose structure was assigned as 3-methyl-2,3,3a,4-tetrahydro[1]benzopyrano[4,3-*b*]pyrrole (**19**): IR (neat) 3.44, 3.52, 6.13, 6.19, 6.35, 6.75, 6.89, 7.27, 7.49, 7.66, 8.19, 8.70, 8.92, 9.30, 10.01, 10.35, 12.04, and 13.15 μ; UV (cyclohexane) 316 nm (ϵ 3700), 304 (3900), and 249 (21 000); NMR ($CDCl_3$, 100 MHz) τ 8.76 (d, 3 H, J = 6.5 Hz), 7.20 (m, 1 H), 6.60 (ddd, 1 H, J = 13.0, 6.0, and 3.0 Hz), 6.10 (dd, 1 H, J = 13.0 and 10.0 Hz), 5.72 (dd, 1 H, J = 13.0 and 8.0 Hz), 5.80 (m, 1 H), 5.36 (dd, 1 H, J = 10.0 and 6.0 Hz), 2.40–3.20 (m, 3 H), and 2.04–2.10 (m, 1 H); *m/e* 187 (M^+), 186, 185, 174, 173, 171, 159, 119 (base), and 91. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.49. Found: C, 76.62; H, 7.34; N, 7.27.

The photolysis of **17** was also carried out in the presence of methyl acrylate. A solution containing 300 mg of **17** and 15 mL of methyl crotonate in 150 mL of cyclohexane was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent left a yellow oil which was subjected to preparative thick layer chromatography using a 15% acetone–hexane mixture as the eluent. The major component contained 375 mg (82%) of a clear oil whose structure was assigned as 2-(*o*-(2-butenyloxyphenyl))-3-methyl-4-carbomethoxy-Δ^1-pyrroline on the basis of its spectral data: IR (neat) 3.42, 3.49, 5.80, 6.25, 6.76, 6.89, 7.30, 8.12, 8.95, 9.90, 10.29, 10.91, and 13.20 μ; NMR ($CDCl_3$, 100 MHz) τ 8.92 (d, 3 H, J = 7.5 Hz), 8.24 (d, 3 H, J = 5.0 Hz), 7.20 (p, 1 H, J = 7.5 Hz), 6.32 (s, 3 H), 6.20 (q, 1 H, J = 7.5 Hz), 5.96 (t, 2 H, J = 8.0 Hz), 5.54 (d, 2 H, J = 4.5 Hz), 4.26 (m, 2 H), 2.08–3.28 (m, 4 H); *m/e* 287 (M^+), 178 (base), 105, and 77.

Irradiation of 5,5,5-Trimethoxy-2-(*o*-allyloxyphenyl)-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,5-oxazaphosph(V)ol (20). A solution containing 450 mg of 1,3,5-oxazaphosph(V)ol **20** in 500 mL of benzene under an argon atmosphere was irradiated for 4 h using a Vycor filter sleeve. Removal of the solvent left behind a crystalline solid which was recrystallized from an 80% ethanol solution to give 2,2-di(trifluoromethyl)-2,3,3a,4-tetrahydro[1]benzopyrano[4,3-*b*]pyrrole (**22**) as a white solid: mp 140–141 °C; IR (KBr) 3.38, 6.15, 6.23, 6.82, 6.90, 7.27, 7.75, 8.00, 8.28, 8.80, 8.95, 9.22, 9.71, 10.02, 10.50, 12.13, 13.04, 13.76, and 14.35 μ; *m/e* 309 (M^+), 290, 240 (base), 171, 145; NMR (100 MHz, CCl_4) τ 8.12 (dd, 1 H, J = 14.0 and 9.0 Hz), 7.36 (dd, 1 H, J = 14.0 and 8.0 Hz), 6.52 (dddd, 1 H, J = 12.3, 9.0, 8.0, and 5.4 Hz), 6.08 (dd, 1 H, J = 12.3 and 9.5 Hz), 5.37 (dd, 1 H, J = 9.5 and 5.4 Hz), 2.60–3.28 (m, 3 H), and 2.0–2.20 (m, 1 H); NMR (benzene-d_6, 94.1 MHz) τ 16.07 (q, J = 7.5 Hz, 3 F) and 16.40 (q, J = 7.5 Hz, 3 F) relative to hexafluorobenzene.

