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).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-24449) and the National Institutes of Health (Grant No. CA-12195-06).

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

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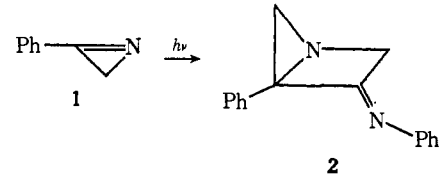
Abstract: Mechanistic studies on the photocycloaddition and photodimerization of arylazirines are reported. Irradiation of a number of substituted arylazirines in an inert solvent gives 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts. The formation of these dimers can be rationalized by 1,3-dipolar 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).

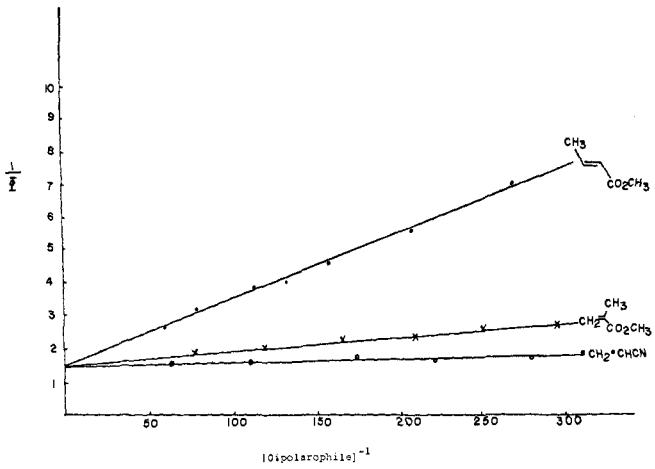


Figure 1. Plot of [quantum yield of cycloaddition]$^{-1}$ against [dipolarophile]$^{-1}$.

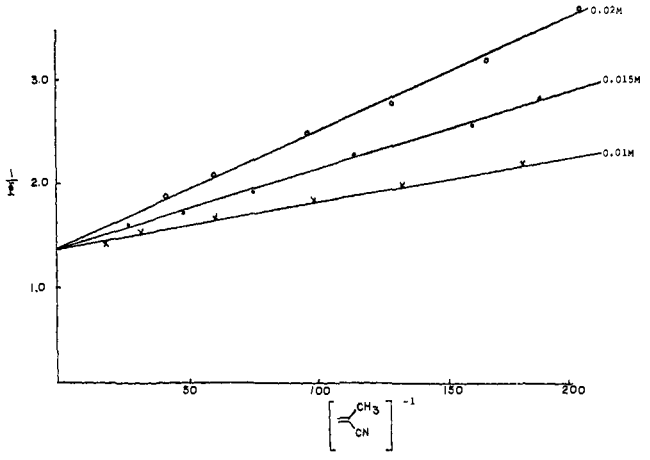
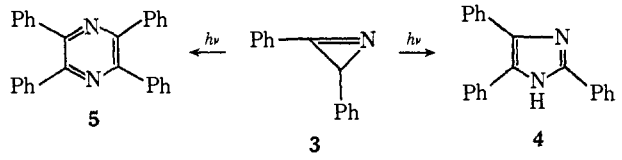


Figure 2. Plot of [quantum yield of cycloaddition]$^{-1}$ against [α-methylacrylonitrile]$^{-1}$ as a function of diphenylazirine concentration.

phenylimidazole (**4**). Hassner and Levy,[6] however, report the formation of tetraphenylpyrazine (**5**) from the irradiation of diphenylazirine.

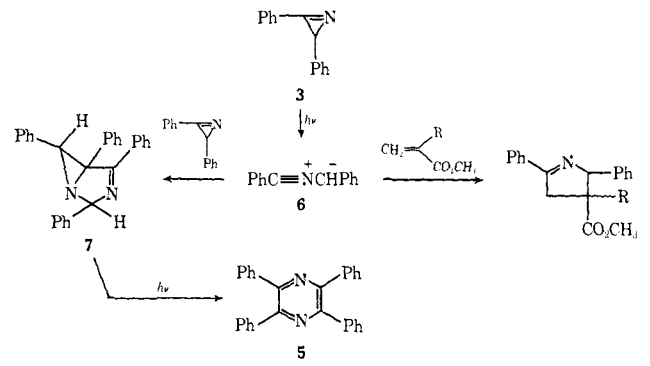


At the time our investigations began, there had been no attempt to arrive at a systematic view of the photodimerization reaction which arylazirines undergo on irradiation. In view of the widespread interest in the photochemistry of small ring nitrogen heterocycles,[7] we have studied the photodimerization of a number of substituted arylazirines in order to determine the generality and mechanistic details of the process. The data which follow allow postulation of a complete mechanistic scheme for both the photodimerization and photocycloaddition reactions of arylazirines.

