Observations on the Scope of the Photoinduced 1,3-Dipolar Addition Reactions of Arylazirines[1]

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Abstract: The scope of the photoinduced cycloaddition reaction of arylazirines with electron-deficient olefins has been examined. Upon irradiation with ultraviolet light, arylazirines undergo ring opening to produce nitrile ylides. These reactive 1,3-dipoles are trapped with a variety of dipolarophiles to produce Δ^1-pyrrolines. The cycloaddition reaction shows all the characteristics of a concerted reaction, including stereospecificity and regioselectivity. When the azirine is photolyzed in the presence of an unsymmetrically substituted dipolarophile, two photoadducts are formed. The ratio of adducts provides a probe into the interplay of steric and electronic factors in the cycloaddition. Mechanistic discussion of the cycloaddition is given in the following paper.

Although kinetic and spectroscopic studies of the electronically excited carbonyl group are legion,[3-6] relatively little mechanistic effort has been devoted to the photochemistry of the structurally related imine system. This is surprising in view of the many examples of imine photochemistry appearing in the literature[7-40] and the interest which has been shown in the spectroscopic states of these compounds.[41] The combination of $n-\pi^*$ and $\pi-\pi^*$ states present in this chromophore should provide for a variety of interesting physical and chemical conversion processes. Previous study of the photochemistry of imines has shown that this functional group resembles the carbonyl group in its ability to undergo photoreduction in the presence of a suitable hydrogen-atom donor.[22,23] Although attractive mechanistic analogies can be drawn between this reaction and the photoreduction of excited carbonyl compounds, the available data indicate that imine photoreduction is quite different mechanistically in that it appears not to involve the excited state of the imine.[22] Instead, ketyl radicals were clearly implicated as the active reducing agent. These ketyl radicals were derived from carbonyl compounds present in the reaction mixture as an impurity, an added sensitizer, or as a photogenerated species.[22] While chemical reaction of the excited state of an imine has been observed with a number of systems, a more frequently encountered phenomenon for simple imines is a high rate and efficiency of radiationless deactivation. The low photoreactivity of the imine system can be attributed to rotation about the π bond in the excited state, thereby allowing for dissipation of electronic energy.[42-49] In rigid systems, this mode of energy

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(2) (a) Alfred P. Sloan Foundation Fellow, 1968–1972; National Institutes of Health Special Postdoctoral Fellow, 1972–1973; (b) NDEA Title IV Fellow, 1969–1971; (c) NSF Science Faculty Fellow, 1970–1971; Virginia Military Institute Faculty Fellow, 1971–1973.
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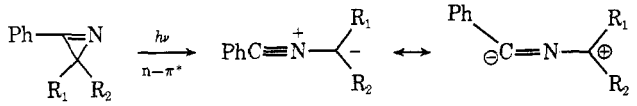
dissipation would not be available and these cyclic imines would have maximum opportunity to undergo reaction from an electronically excited state.

It was the purpose of the present study to investigate the behavior of small ring cyclic imines, in which syn–anti photoisomerization about the C–N double bond should be a high-energy, structurally prohibited, process. The photochemical behavior of the three-membered azirine ring has been little studied except for a few instances in which either photodimerization[50–54] or photorearrangement[55–57] occurred. The present paper is the first of a set which describes a pioneering, exploratory study on the photocycloaddition of arylazirines with electron deficient olefins.[58] The accompanying paper presents further studies which probe more deeply into the mechanistic features of the cycloaddition.

Results

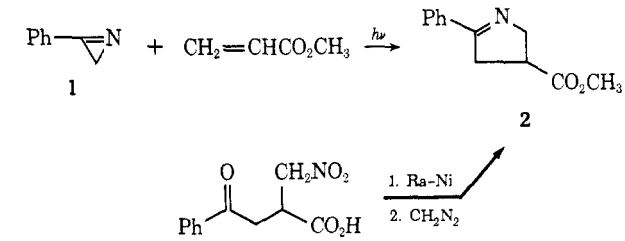
Spectral Properties. The ultraviolet absorption spectra of substituted arylazirines in cyclohexane exhibit strong (ϵ ~10,000) absorption at *ca.* 240 nm with a weak inflection on the long-wavelength side of the principal absorption band (*i.e.*, *ca.* 285 nm (ϵ ~500)). This weak band undergoes a hypsochromic shift with increasing polarity of the medium. By the empirical criteria of low intensity and shift of the absorption to shorter wavelengths in hydrogen-bonding solvents, this latter band can be attributed to an n–π^* transition. The weakening of the C–C bond of the azirine ring as a result of this transition was rationalized earlier[56,57] in terms of an electrocyclic transformation by analogy with the cyclopropyl → allyl cation rearrangement.[59] The intermediate 1,3-dipole which would be expected to be formed as a result of C–C bond cleavage should react with suitable dipolarophiles.



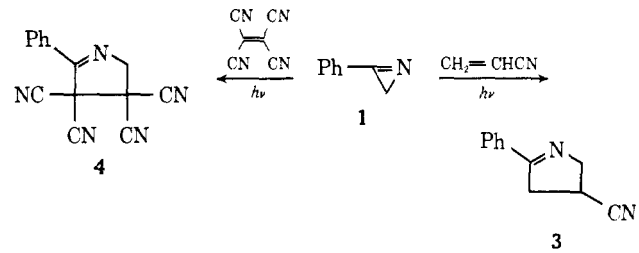
1a

This paper describes the products of photolysis of several substituted arylazirines with electron-deficient olefins, including detailed structure proofs for new compounds.

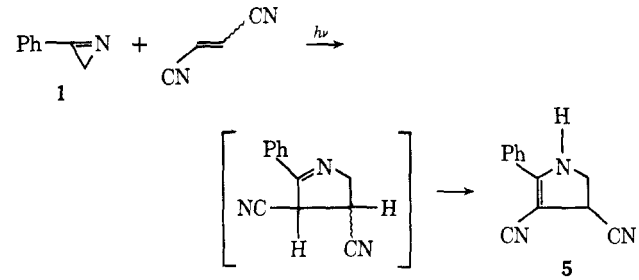
Cycloaddition Reactions of Arylazirines. Irradiation of a solution of phenylazirine (**1**) in excess methyl acrylate using a 450-W high-pressure mercury resonance lamp with a Vycor filter for 3 hr yields 80% 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**2**). Structure **2** was confirmed by its unequivocal synthesis from 3-benzoyl-2-nitromethylpropionic acid[60] by Raney nickel



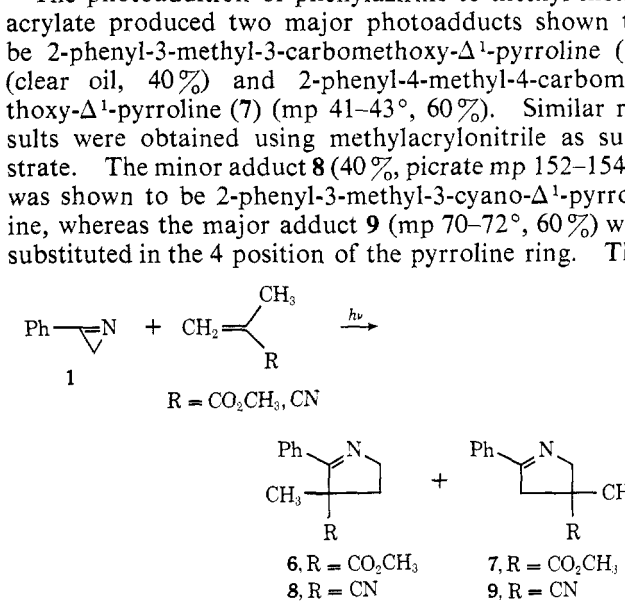
(W2) reduction followed by esterification with diazomethane. Similarly, when acrylonitrile or tetracyanoethylene was used as substrate, Δ^1-pyrroline **3** (mp 95–96°, 70%) and 2-phenyl-3,3,4,4-tetracyano-Δ^1-pyrroline (**4**) (mp 191–192°, 95%) were formed in high yield.



Photolysis of phenylazirine with *cis*- (or *trans*-)-dicyanoethylene affords 2-phenyl-3,4-dicyano-4,5-dihydropyrrole (**5**) as the only identifiable product in 72% yield. The structure of **5** is based on analytical and infrared, ultraviolet, nmr, and mass spectral data (see Experimental Section). The formation of this product presumably proceeds by way of a transient Δ^1-pyrroline intermediate which undergoes a subsequent 1,3-hydrogen shift.



The photoaddition of phenylazirine to methyl methacrylate produced two major photoadducts shown to be 2-phenyl-3-methyl-3-carbomethoxy-Δ^1-pyrroline (**6**) (clear oil, 40%) and 2-phenyl-4-methyl-4-carbomethoxy-Δ^1-pyrroline (**7**) (mp 41–43°, 60%). Similar results were obtained using methylacrylonitrile as substrate. The minor adduct **8** (40%, picrate mp 152–154°) was shown to be 2-phenyl-3-methyl-3-cyano-Δ^1-pyrroline, whereas the major adduct **9** (mp 70–72°, 60%) was substituted in the 4 position of the pyrroline ring. The



6, R = CO_2CH_3
8, R = CN

7, R = CO_2CH_3
9, R = CN

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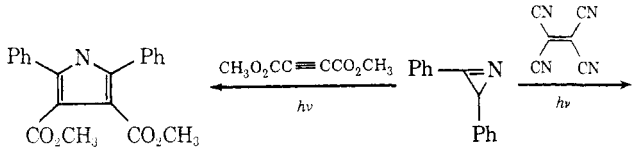
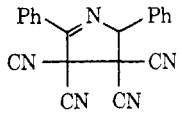
analytical and spectral data support the formulation of these compounds as Δ^1-pyrrolines. A choice between the alternative 3,3- and 4,4-disubstituted Δ^1-pyrrolines can be readily made on the basis of their characteristic nmr spectra.[61] The 60-MHz nmr spectra of adducts **6** and **8** show a complicated pattern for the methylene protons. Structures **7** and **9**, on the other hand, show well-defined AB quartets for both sets of methylenic protons.