Anal. Calcd for $C_{13}H_{19}F_6NO$: C, 50.49; H, 2.93; N, 4.53. Found: C, 50.42; H, 2.97; N, 4.56.

The same compound was also formed in quantitative yield when a sample of **20** was refluxed in xylene for 24 h.

The photolysis of **20** was also carried out in the presence of methyl acrylate. A solution containing 50 mg of **20** and 50 mL of methyl acrylate in 50 mL of benzene was irradiated for 4 h with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent followed by thick layer chromatography resulted in the separation of two bands. The minor band contained 10 mg (29%) of the internal 1,3-dipolar adduct **22**. The major band contained 20 mg (43%) of a clear oil which contained a mixture of 3-carbomethoxy- and 4-carbomethoxy-2-(*o*-allyloxyphenyl)-5,5-di(trifluoromethyl)-Δ^1-pyrroline. All attempts to separate the mixture into its component parts failed. The NMR spectrum of the mixture (100 MHz, $CDCl_3$) showed bands at τ 7.04–7.60 (m, 1 H), 6.00–6.80 (m, 1 H), 6.18 (s) and 6.39 (s) (3 H, ratio 2:3), 5.26–5.48 (m, 2 H), 4.48–4.74 (m, 2 H), 3.72–4.14 (m, 1 H), 2.88–3.14 (m, 2 H), 2.66–2.74 (m, 1 H), and 1.90–3.04 (m, 1 H); *m/e* 397 (M^+).

Irradiation of (*E*)-3-[o-(4-Carbomethoxy-3-butenyl)phenyl]-2,2-dimethyl-2*H*-azirine (29). A solution containing 100 mg of **29** 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 chromatographed on a thick layer plate using a 15% ethyl acetate–hexane mixture as the eluent. The major band contained a single product (85%) whose structure was assigned as methyl 3,3a,4,5-tetrahydro-2,2-dimethyl-2*H*-benz[*g*]indole-3-carboxylate (**30**) on the basis of the following data: IR (neat) 3.30, 5.65, 6.00, 6.85, 7.30, 8.20, 8.50, and 13.00 μ; NMR (100 MHz) τ 8.92 (s, 3 H), 8.40 (s, 3 H), 8.20–8.58 (m, 1 H), 7.60–7.90 (m, 1 H), 7.36 (d, 1 H, J = 10.0 Hz), 6.98–7.12 (m, 2 H), 6.50–6.72 (m, 1 H), 6.32 (s, 3 H), 2.82 (m, 3 H), 2.00 (d, 1 H, J = 6.0 Hz); *m/e* 257 (M^+), 256, 242, 198, 184 (base), 141, 77; UV (methanol) 270 nm (ϵ 3000) and 245 (18 600).

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.45; H, 7.38; N, 5.11.

A photolysis of **29** was also carried out in the presence of methyl acrylate. A solution containing 100 mg of **29** and 20 mL of methyl acrylate in 120 mL of benzene was irradiated under an argon atmosphere using a Vycor filter sleeve. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate to give a single component whose structure is assigned as (*E*)-2-(4-carbomethoxy-3-butenylphenyl)-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline: IR (neat) 3.30, 5.70, 5.95, 6.90, 7.50, 8.55, 9.30, and 13.05 μ; NMR (100 MHz) τ 8.84 (s, 3 H), 8.50 (s, 3 H), 7.40–7.80 (m, 2 H), 6.90–7.20 (m, 3 H), 6.20–6.80 (m, 2 H), 6.34 (s, 3 H), 6.32 (s, 3 H), 4.20 (d, 1 H, J = 14.0 Hz), 2.30–3.14 (m, 5 H); *m/e* 343 (M^+), 328, 257, 198, 183, 116 (base), 105, 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 giving a reproducible lamp output of 1.63×10^{17} quanta s^{-1}.[45] After irradiation, the degree of reaction was determined by quantitative NMR spectroscopy. The conversions were run to 20% or less. Competitive studies were carried out photochemically on mixtures of the 2*H*-azirine, an internal standard, and methyl acrylate as an external dipolarophile. All measurement were made on a "merry-go-round" assembly at room temperature using a 2537-Å source. Varying quantities of methyl acrylate were added to solutions of the azirine, and the amount of rearranged product was determined by quantitative NMR after ca. 20% of starting material had been consumed.

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