Results and Discussion

Photocycloaddition and Photodimerization in the Diphenylazirine System. The photochemical cycloaddition of diphenylazirine with a variety of substituted dipolarophiles was shown to give Δ^1-pyrrolines as cycloadducts.[1] When the irradiation of **3** was carried out with olefins of low dipolarophilic activity (such as methyl β-methylcrotonate), no photoadduct was obtained, but instead tetraphenylpyrazine (**5**) was isolated on extended photolysis. As indicated by observations described and interpreted in more detail below, the formation of tetraphenylpyrazine proceeds by addition of nitrile ylide **6** onto ground-state azirine with the formation of a 1,3-diazabicyclo[3.1.0]hex-3-ene intermediate (**7**). On further irradiation, this species is converted to tetraphenylpyrazine (**5**).

These conclusions are confirmed by a study of the variation of the quantum yield of adduct formation as a function of the reciprocal of the concentration of added dipolarophile at 3130 Å. The quantum yield of adduct formation was determined by using benzo-



phenone–benzhydrol actinometry.[8] Degassed and sealed Pyrex tubes containing solutions of diphenylazirine and the dipolarophile were irradiated along with actinometer tubes in the rotating photochemical assembly. The light from a 450-W Hanovia lamp was filtered through a nickel–cobaltous solution (transmission 300–340 nm). Reactions were carried to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by glpc using internal standards. The results of the quantum yield measurements in degassed pentane solution are given in Figures 1 and 2. The quantum yield for adduct formation as a function of the concentration of diphenylazirine at a fixed dipolarophile concentration was also studied. The data are presented graphically in Figure 3 for the case of methyl methacrylate.

To establish the multiplicity of the photocycloaddition reaction, quenching and sensitization experiments were carried out. Identical diphenylazirine–methyl acrylate solutions containing naphthalene, 1,3-cyclohexadiene, and piperylene were irradiated. Neither the rate of diphenylazirine disappearance nor that of adduct formation was affected by the quenchers, each of which was present in concentrations known to diminish markedly the rates of established triplet processes.[9,10] Quantum yields for acetophenone-sensitized cycloaddition runs were also determined. The

(6) A. Hassner and L. A. Levy, *J. Amer. Chem. Soc.*, 87, 4203 (1965).
(7) For a recent review, see S. T. Reid, *Advan. Heterocycl. Chem.*, **11**, 1 (1970).
(8) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).
(9) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *ibid.*, **88**, 4781 (1966).
(10) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, **27**, 4111 (1962).

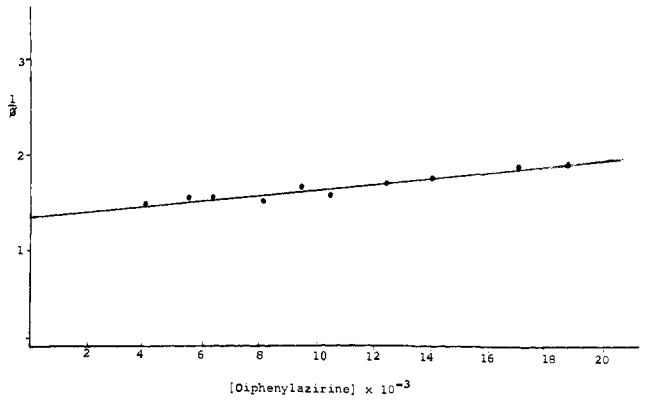


Figure 3. Plot of [quantum yield of cycloaddition]$^{-1}$ against [diphenylazirine] at 0.008 *M* methyl methacrylate.

concentrations were adjusted so that acetophenone absorbed more than 98% of the light. The concentration of diphenylazirine was kept sufficiently low to ensure unimolecular destruction of acetophenone excited singlet molecules prior to collision with ground state azirine, yet sufficiently high to guarantee collision of acetophenone triplets with azirine at a rate faster than acetophenone decay.[11,12] Under these conditions, no photocycloaddition whatever was detected. The quenching and sensitization experiments suggest that the overall transformations of diphenylazirine occur from the excited singlet manifold.[13] No fluorescence emission from **3** was observed.