Irradiation of phenylazirine in the presence of electron-rich acyclic or cyclic olefins (*i.e.*, 1-octene, cyclohexene, etc.) produced no photoadduct but instead gave a dimeric material.[64]

The photochemical cycloaddition reactions of diphenylazirine (**10**) with electron-deficient olefins were



12 **10**



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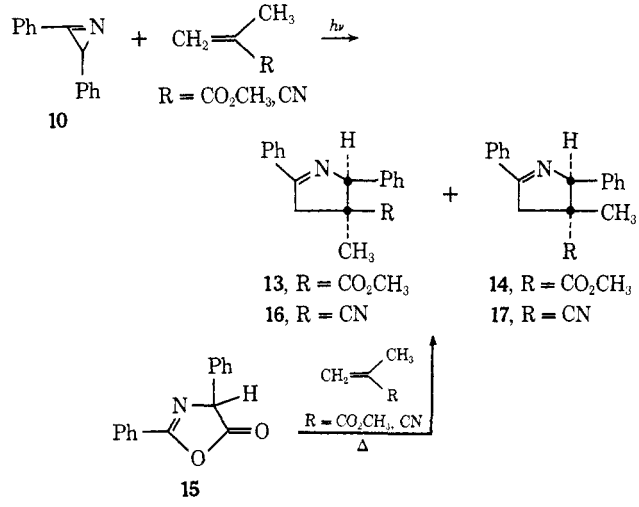
also investigated. Irradiation of an acetonitrile solution of **10** with tetracyanoethylene gave Δ^1-pyrroline **11** in 85% yield. Similarly, photolysis of **10** with dimethyl acetylenedicarboxylate afforded the known pyrrole **12**[65] in excellent yield.[66]

Irradiation of a pentane solution of methyl methacrylate and diphenylazirine produced a mixture of 2,5-diphenyl-4-methyl-4-carbomethoxy-Δ^1-pyrrolines (**13**, 40%, and **14**, 60%). The stereochemical relationship

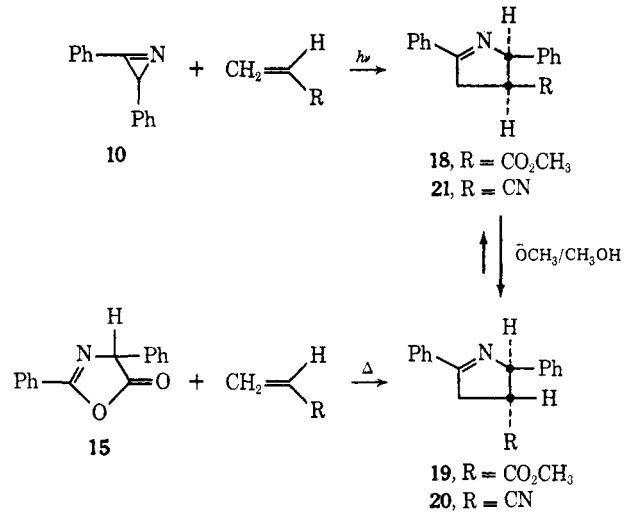


10 **13**, R = CO_2CH_3 **14**, R = CO_2CH_3
16, R = CN **17**, R = CN

15

of photoadducts **13** and **14** is apparent from the similar spectral data (uv, ir, *m/e*) of the two compounds. The basis for the assignment of geometry rests on the nmr data. Compound **13** has signals attributable to the methyl and carbomethoxy groups at τ 8.45 and 7.00, whereas the methyl and carbomethoxy signals of **14** appeared at τ 9.27 and 6.40. The strong upfield shift of the methyl signal of **14** can be attributed to shielding by the π electrons of the neighboring phenyl ring. The appearance of the carbomethoxy signal at τ 7.00 in adduct **13** is also consistent with this principle.[67] The same two adducts were prepared by heating 2,4-diphenyl-Δ^2-oxazolin-5-one (**15**) with methyl methacrylate in xylene. Photocycloaddition using methylacrylonitrile as substrate gave Δ^1-pyrrolines **16** (10%) and **17** (70%). These two compounds were also prepared from the thermolysis of **15** with methylacrylonitrile.[68] Again, the assignment of stereochemistry rests on the location of the methyl group in the nmr spectrum.

Photolysis of a mixture of diphenylazirine and methyl acrylate gave 2,5-diphenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline (**18**) as the major photoadduct (mp 101–102°,



10 **18**, R = CO_2CH_3
21, R = CN

15 **19**, R = CO_2CH_3
20, R = CN

85%). In contrast, heating oxazolinone **15** with methyl acrylate afforded the isomeric *trans*-pyrroline **19**. Control experiments demonstrated that **18** was stable to the thermal conditions. Proof of the cis relationship of the groups in **18** was obtained by nmr analysis as well as by the base-catalyzed epimerization of **18** to **19** (equilibrium ratio **18**/**19** = 1/4).

Reaction of diphenylazirine with acrylonitrile in benzene took a different course and produced 2,5-diphenyl-4-*trans*-cyano-Δ^1-pyrroline (**20**, 90%) in addition to the corresponding cis isomer **21** (10%). The cis isomer **21** epimerizes at 80° in methanol (containing a catalytic amount of sodium methoxide) to the trans isomer **20** until a 77:23 (**20**/**21**) equilibrium is reached. Heating oxazolinone **15** with acrylonitrile in xylene gave a mixture of the same two 1:1 adducts which consisted, however, of 10% of **20** and 90% of **21** according to vpc analysis. The difference in product distribution from the reactions of diphenylazirine (**10**) and diphenyloxazolinone (**15**) with methyl acrylate

(61) The nmr spectra of all the Δ^1-pyrrolines isolated in this study show a chemical-shift pattern consistent with previous assignments in related systems.[62,63]

(62) R. Bonnett and D. E. McGreer, *Can. J. Chem.*, **40**, 177 (1962).

(63) R. Huisgen, G. Gotthardt, and H. O. Bayer, *Tetrahedron Lett.*, 481 (1964); R. Huisgen and R. Raab, *ibid.*, 649 (1966).

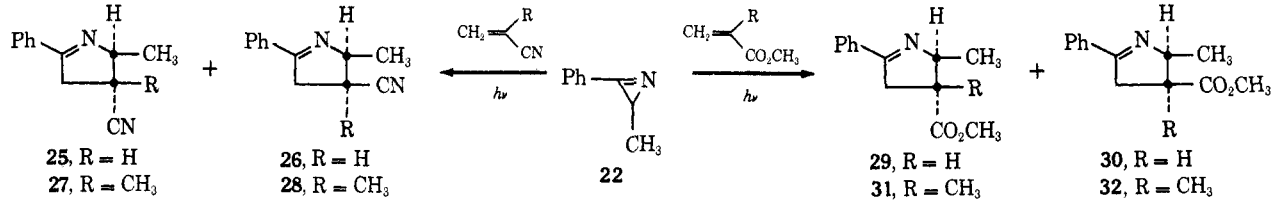
(64) The structure and mechanism for dimer formation from the irradiation of phenylazirine will be described in the accompanying paper.

(65) R. Huisgen, H. Gotthardt, and H. O. Bayer, *Angew. Chem., Int. Ed. Engl.*, **3**, 135 (1964).

(66) Schmid and coworkers have also reported that arylazirines undergo photocycloaddition with dipolarophiles; see H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 745 (1972).

(67) For additional examples of this effect, see J. H. Hall and R. Huisgen, *Tetrahedron Lett.*, 1187, 1188 (1971).

(68) R. Huisgen, H. Gotthardt, and H. O. Bayer, *Chem. Ber.*, **103** 2368 (1970).



25, R = H
27, R = CH_3

26, R = H
28, R = CH_3

22

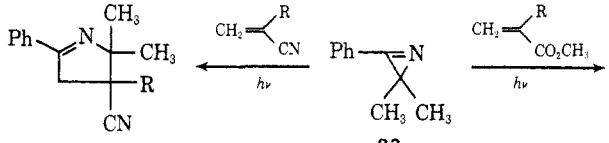
29, R = H
31, R = CH_3

30, R = H
32, R = CH_3

and acrylonitrile suggests the absence of a common reactive intermediate.

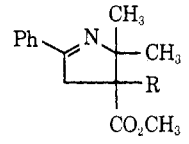
Additional cases of photoaddition reactions are provided by the photolyses of 3-methyl-2-phenylazirine (**22**), 2-phenyl-3,3-dimethylazirine (**23**), and 2-(β-naphthyl)azirine (**24**). Cycloaddition of **22** with acrylonitrile, methylacrylonitrile, methyl acrylate, and methyl methacrylate follows the same general pattern and gives rise to Δ^1-pyrrolines **25–32** in good yield (see Experimental Section).

In an analogous manner, photoaddition of phenyldimethylazirine (**23**) with the same electron-deficient olefins affords Δ^1-pyrrolines **33–36**. The configurations of the adducts were readily established by examination of their characteristic nmr spectra (see Experimental Section).



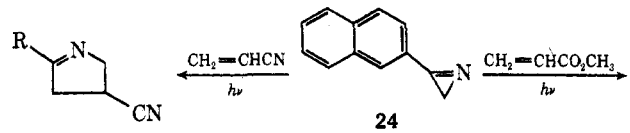
33, R = H
34, R = CH_3

23



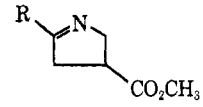
35, R = H
36, R = CH_3

Finally, cycloaddition of naphthylazirine (**24**) with methyl acrylate and acrylonitrile takes place very readily and gives good yields of photoadducts **37** and **38**.



37, R = naphthyl

24



38, R = naphthyl

Discussion

The major objective of the present work was to study the detailed mechanism of the photocycloaddition reaction leading to the Δ^1-pyrroline system. The structures of all of the photoadducts were established in a convincing manner so that there would be no question about the regiospecificity of the cycloaddition. The photocycloaddition of arylazirines with electron-deficient olefins can be rationalized by the assumption that the electronically excited n–π^* state of the azirine ring undergoes C–C bond cleavage to give a nitrile ylide intermediate **1a**. As a 1,3-dipole, **1a** can be intercepted with suitable dipolarophiles to form five-membered rings.[69]

1,3-Dipolar additions of nitrile oxides, nitrile imines, and nitrile ylides are considered to be multicentered cycloaddition processes.[69] The independence of solvent polarity,[70] the very negative entropies of activation,[71] and the stereospecificity and regiospecificity[72] point to a highly ordered transition state. In most instances of 1,3-dipolar cycloaddition reactions, when two isomers are possible as a result of the use of unsymmetrical reagents, one isomer usually predominates, often to the exclusion of the other isomer.[73,74] The principal question that arises when considering the regiospecificity of 1,3-dipolar additions is whether the two new σ bonds formed on addition of the 1,3-dipolar compound to the dipolarophile are formed simultaneously or one after the other. The mechanism that has emerged from Huisgen's group is that of a single-step, four-center, "no-mechanism" cycloaddition, in which the two new bonds are both partially formed in the transition state, although not necessarily to the same extent.[69,72] A symmetry–energy correlation diagram reveals that such a thermal cycloaddition reaction is an allowed process.[72,75,76] An alternative mechanism that has been proposed is a two-step process involving a spin-paired diradical intermediate.[77]

The orientation of the groups in the Δ^1-pyrrolines obtained from the photoaddition process is essentially identical with that observed by Huisgen in related 1,3-dipolar additions.[72,78] For example, treatment of *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**39**) with triethylamine in the presence of acrylonitrile has been found to give Δ^1-pyrroline **41**.[78] This reaction has been interpreted as proceeding *via* a nitrile ylide intermediate **40**. As Huisgen has pointed out, this orientation is opposite to that expected on the basis of the nitrilium resonance representation **40**.[78,79] It should be noted, however, that it is not meaningful to assign an electrophilic and nucleophilic end to a 1,3 dipole.[80] To date,

(69) For recent reviews, see (a) R. Huisgen, *Angew. Chem.*, **75**, 741 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963); (b) R. Huisgen R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, pp 806–878; (c) G. L. Abbé, *Chem. Rev.*, **69**, 345 (1969).

(70) R. Huisgen, G. Szeimies, and L. Mobius, *Chem. Ber.*, **100**, 2494 (1967); R. Huisgen, H. Stangl, H. J. Stern, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(71) R. Huisgen, L. Mobius, G. Muller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965).

(72) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

(73) R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968).

(74) M. Christl and R. Huisgen, *Tetrahedron Lett.*, 5209 (1968).

(75) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).

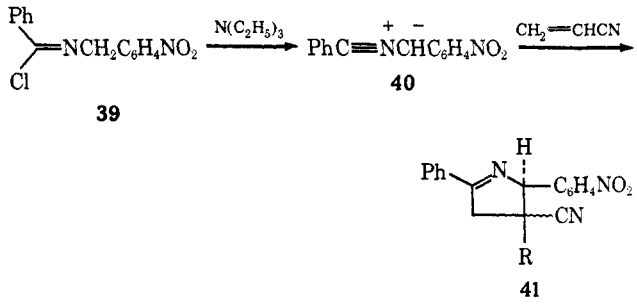
(76) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 20 (1968).

(77) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); **37**, 2181 (1972); *J. Chem. Soc. A*, 1570 (1970).

(78) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem., Int. Ed. Engl.*, **1**, 50 (1962); *Chem. Ber.*, **105**, 1258 (1972).

(79) R. Huisgen, *Angew. Chem., Int. Ed., Engl.*, **2**, 565 (1963).

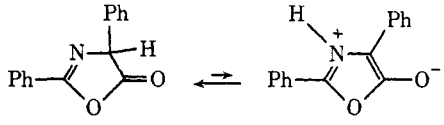
(80) R. Huisgen, *Bull. Soc. Chim. Fr.*, 3431 (1965).



39 40 41

the whole question of orientation or regiospecificity is still shrouded with uncertainty.[80a] The rationalization that best accounts for the orientation phenomena in 1,3-dipolar additions is that there exists a subtle interplay of steric and electronic factors which controls the regiospecificity of addition. Presumably, the interplay of these same factors controls the orientation of addition in the arylazirine system.

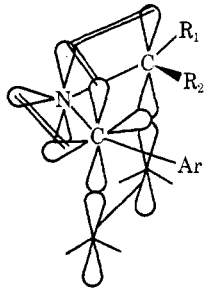
The difference in product stereochemistry found in the reactions of diphenylazirine (**10**) and 2,4-diphenyl-Δ^2-oxazolin-5-one (**15**) with methyl acrylate and acrylonitrile indicates the absence of a common reactive intermediate. 1,3-Dipolar cycloadditions of azalactones such as **15** have been suggested to proceed by tautomerization to a mesoionic oxazolium 5-oxide (**42**) which then



15 42

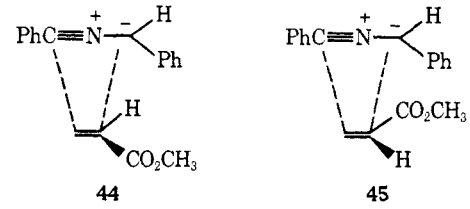
combines with the dipolarophile.[81] This scheme is consistent with the difference in product orientation found in the reactions of **10** and **15** with methyl acrylate and acrylonitrile.

Concerted 1,3-dipolar additions are known to proceed *via* a "two-plane" orientation complex.[72] Formula **43** depicts the orientation complex involved in



43

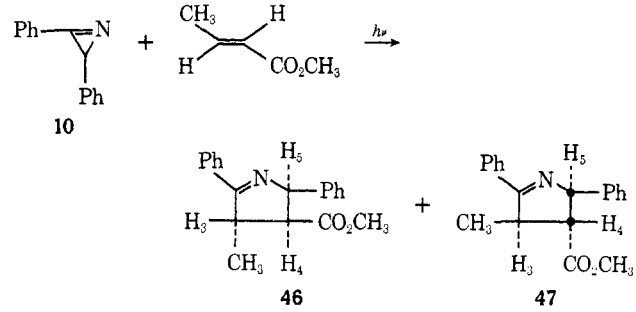
the addition of a nitrile ylide with a dipolarophile. For the case of diphenylazirine and methyl acrylate, there are two possible orientation complexes (**44** or **45**). The interaction of the substituent groups in the syn complex **44** can be of an attractive (π-overlap, dipole–dipole interaction) or of a repulsive nature (van der Waals strain). Both effects are probably negligible in the anti complex **45**. The results found in the diphenylazirine–methyl acrylate system indicate that the syn complex is favored over the anti arrangement (*i.e.*,



44 45

cis-Δ^1-pyrroline **18** is the dominant adduct). The π overlap of the ester and phenyl groups in the syn complex **44** presumably overcomes the adverse van der Waals repulsion of these substituents.[82] With acrylonitrile as the dipolarophile, syn addition becomes slower than anti addition (*i.e.*, *trans*-Δ^1-pyrroline **20** is the major adduct). In this case, the adverse van der Waals repulsion of the substituent groups overcomes the attractive π-overlap interactions, thereby favoring the anti arrangement.

All octet-stabilized 1,3-dipoles examined so far in the literature have been shown to undergo stereospecific cis cycloaddition.[69] In order to determine whether the nitrile ylide generated from the photolysis of an arylazirine behaves similarly, we have studied the photoaddition of diphenylazirine with cis- and trans-disubstituted dipolarophiles. Irradiation of **10** with methyl *trans*-crotonate gave a quantitative yield of a mixture of two 1:1 adducts which consisted of 60% of **46** and 40% of **47** according to vpc and nmr analysis. The two adducts



10 46 47

obtained can be derived from the two possible orientation complexes for concerted addition of the nitrile ylide to the dipolarophile. It is interesting to note that the major adduct **46** has the phenyl and carbomethoxy groups cis, just as was the case with the simpler methyl acrylate system.

When the irradiation of diphenylazirine was carried out with methyl *cis*-crotonate, no photoadduct was obtained, but instead tetraphenylpyrazine (**48**) was isolated on extended photolysis. The formation of tetraphenylpyrazine (**48**) from the irradiation of diphenylazirine was found to be quite general when the dipolarophile used was tri- or tetrasubstituted.[83] The mechanism of dimer formation will be considered in detail in the accompanying paper.

Since the *cis*-crotonate ester reacts so sluggishly with the nitrile ylide, it became of interest to study the photochemistry of diphenylazirine with another set of stereochemically labeled dipolarophiles. To this end, the photoaddition of **10** with *cis*- and *trans*-dicyanoethylene

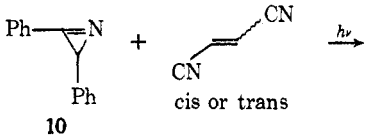
(80a) Note Added in Proof. See, however, K. N. Houk, *J. Amer. Chem. Soc.*, **94**, 8953 (1972), for a recent rationale.

(81) H. Gotthardt, R. Huisgen, and H. O. Bayer, *J. Amer. Chem. Soc.*, **92**, 4340 (1970).

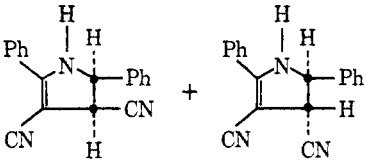
(82) Similar results to these have been observed by Huisgen and Eberhard in the 1,3-dipolar addition of aliphatic diazo compounds to α,β-unsaturated carboxylic acids; see R. Huisgen and P. Eberhard, *Tetrahedron Lett.*, 4337, 4343 (1971).

(83) Irradiation of diphenylazirine in the presence of methyl β-methylcrotonate, the dimethyl ester of dimethylmaleic acid, or the dimethyl ester of citraconic acid, gave no photoadduct. Instead, pyrazine **48** formation occurred on extended irradiation.

was examined. As is shown below, irradiation of **10** with either olefin gave 90% of a 1:1 mixture of **49** and **50**. It would appear as though the initially formed



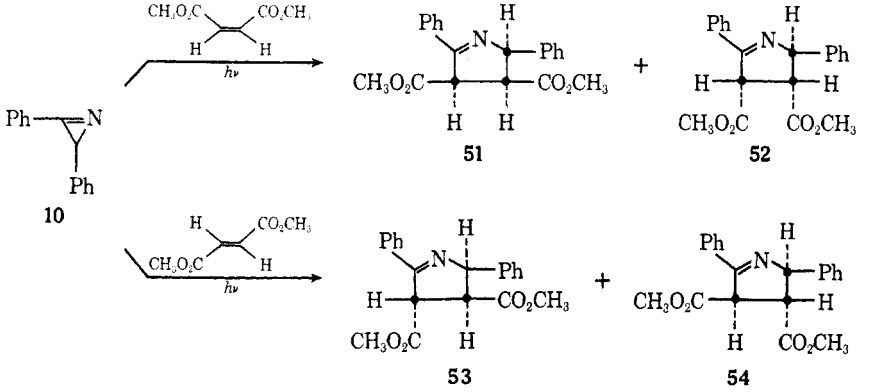
10



49 **50**

Δ^1-pyrroline system undergoes a facile 1,3-hydrogen shift during the course of the reaction.[84] All attempts to detect the transient Δ^1-pyrroline ring failed.

It was found, however, that photoaddition of diphenylazirine with dimethyl maleate and fumarate proceeds stereospecifically and yields the diastereoisomeric Δ^1-pyrrolines **51**, **52**, and **53**, **54**. All of these



10 **51** **52** **53** **54**

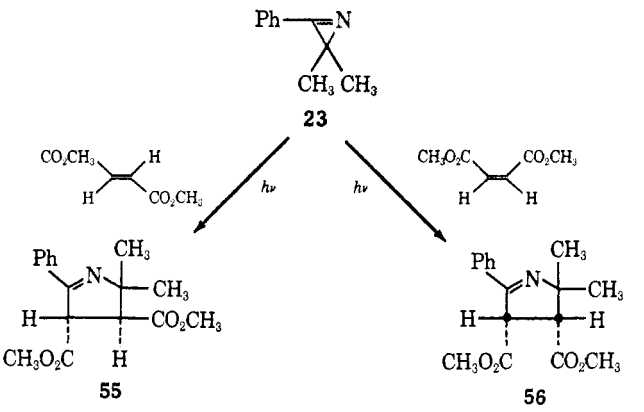
compounds can be dehydrogenated to the same pyrrole (**12**). The appearance of the carbomethoxy signal at relatively high field in adducts **51** and **53** is consistent with the vicinal shielding effect of the neighboring cis-phenyl ring. The observed coupling constants are in good agreement with model systems.[62-64] Additional information which supports the stereochemical assignments was obtained from some base-catalyzed epimerization experiments. The major fumarate adduct **53** was found to isomerize to the thermodynamically more favored isomer **54**. Treatment of adducts **51** and **52** with sodium methoxide in methanol, however, results in the exclusive formation of pyrrole **12**.

Complementary results were obtained by irradiating dimethylphenylazirine (**23**) with dimethyl fumarate and maleate. The data obtained indicate that **23** reacts stereospecifically with the fumaric and maleic esters, producing the respective adducts (**55** and **56**) nearly quantitatively with no admixtures of their diastereoisomers. Maleate adduct **56** was found to isomerize to fumarate adduct **55** on standing in the dark.

Conclusions

The photocycloaddition of arylazirines with electron-deficient olefins has been shown to produce Δ^1-pyrrolines as primary photoproducts. These reactions show all

(84) Conceivably a photoinduced process.



23 **55** **56**

the characteristics of concerted reactions, including stereospecificity and regioselectivity. The mechanism for product formation can best be rationalized by C–C bond cleavage of the electronically excited azirine ring to give a nitrile ylide intermediate. As a 1,3-dipole, the nitrile ylide can be intercepted with a variety of dipolarophiles to form five-membered rings. When the arylazirine is allowed to react with an unsymmetrically substituted dipolarophile, a mixture of two adducts is obtained. This mixture corresponds to the two orientations of the 1,3 dipole and the dipolarophile in the activated complex leading to the transition state. The ratio of the two steric courses (syn and anti) functions as a probe and gives insight into the interplay of steric and electronic substituent effects in the transition state of 1,3-dipolar addition. The effect of π overlap and van der Waals strain plays an important role in controlling the distribution of products. It is interesting to note that Huisgen has reported that diarylazirines do not undergo thermal cycloaddition with dipolarophiles.[63] Further discussion of the reaction mechanism and the nature and reactvity of the excited state responsible for the cycloaddition is deferred to the following paper.

Experimental Section[85]

Photoaddition of Methyl Acrylate with Phenylazirine. A solution

(85) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associate high-resolution spectrometer and at 100 MHz using a Jeol-MH-100 spectrometer.

of 0.5 g of 2-phenylazirine[86] (**1**) in 250 ml of methyl acrylate was irradiated through a Vycor filter sleeve for 3 hr. Removal of the methyl acrylate under reduced pressure afforded a yellow oil which was purified by preparative vpc using a 5% DEGS column at 150° to give 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**2**) in high yield (80%): ir (neat) 5.75 and 6.15 μ; uv (95% ethanol) 243 nm (ϵ 14,000); nmr ($CDCl_3$, 60 MHz) τ 6.80 (3 H, m), 6.38 (3 H, s), 5.80 (2 H, m), and 2.65 (5 H, m); *m/e* 203 (parent), 144, 117 (base), 103, and 77.

A picrate derivative was prepared and recrystallized from ethanol to give an analytical sample, mp 161–163°.

Anal. Calcd for $C_{18}H_{16}N_4O_9$: C, 50.00; H, 3.73; N, 12.96. Found: C, 49.91; H, 3.79; N, 12.63.

The structure of the photoadduct **2** was further confirmed by its unequivocal synthesis from 2-phenyl-4-carboxy-Δ^1-pyrroline[60] and diazomethane.

Photoaddition of Methyl Methacrylate with Phenylazirine. A solution of 0.5 g of phenylazirine (**1**) in 250 ml of methyl methacrylate was irradiated through a Vycor filter for 4 hr. The methyl methacrylate was removed under reduced pressure, and the residual oil was subjected to preparative glc using a 5% DEGS column on Chromosorb P at 150°. The two major products were identified as 2-phenyl-3-methyl-3-carbomethoxy-Δ^1-pyrroline (**6**, 40%) and 2-phenyl-4-methyl-4-carbomethoxy-Δ^1-pyrroline (**7**), *mp* 41–43° (60%). Compound **6** was a clear oil: ir (neat) 5.79 and 6.15 μ; uv (95% ethanol) 245 nm (ϵ 14,000); *m/e* 217 (parent), 158, 117, 114 (base), and 77; nmr (60 MHz, $CDCl_3$), τ 8.55 (3 H, s), 7.85 (2 H, m), 6.40 (3 H, s), 5.97 (2 H, m), and 2.71 (5 H, m).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.41; H, 6.99; N, 6.18.

The major isomer **7** was a low-melting solid, mp 41–43°: ir (neat) 5.78 and 6.15 μ; uv (95% ethanol) 245 nm (ϵ 12,800); nmr ($CDCl_3$, 60 MHz) τ 8.73 (3 H, s), AB quartet centered at 6.90 (2 H, J = 15 Hz), 6.38 (3 H, s), 5.91 (2 H, d, J = 15 Hz), 2.70 (5 H, m); *m/e* 217 (parent), 158, 117 (base), and 77.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.50; H, 6.89; N, 6.44.

Photoaddition of Acrylonitrile with Phenylazirine. A solution containing 0.5 g of phenylazirine and 5 ml of acrylonitrile in 250 ml of pentane was irradiated using a Vycor filter for 2 hr. The residual oil that remained on removal of the solvent was recrystallized from hexane to give 2-phenyl-4-cyano-Δ^1-pyrroline (**3**) (70%): mp 95–96°; ir (KBr) 4.46 and 6.2 μ; uv (95% ethanol) 245 nm (ϵ 12,400); nmr ($CDCl_3$, 60 MHz), τ 6.80 (3 H, m), 5.75 (2 H, m), and 2.50 (5 H, m); *m/e* 170 (parent), 117 (base), 103, and 99.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.59; H, 5.85; N, 16.50.

Photoaddition of Methylacrylonitrile with Phenylazirine. A solution containing 0.5 g of phenylazirine and 5 ml of methylacrylonitrile in 500 ml of pentane was photolyzed for 4 hr using a Vycor filter. Liquid–liquid partition chromatography of the residue showed the presence of two adducts. The minor adduct **8** (40%) was a pale yellow oil whose structure was assigned as 2-phenyl-3-methyl-3-cyano-Δ^1-pyrroline (**8**): ir (neat) 4.50 and 6.21 μ; uv (95% ethanol) 248 nm (ϵ 12,000); nmr (60 MHz, $CDCl_3$) τ 8.42 (3 H, s), 7.51 (2 H, m), 6.03 (2 H, m), 2.40 (5 H, m); *m/e* 184 (parent), 117 (base), 104, 103, 91, and 77. A picrate derivative was prepared and recrystallized from ethanol, mp 152–154°.

Anal. Calcd for $C_{18}H_{15}N_3O_7$: C, 52.30; H, 3.55; N, 16.94. Found: C, 52.18; H, 3.66; N, 16.96.

The major adduct (60%) was assigned the structure of 2-phenyl-4-methyl-4-cyano-Δ^1-pyrroline (**9**) on the basis of the following data: mp 70–72°; ir (KBr) 4.50 and 6.20 μ; uv (95% ethanol) 245 nm (ϵ 13,500); nmr (60 MHz, $CDCl_3$) τ 8.60 (3 H, s) 6.75 (2 H, AB quartet, J = 17.0 Hz), 5.80 (2 H, AB quartet, J = 16.0 Hz), 2.45 (5 H, m); *m/e* 184 (parent), 117 (base), and 77.

Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 77.95; H, 6.48; N, 15.14.

Photoaddition of Tetracyanoethylene with Phenylazirine. A solution of 0.5 g of phenylazirine and 0.54 g of tetracyanoethylene in 250 ml of acetonitrile was irradiated for 3 hr using a Vycor filter. The black solid obtained on removal of the solvent was decolorized with Norite and recrystallized from 95% ethanol to give 2-phenyl-3,3,4,4-tetracyano-Δ^1-pyrroline (**4**) (95%) as white crystals: mp 191–192°; ir (KBr) 6.05 μ; uv (95% ethanol) 242 nm (ϵ 18,000); nmr (60 MHz, DMSO) τ 4.58 (2 H, s), 2.5–1.8 (5 H, m); *m/e* 245, 117 (base), 103, and 77.

Anal. Calcd for $C_{14}H_7N_5$: C, 68.56; H, 2.88; N, 28.56. Found: C, 68.49; H, 3.00; N, 28.68.

Photoaddition of Phenylazirine with *cis*- or *trans*-Dicyanoethylene. A solution containing 0.3 g of phenylazirine and 0.2 g of *cis*- (or *trans*-) dicyanoethylene in 250 ml of benzene was irradiated for 4 hr using a Vycor filter. Removal of the solvent under reduced pressure afforded a brown solid which was recrystallized from 95% ethanol to give 2-phenyl-3,4-dicyano-4,5-dihydropyrrole (**5**) (72%) as a white crystalline solid: mp 142–143°, ir (KBr) 3.10 and 4.55 μ; uv (95% ethanol) 229 and 315 nm (ϵ 12,500 and 6900); nmr (60 MHz, CD_3CN) τ 6.0 (3 H, m), 4.31 (1 H, broad s), 2.40 (5 H, m); *m/e* 195, 169, 168 (base), 141, 140, 117, and 77.

Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.64; H, 4.64; N, 21.38.

Photoaddition of Diphenylazirine with Methyl Methacrylate. A solution containing 0.5 g of diphenylazirine (**10**) and 5 ml of methyl methacrylate in 250 ml of pentane was irradiated for 3 hr using a Vycor filter sleeve. The residue obtained on removal of the solvent was subjected to preparative gas chromatography using a 5 ft × 0.25 in. column of SE-30 on Chromosorb P at 220°. The minor component (40%) **13** was a clear oil: ir (neat) 5.79 and 6.20 μ; nmr ($CDCl_3$, 60 MHz) τ 8.45 (3 H, s), 7.0 (3 H, s), 4.4 (1 H, broad s), and 3.0–2.0 (10 H, m). The major component of the mixture (60%) **14** showed bands at 5.79 and 6.15 μ in the infrared. Its nmr spectrum showed a three proton singlet at τ 9.27, a doublet of doublets at 7.1 (J = 17 and 2.0 Hz), a doublet of doublets at 6.35 (J = 17 and 2.0 Hz), a singlet at 6.40 (3 H), a broad singlet at 3.40, and the aromatic protons at 2.61 (10 H, m). A picrate derivative of the major component was prepared and recrystallized from 95% ethanol, mp 160–162°.

Anal. Calcd for $C_{25}H_{22}N_4O_9$: C, 57.47; H, 4.24; N, 10.72. Found: C, 57.38; H, 4.24; N, 10.57.

The same two adducts were prepared by the thermolysis of 2,4-diphenyl-Δ^2-oxazolin-5-one (**15**) with methyl methacrylate.[81]

Photoaddition of Diphenylazirine with Methyl Acrylate. A solution of 0.3 g of diphenylazirine and 5 ml of methyl acrylate in 250 ml of pentane was irradiated for 3 hr using a Vycor filter sleeve. Recrystallization of the residual oil from heptane gave a single photoadduct, whose structure is assigned as 2,5-diphenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline (**18**) (85%): mp 101–102°; ir (KBr) 5.75 and 6.10 μ; uv (95% ethanol) 247 nm (ϵ 18,000); nmr ($CDCl_3$, 60 MHz), τ 6.92 (3 H, s), 6.50 (3 H, m), 4.33 (1 H, d, J = 8.0 Hz), and 2.50 (5 H, m); *m/e* 279, 248, 220, 193 (base), 103, 91, and 77.

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.20; H, 6.13; N, 4.89.

Treating the cis adduct **18** (0.1 g) with potassium *tert*-butoxide (0.01 g) in anhydrous methanol (20 ml) under nitrogen at reflux for 30 min gave 2,5-diphenyl-*trans*-4-carbomethoxy-Δ^1-pyrroline (**19**) in 80% yield as a colorless oil: ir (neat) 5.72 and 6.15 μ; nmr ($CDCl_3$, 60 MHz) τ 6.65 (3 H, m), 6.42 (3 H, s), 4.62 (1 H, broad *d*), and 2.60 (10 H, *m*). The remaining 20% consisted of recovered starting material. The trans adduct **19** was also prepared by heating 2,4-diphenyloxazolin-5-one (**15**) with methyl acrylate.

Photoaddition of Diphenylazirine with Acrylonitrile. A solution containing 0.7 g of diphenylazirine and 10 ml of acrylonitrile in 500 ml of benzene was irradiated for 5 hr through a Pyrex filter. The residual oil solidified on standing and was analyzed by vpc using a 5 ft × 0.25 in. column of 5% SE 30 on Chromosorb P at 240°. The chromatogram showed the presence of two components. The major component of the mixture **20** (90%) was obtained in high purity by recrystallization of the photolysate from methanol. This material is assigned the structure of 2,5-diphenyl-4-*trans*-cyano-Δ^1-pyrroline (**20**), mp 120–121°; ir (KBr) 4.49 and 6.20 μ; uv (95% ethanol) 247 nm (ϵ 15,100); nmr ($CDCl_3$, 100 MHz) τ 7.0 (1 H, m), 6.60 (2 H, m), 4.52 (1 H, m), 2.40 (10 H, m). Spin-decoupling experiments were carried out in order to obtain the coupling constants. External irradiation of the proton at τ 4.52 allowed the following coupling constants to be determined: J_{2AB} = 16.0 Hz, J_{2A3} = 10 Hz, J_{2B3} = 8.0 Hz, J_{34} = 7 Hz, and J_{2A4} = J_{2B4} = 2.0 Hz; *m/e* 245, 220, 193 (base), 165, and 103.

Anal. Calcd for $C_{17}H_{13}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.89; H, 5.83; N, 11.22.

The minor component of the mixture (10%) was identified as 2,5-diphenyl-4-*cis*-cyano-Δ^1-pyrroline (**21**), *mp* 127–128°. This material was identical with the adduct reported by Huisgen from the thermolysis of 2,4-diphenyl-Δ^2-oxazolin-5-one (**15**) with acrylonitrile.[68]

A solution containing 50 mg of the major photoadduct **20** and

(86) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

50 mg of sodium methoxide in 25 ml of methanol was heated under nitrogen at reflux for 1.5 hr. Analysis of the mixture by vpc showed that it contained 77% of trans adduct **20** and 23% cis adduct **21**. The same equilibrium mixture was obtained by the base-catalyzed epimerization of the minor photoadduct **21**.

Photoaddition of Diphenylazirine with Methylacrylonitrile. A solution of 0.5 g of diphenylazirine and 5 ml of methylacrylonitrile in pentane was irradiated for 2 hr using a Vycor filter sleeve. The crude residue showed the presence of two components by vpc analysis. The major component (70%) was separated by liquid–liquid partition chromatography and was assigned as 2,5-diphenyl-4-cyano-4-*cis*-methyl-Δ^1-pyrroline (**17**), mp 109–110°; ir (KBr) 4.50 and 6.25 μ; uv (95% ethanol) 248 nm (log ϵ 4.26); nmr ($CDCl_3$, 100 MHz) τ 9.14 (3 H, s); 6.68 (2 H, AB quartet, J = 16.3 Hz, fine splitting J = 2.2 and 1.4 Hz), 4.31 (1 H, broad t), 2.50 (10 H, m); *m/e* 260, 233, 193 (base), 165, 91, 90, 89, and 77.

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.76; H, 6.24; N, 10.94.

This material is identical in all respects with the product reported by Huisgen, *et al.*, from the thermolysis of 2,4-diphenyloxazolin-5-one (**15**) with methylacrylonitrile.[68]

The minor component **16** from the irradiation experiment (*ca.* 10%) could not be separated from the major component on all chromatographic columns tried.

Photoaddition of Diphenylazirine with Tetracyanoethylene. A solution of 0.5 g of diphenylazirine (**10**) and 0.32 g of tetracyanoethylene in 250 ml of acetonitrile was irradiated for 2 hr through a Vycor filter. Recrystallization of the dark solid from ethanol gave a crystalline solid **11**: mp 178–179°; ir (KBr) 6.10 μ; uv (95% ethanol) 263 nm (ϵ 10,500); nmr (60 MHz, DMSO) τ 2.95 (1 H, s) and 2.5–1.9 (10 H, m); *m/e* 269, 193 (base), 165, 164, 103, and 77, in high yield (85%).

Anal. Calcd for $C_{20}H_{11}N_5$: C, 74.75; H, 3.45; N, 21.80. Found: C, 74.71; H, 3.61; N, 21.63.

Photoaddition of Diphenylazirine with *cis*- and *trans*-Dicyanoethylene. A solution containing 0.62 g of *cis*- (or *trans*-) dicyanoethylene in 125 ml of acetonitrile was irradiated using a Vycor filter for 2 hr. Removal of the solvent followed by recrystallization of the solid from ethanol gave a 90% yield of a 1:1 eutectic mixture, mp 148–149°. All attempts to separate the eutectic mixture into its separate components failed; consequently the mixture was analyzed without separation: ir (KBr) 3.10 and 4.61 μ; uv (95% ethanol) 238, 315, and 377 nm (ϵ 10,000, 4400, 4400); nmr (100 MHz, CD_3CN) τ 5.82 (0.5 H, d, J = 8.5 Hz), 5.36 (0.5 H, d, J = 11.0 Hz), 4.68 (0.5 H, d, J = 8.5 Hz), 4.62 (0.5 H, d, J = 11.0 Hz), 3.80 (1 H, broad s), 2.35 (10 H, m); *m/e* 271, 244 (base), 193, 140, and 77.

Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.68; H, 4.83; N, 15.49. Found: C, 79.26; H, 4.83; N, 15.23.

The same 1:1 eutectic mixture was obtained from the thermolysis of 2,4-diphenyloxazolin-5-one (**15**) with *cis*- or *trans*-dicyanoethylene.

Photoaddition of Diphenylazirine with Methyl *trans*-Crotonate. A solution containing 0.125 g of diphenylazirine and 0.64 g of methyl *trans*-crotonate in 50 ml of benzene was irradiated for 1.5 hr at 3130 Å. The crude reaction mixture contained two photoadducts. The major component (60%) was obtained as a crystalline solid, **46**, mp 146–148°, by fractional crystallization from 95% ethanol: ir (KBr) 5.85 and 6.20 μ; uv (95% ethanol) 244 nm (ϵ 13,900); nmr ($CDCl_3$, 100 MHz) τ 8.75 (3 H, d, J = 7.5 Hz), 6.91 (3 H, s), 6.71 (1 H, dd, J = 9.0 and 4.5 Hz), 5.93 (1 H, m), 4.32 (1 H, quartet of doublets, J = 9.0 and 2.0 Hz), 2.40 (10 H, m); *m/e* 293, 234, 193 (base), 165, 131, 115, 91, 90, 89, and 77.

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.52; H, 6.52; N, 4.83.

The minor component (40%) of the reaction mixture **47** was separated from the major adduct by passage through a neutral alumina column using 10% ethyl acetate–benzene and was found to be a colorless oil: ir (neat) 5.78 and 6.18 μ; uv (95% ethanol) 246 nm (ϵ 12,500); nmr ($CDCl_3$, 100 MHz), τ 8.70 (3 H, d, J = 7.5 Hz), 7.22 (1 H, dd, J = 5.5 Hz), 6.33 (3 H, s), 6.35 (1 H, m), 4.45 (1 H, d, J = 5.5 Hz), 2.40 (10 H, m); *m/e* 290, 234, 193 (base), 163, 131, 115, 91, and 77.

A picrate derivative was prepared and recrystallized from 95% ethanol, mp 150–152°.

Anal. Calcd for $C_{25}H_{22}N_4O_9$: C, 57.47; H, 4.24; N, 10.72. Found: C, 57.18; H, 4.31; N, 10.67.

The same two adducts were obtained by heating a mixture of 2,4-diphenyloxazolin-5-one (**15**) with methyl *trans*-crotonate.

Photoaddition of Diphenylazirine with Dimethyl Acetylenedicarboxylate. A solution of 0.5 g of diphenylazirine and 0.335 g of dimethyl acetylenedicarboxylate in 500 ml of pentane was photolyzed for 3 hr using a Vycor filter. Removal of the solvent left a tan solid which was recrystallized from heptane–benzene to give 2,5-diphenyl-3,4-dicarbomethoxypyrrole (**12**, 95%), mp 146–148°. The pyrrole obtained in this manner was identical in all respects with an authentic sample of **12** prepared according to the procedure of Huisgen and coworkers.[66]

Photoaddition of Diphenylazirine with Dimethyl Fumarate. A solution of 0.5 g of diphenylazirine and 0.4 g of dimethyl fumarate in 500 ml of benzene was irradiated for 1 hr through a uranium glass filter. Liquid–liquid partition chromatography of the photolysis residue separated two photoadducts. The major adduct (70%), mp 108–109°, was identified as 2,5-diphenyl-*trans,cis*-3,4-dicarbomethoxy-Δ^1-pyrroline (**53**) on the basis of the following data: ir (KBr) 5.71, 6.20 μ; uv (95% ethanol) 249 nm (ϵ 17,800); nmr ($CDCl_3$, 60 MHz) τ 6.89 (3 H, s), 6.34 (3 H, s), 6.02 (1 H, dd, J = 9.0 and 4.5 Hz), 5.12 (1 H, dd, J = 4.5 and 1.5 Hz), 4.11 (1 H, dd, J = 9.0 and 1.5 Hz), 2.40 (10 H, m); *m/e* 337, 277, 246, 219, 193 (base), 147, 115, 90, and 77.

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 70.82; H, 5.69; N, 4.15.

The minor adduct (30%), mp 108–110°, was identified as 2,5-diphenyl-*trans,trans*-3,4-dicarbomethoxy-Δ^1-pyrroline (**54**) on the basis of the spectral data: ir (KBr) 5.75, 6.10 μ; nmr (60 MHz, $CDCl_3$) τ 6.50 (3 H, s), 6.45 (1 H, dd, J = 6.5 and 6.0 Hz), 6.35 (3 H, s), 5.41 (1 H, dd, J = 6.5 and 1.5 Hz), 4.62 (1 H, dd, J = 6.0 and 1.5 Hz), 2.80 (10 H, m); *m/e* 337, 277, 246, 219, 193 (base), 147, 115, 90, and 77.

The minor photochemical adduct **54** could be independently synthesized[68] in high yield by heating a mixture of 2,4-diphenyloxazolin-5-one (**15**) with dimethyl fumarate at 80°. The nmr spectrum of the crude thermolysis mixture showed the presence of only adduct **54**. Further proof for the structure of the trans–trans adduct **54** was obtained by oxidation of **54** to 2,5-diphenyl-3,4-dicarbomethoxypyrrole (**12**).[66]

The trans–cis adduct **53** could be epimerized to the trans–trans adduct **54** by heating in methanol in the presence of base. A solution of 50 mg of the trans–cis adduct **53** and 25 mg of sodium methoxide in 50 ml of methanol was heated at reflux for 4 hr. Removal of the solvent left a residual solid whose nmr spectrum was identical with that of the trans–trans adduct **54**.

Photoaddition of Diphenylazirine with Dimethyl Maleate. A solution of 0.5 g of diphenylazirine and 0.325 g of dimethyl maleate in 450 ml of hexane was irradiated for 4 days through a uranium glass filter. A white crystalline solid precipitated out of solution during the course of the reaction. This material was subsequently identified as 2,5-diphenyl-*cis,cis*-3,4-dicarbomethoxy-Δ^1-pyrroline (**51**): mp 163–165° (70%); ir (KBr) 5.71, 5.76, 6.16 μ; uv (95% ethanol) 254 nm (ϵ 18,900); nmr (60 MHz, DMF) 6.94 (3 H, s), 6.55 (3 H, s), 6.23 (1 H, t, J = 9.5 Hz), 5.59 (1 H, d, J = 9.5 Hz), 4.21 (1 H, d, J = 9.5 Hz), 2.80 (10 H, m); *m/e* 337, 335 (base), 304, 272, 246, 217, 189, 103, and 77.

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 70.78; H, 5.88; N, 4.18.

The solvent was removed from the original mother liquors and the residue was chromatographed using liquid–liquid partition chromatography. The second photoadduct **52** (30%) was slightly contaminated with the major adduct and all attempts to crystallize this material failed. The structure of this minor photoadduct **52** (30%) rests on its spectral properties: ir (neat) 5.72 and 6.10 μ; nmr (60 MHz, $CDCl_3$) τ 6.45 (3 H, s), 6.28 (3 H, s) 5.42 (1 H, d, J = 6.5 Hz), 4.52 (1 H, d, J = 6.5 Hz); *m/e* 337, 335, 277, 246, 218, 193, 131, 121, 115, 105 (base).

Treatment of both the *cis,cis*-**51** and *cis,trans*-**52** adducts with sodium methoxide in methanol resulted in the formation of 2,5-diphenyl-3,4-dicarbomethoxypyrrole (**12**).

Photoaddition of 3-Methyl-2-phenylazirine with Acrylonitrile. A solution of 1.0 g of 3-methyl-2-phenylazirine (**22**) and 25 ml of acrylonitrile in 200 ml of pentane was irradiated for 1 hr using a Vycor filter. The crude reaction mixture contained two photoadducts. These materials could be separated by preparative thick layer chromatography using a 1:1 hexane–ethyl acetate mixture. The major isomer (50%) was assigned the structure of *trans*-2-phenyl-4-cyano-5-methyl-Δ^1-pyrroline (**25**): mp 50–51°; ir (KBr) 4.50 and 6.19 μ; uv (cyclohexane) 245 nm (ϵ 16,100); nmr ($CDCl_3$, 100 MHz) τ 8.53 (3 H, d, J = 6.5 Hz), 6.73 (3 H, m), 5.53 (1 H, m), 2.2–2.9 (5 H, m); *m/e* 184, 131 (base), and 103.

Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.24; H, 6.71; N, 15.27.

The minor component (20%) isolated from the thick layer plate was assigned the structure of *cis*-2-phenyl-4-cyano-5-methyl-Δ^1-pyrroline (**26**), mp 82–83°; ir (KBr) 4.48 and 6.17 μ; uv (cyclohexane) 243 nm (ϵ 16,700); nmr ($CDCl_3$, 100 MHz) τ 8.50 (3 H, d, J = 6.5 Hz), 7.40 (1 H, q, J_{3A4} = 9.5 Hz, J_{3B4} = 8.0 Hz, J_{45} = 7.0 Hz), 6.80 (2 H, m), 5.59 (1 H, t, J = 7.0 and 6.5 Hz); *m/e* 184, 131 (base).

Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.14; H, 6.54; N, 15.07.

Further support for the assignments was obtained by the oxidation of both adducts to the same pyrrole. A solution of 100 mg of **25** (and/or **26**) and 100 mg of 2,3-dichloro-5,6-dicyanobenzoquinone in 10 ml of benzene was refluxed for 1 hr. The crude reaction residue was filtered through a short florisil column. The solvent was removed under reduced pressure and the residue was recrystallized from benzene to give 2-phenyl-4-cyano-5-methylpyrrole (90%) as a white crystalline solid: mp 178–179°; ir (KBr) 4.55 and 6.24 μ; nmr (60 MHz, acetone-d_6) τ 7.57 (3 H, s), 3.30 (1 H, m), 2.30–2.80 (5 H, m); *m/e* 182 (base), 154, 140, and 127.

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.07; H, 5.45; N, 15.32.

The same two photoadducts (**25** and **26**) could be independently synthesized by heating a mixture of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one and acrylonitrile in xylene.[81]

Photoaddition of 3-Methyl-2-phenylazirine with Methylacrylonitrile. A solution of 0.5 g of 2-methyl-2-phenylazirine and 1.0 g of methylacrylonitrile was irradiated in 200 ml of pentane for 2 hr using a Vycor filter. The nmr spectrum of the crude reaction mixture revealed the presence of two photoadducts in a ratio of 3:1. The two components could not be separated by chromatography on all columns tried. Characterization was accomplished by nmr spectroscopy. The major adduct (46%) showed a singlet at τ 8.36 (3 H), doublets at 7.08 (1 H, J = 16 Hz) and 6.52 (1 H, J = 16.0 Hz), and a quartet at 5.95 (1 H, J = 7.0 Hz). The minor adduct (15%) showed a singlet at τ 8.30 (3 H) and had doublets at 7.00 (1 H, J = 16 Hz) and 6.64 (1 H, J = 16 Hz), and had a quartet at 5.63 (1 H, J = 8.0 Hz).

Photoaddition of 3-Methyl-2-phenylazirine with Methyl Acrylate. Photoaddition of 3-methyl-2-phenylazirine with methyl acrylate in pentane for 3 hr using a Vycor filter gave a mixture (ratio 2:1) of two photoadducts. The mixture could not be separated into its component parts. Characterization was accomplished by nmr spectroscopy ($CDCl_3$, 100 MHz). The major adduct (31%) showed a doublet at τ 8.80 (3 H, J = 7.0 Hz), a multiplet at 6.9 (3 H), a singlet at 6.28 (3 H), a multiplet at 5.30 (1 H), and a multiplet from 2.1 to 2.9 (5 H). The minor adduct (15%) showed a doublet at τ 8.53 (3 H, J = 7.0 Hz), a multiplet at 6.90 (3 H), a singlet at 6.31 (3 H), a multiplet at 5.63 (1 H), and a multiplet from 2.1 to 2.9 (5 H).

Photoaddition of 3-Methyl-2-phenylazirine with Methyl Methacrylate. Photoaddition of 3-methyl-2-phenylazirine with methyl methacrylate for 18 hr using a Vycor filter gave a mixture of two photoadducts (3:2). The mixture could not be separated into its component parts but was characterized by nmr spectroscopy ($CDCl_3$, 100 MHz). The major component (53%) showed a doublet at τ 8.55 (3 H, J = 7 Hz), a singlet at 6.32 (3 H), a quartet at 5.82 (1 H, J = 7 Hz), a singlet at 8.64 (3 H), and an AB quartet centered at 6.8 (2 H, J = 16 Hz). The minor component showed a doublet at 8.84 (3 H, J = 7 Hz), a singlet at 8.81 (3 H), a singlet at 6.34 (3 H), an AB quartet centered at 6.75 (2 H, J = 16 Hz), a quartet at 5.60 (1 H, J = 7 Hz,) and a multiplet from 2.1 to 2.9 (5 H).

Photoaddition of 2-Phenyl-3,3-dimethylazirine and Acrylonitrile. Photoaddition of 2-phenyl-3,3-dimethylazirine and acrylonitrile using standard irradiation procedures gave 2-phenyl-4-cyano-5,5-dimethyl-Δ^1-pyrroline (**33**, 78%) as a crystalline solid: mp 65–66°; ir (KBr) 4.50 and 6.19 μ; uv (cyclohexane) 244 nm (ϵ 17,100); nmr ($CDCl_3$, 100 MHz) τ 8.56 (3 H, s), 8.50 (3 H, s), 7.09 (1 H, dd, J = 10.0 and 8.0 Hz), 6.76 (1 H, dd, J = 17.0 and 8.0 Hz), 6.58 (1 H, dd, J = 17.0 and 10.0 Hz), 2.2–2.8 (5 H, m); *m/e* 198, 145 (base), 104, and 77.

Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.51; H, 7.06; N, 14.13.

Photoaddition of 2-Phenyl-3,3-dimethylazirine and Methylacrylonitrile. Photoaddition of a mixture of 2-phenyl-3,3-dimethylazirine and methylacrylonitrile using standard irradiation conditions gave 2-phenyl-4-cyano-4,5,5-trimethyl-Δ^1-pyrroline (**34**) (59%) as a colorless oil: nmr ($CDCl_3$, 100 MHz) τ 8.70 (3 H, s), 8.68 (3 H, s), 8.57 (3 H, s), 7.11 (1 H, d, J = 16.5 Hz), 6.60 (1 H, d, J = 16.5 Hz), 2.2–2.9 (5 H, m).

Photoaddition of 2-Phenyl-3,3-dimethylazirine and Methyl Acrylate. Irradiation of a mixture of 2-phenyl-3,3-dimethylazirine and methyl acrylate using standard conditions gave 2-phenyl-4-carbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**35**) (26%) as a crystalline solid: mp 55–56°; ir (KBr) 5.80 and 6.20 μ; uv (cyclohexane) 243 nm (ϵ 17,700); nmr ($CDCl_3$, 100 MHz) τ 8.85 (3 H, s), 8.45 (3 H, s), 6.72 (3 H, m), 6.26 (3 H, s), 2.1–2.8 (5 H, m); *m/e* 231, 200, 172, 145 (base) 115, and 104.

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.71; H, 7.56; N, 6.07.

Photoaddition of 2-Phenyl-3,3-dimethylazirine and Methyl Methacrylate. Irradiation of a mixture of 2-phenyl-3,3-dimethylazirine and methyl methacrylate gave 2-phenyl-4-carbomethoxy-4,5,5-trimethyl-Δ^1-pyrroline (**36**) (58%) as a crystalline adduct: mp 95–96°; ir (KBr) 5.80 and 6.20 μ; uv (cyclohexane) 243 nm (ϵ 14,800); nmr ($CDCl_3$, 100 MHz) τ 8.87 (3 H, s), 8.54 (3 H, s) 7.20 (1 H, d, J = 16.5 Hz) 6.20 (1 H, d, J = 16.5 Hz), 2.1–2.8 (5 H, m); *m/e* 245, 186, 145 (base), 104, and 77.

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.46; H, 7.88; N, 5.70.

Photoaddition of 2-Phenyl-3,3-dimethylazirine with Dimethyl Fumarate. A solution of 2.0 g of 2-phenyl-3,3-dimethylazirine and 1.4 g of dimethyl fumarate in 500 ml of cyclohexane was irradiated for 9 hr using a Pyrex filter. Recrystallization of the residue from absolute ethanol gave 2-phenyl-3,4-*trans*-dicarbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**55**) (86%) as a crystalline solid: mp 84–85°; ir (KBr) 3.40, 5.82, 7.00, 7.60, 8.65, 12.78, 13.00, and 14.35 μ; uv (cyclohexane) 242 nm (ϵ 14,200); nmr ($CDCl_3$, 100 MHz) τ 8.80 (3 H, s), 8.37 (3 H, s), 6.64 (1 H, d, J = 8.0 Hz), 6.38 (3 H, s), 6.25 (3 H, s), 5.21 (1 H, d, J = 8.0 Hz), 2.1–2.8 (5 H, m); *m/e* 289, 230, 170, 145 (base), 127, 104, and 77.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.36; H, 6.54; N, 4.82.

Photoaddition of 2-Phenyl-3,3-dimethylazirine with Dimethyl Maleate. A solution of 2.0 g of 2-phenyl-3,3-dimethylazirine and 1.4 g of dimethyl maleate in 500 ml of cyclohexane was irradiated with a 550-W lamp for 1 hr using a Pyrex filter. A nmr spectrum of the reaction mixture indicated the presence of starting material and 2-phenyl-3,4-*cis*-dicarbomethoxy-5,5-dimethyl-Δ^1-pyrroline (**56**, 85%). The nmr spectrum showed doublets at τ 5.62 (1 H, J = 10.0 Hz) and 6.71 (1 H, J = 10.0 Hz). After standing in the nmr tube for 24 hr, the cis adduct had partially isomerized (*ca.* 30%) to the trans form. All attempts to isolate cis adduct **56** by chromatography or crystallization failed; instead, only trans adduct **55** was obtained in good yield.

Preparation of 2-(β-Naphthyl)azirine (24). To a stirred slurry of 15.0 g of sodium azide in 100 ml of acetonitrile in a methanol–ice bath was added slowly 18.3 g of iodine monochloride over a period of 20 min. The reaction mixture was stirred for an additional 30 min and, after 13.8 g of 2-vinylnaphthalene was added, allowed to warm to room temperature for 12 hr. The red-brown slurry was added to 600 ml of water, and the mixture was extracted with 500 ml of ether in four portions. These were combined and washed with three 100-ml portions of 5% sodium thiosulfate followed by four 200-ml portions of cold water. The ethereal layer was dried over magnesium sulfate and the crude 1-azido-2-iodo-1-(β-naphthyl)ethane (23.1 g, 79%) was used in the next step without further purification: nmr ($CDCl_3$, 100 MHz) τ 6.65 (2 H, d, J = 7.0 Hz), 5.25 (1 H, t, J = 7.0 Hz), 1.7–2.7 (7 H, m); ir (neat) 4.72, 7.90, 12.21, and 13.30 μ.

To a stirred solution of 23.1 g of the crude iodo azide adduct in 250 ml of ether in a methanol–ice bath was added 12.5 g of potassium *tert*-butoxide over a period of 1 hr. The reaction was stirred for an additional 7 hr and the resulting brown suspension was washed twice with 200 ml of water. The ethereal layer was dried over magnesium sulfate. Removal of the ether under reduced pressure gave 12.1 g (94%) of crude 1-(β-naphthyl)vinyl azide. The dark solid was purified by passing it through a column of neutral alumina with benzene. The light yellow solid which remained (8.5 g) was recrystallized from hexane: mp 53–54°; ir (neat) 4.76, 7.80, 12.21, and 13.40 μ; nmr ($CDCl_3$, 100 MHz) τ 5.00 (1 H, d, J = 2.0 Hz), 4.49 (1 H, d, J = 2.0 Hz), 1.9–2.6 (7 H, m).

A solution of 1.0 g of the above vinyl azide in 10 ml of chloroform was heated at reflux for 62 hr. Removal of the solvent left a crude solid which was sublimed at 40° at 0.05 mm to give 0.47 g (54%) of 2-(β-naphthyl)azirine as a white cyrstalline solid: mp 48–49°; ir (KBr) 5.75, 7.40, 10.10, 11.12, 11.60, 12.20, and 13.43 μ; uv (cyclohexane) 339, 322, 296, 293, 284, 275, 248, and 240 nm (ϵ 1400, 1200, 9600, 9400, 11,200, 9100, 54,500, 51,300); nmr ($CDCl_3$, 100 MHz) τ 8.15 (2 H, s), 1.6–2.5 (7 H, m); *m/e* 167, 153, 139, and 127.

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.03; H, 5.58; N, 8.23.

Photoaddition of 2-(β-Naphthyl)azirine with Acrylonitrile. Irradiation of a mixture of 2-(β-naphthyl)azirine and acrylonitrile in benzene for 4 hr using a Pyrex filter gave 2-(β-naphthyl)-4-cyano-Δ^1-pyrroline (**37**) as a crystalline solid (76%). This material was purified by thick layer chromatography using a mixture of 1:1 hexane–ethyl acetate as the eluent and was sublimed at 140° (0.01 mm) to afford an analytical sample, mp 143–144°; ir (KBr) 4.45, 6.20, 11.53, 12.00, and 13.40 μ; uv (cyclohexane) 339 nm (ε 1200), 331 (830), 323 (1100), 305 (2100), 293 (10,900), 282 (12,900), 273 (10,100), 251 (57,500), and 243 (55,000); nmr ($CDCl_3$, 100 MHz) τ 6.60 (3 H, m), 5.56 (2 H, m), 1.9–2.60 (7 H, m); *m/e* 220 (base).

Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.81; H, 5.46; N, 12.64.

Photoaddition of 2-(β-Naphthyl)azirine with Methyl Acrylate. Irradiation of a mixture of naphthylazirine **24** and excess methyl acrylate in benzene for 2 hr using a Pyrex filter gave a mixture of two photoadducts. The major component (62%) was obtained as a crystalline solid by liquid–liquid partition chromatography and was identified as 2-(β-naphthyl)-4-carbomethoxy-Δ^1-pyrroline (**38**) on the basis of the following data: mp 81–82°; ir (KBr) 5.80, 6.20, 7.00, 7.35, 8.62, 12.02, and 13.35; uv (cyclohexane) 337 nm (ε 870), 328 (560), 322 (870), 293 (10,100), 290 (9000), 282 (12,700), 273 (10,400), 264 (7800), 248 (58,600), 241 (60,300), and 233 (45,900); nmr ($CDCl_3$, 100 MHz) τ 6.70 (3 H, m), 6.32 (3, H, s), 5.70 (2 H, m), 1.9–2.90 (7 H, m); *m/e* 253 (parent) and 167 (base).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.86; H, 6.01; N, 5.19.

The minor component (14%) could not be totally separated from the major adduct but showed the following peaks in the nmr ($CDCl_3$, 100 MHz) τ 7.72 (2 H, m), 6.45 (3 H, s), 5.86 (3 H, m), 1.8–2.80 (7 H, m).

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Photochemical Transformations of Small Ring Heterocyclic Compounds. XLVII. Electronic Details of the Photocycloaddition of Arylazirines[1]

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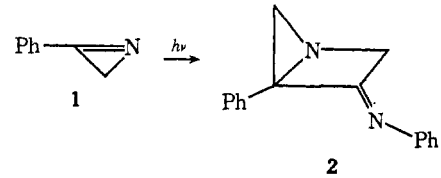
Abstract: Mechanistic studies on the photocycloaddition and photodimerization of arylazirines are reported. Irradiation of a number of substituted arylazirines in an inert solvent gives 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts. The formation of these dimers can be rationalized by 1,3-dipolar addition of the initially generated nitrile ylide onto the arylazirine. In the presence of a good dipolarophile, the nitrile ylide is trapped to give a Δ^1-pyrroline adduct. Support for this conclusion was obtained by a study of the variation of the quantum yield for adduct formation as a function of the concentration of added dipolarophile. The study shows that the amount of adduct formed is dependent on the initial concentration of azirine and on the activity of the dipolarophile. The structure of the dimer obtained from 2-phenylazirine was previously assigned as 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane. This structure is now shown to be 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene. Kinetic studies show that the nitrile ylide generated by the photolysis of an arylazirine is an electronically relaxed species.

Motivated by an interest in the photochemistry of the carbon–nitrogen double bond, we chose to study the photochemical behavior of arylazirines, a class of compounds where syn–anti photoisomerization about the C–N double bond is a structurally prohibited process. In the preceding paper, we reported structural details and preliminary results on the photocycloaddition of arylazirines with electron-deficient olefins to give Δ^1-pyrroline derivatives.[1] The formation of the adducts was interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate which is subsequently trapped by a suitable dipolarophile. During the course of our studies, we found that when the irradiation of the azirine was carried out with an olefin of low dipolarophilic activity, no photoadduct was obtained, but instead, a photodimer was formed. The structure of the photodimer seemed to depend on such factors as the nature of the substituent groups, the length of irradiation, and the particular solvent employed. Other investigators have also noted the formation of dimers on irradiation of arylazirines. For example, Woerner, Reimlinger, and Arnold[3,4] claimed that the irradiation of 2-phenylazirine (**1**) results in the formation of 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane (**2**). In



contrast with the above system, Schmid and coworkers[5] found that irradiation of diphenylazirine (**3**) gave tri-

(1) For part XLVI, see A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, *J. Amer. Chem. Soc.*, **95**, 1945 (1973).

(2) (a) Alfred P. Sloan Foundation Fellow, 1968–1972; National Institutes of Health Special Postdoctoral Fellow, 1972–1973; (b) NDEA Title IV Fellow, 1969–1971; (c) NSF Science Faculty Fellow, 1970–1971; Virginia Military Institute Faculty Fellow, 1971–1973.

(3) F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, 7, 130 (1968).

(4) F. P. Woerner and H. Reimlinger, *Chem. Ber.*, **103**, 1908 (1970).

(5) M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **54**, 1275 (1971).