Several features become apparent upon examination of the data shown in Figures 1–3. (a) Although a good linear relationship is found between the inverse of the quantum yield for adduct formation and the inverse of concentration of dipolarophile, the slope of the line varies both with the structure of the dipolarophile and the concentration of the diphenylazirine used (see Figures 1 and 2). (b) At infinite dipolarophile concentration, the quantum yield for cycloaddition for each dipolarophile used is 0.8 (*i.e.*, intercept = 1.25), indicating that the major pathway from the excited state of azirine involves bond rupture and formation of nitrile ylide **6**. (c) A plot of the reciprocal of the quantum yield for adduct formation *vs.* the concentration of diphenylazirine also gives a value of 1.25 for the intercept (see Figure 3).

These results are consistent with the mechanism shown in Scheme I, where A_0 = diphenylazirine, NY = nitrile ylide **6**, and O = dipolarophile.

Scheme I

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

$$A^{*1} \xrightarrow{k_1} A_0$$

$$A^{*1} \xrightarrow{k_2} NY$$

$$NY + O \xrightarrow{k_3} \text{adduct}$$

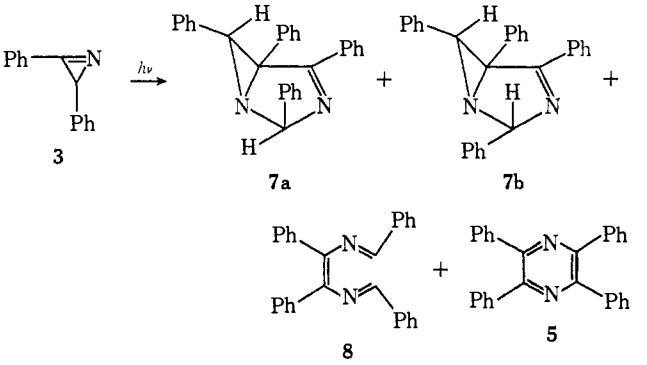
$$NY + A_0 \xrightarrow{k_4} \text{dimer}$$

By making the usual steady-state assumption, we can write

$$\frac{1}{\Phi_{\text{adduct}}} = \frac{1}{\tau k_2}\left[1 + \frac{k_4[A_0]}{k_3[O]}\right]$$

where τ is the excited singlet lifetime. According to this mechanistic scheme, the slope of the plot should be dependent on both the initial concentration of diphenylazirine as well as the magnitude of k_3. Quantitatively, if $k_3 >> k_4[A_0]$, then little variation in slope is to be expected as the concentration of diphenylazirine is increased. This is the case with acrylonitrile, an olefin of high dipolarophilic activity. In cases where k_3 and $k_4[A_0]$ have similar values (such as with methylacrylonitrile or methyl crotonate) the slope of the plot will depend on the concentration of diphenylazirine.

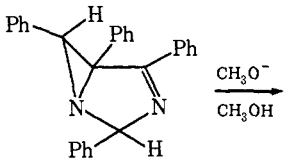
The Stern–Volmer plots shown in Figures 1–3 make it clear that the dimerization of diphenylazirine proceeds by reaction of the nitrile ylide **6** with diphenylazirine. Further support for this contention was obtained by irradiating diphenylazirine in an inert solvent for shorter periods of time. Photolysis of a solution of **3** in cyclohexane for 17 hr led to the complete disappearance of starting material and formation of a complex mixture of photoadducts. Conventional isolation procedures afforded four products (**5**, **7a**, **7b**, and **8**)



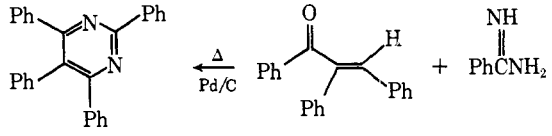
whose relative yields varied as a function of exposure duration. Consideration of the product distribution as a function of time in a number of photolyses showed that as **7a** and **7b** decreased, **8** appeared, and more slowly **5** was formed. Compounds **7a** and **7b** were shown by their elemental analyses and by their mass spectra to be dimeric. The nmr spectra ($CDCl_3$) of **7a** (τ 3.84 (1 H, s), 6.86 (1 H, s), and 2.90 (20 H, m)) and **7b** (τ 4.78 (1 H, s), 7.04 (1 H, s), and 2.85 (20 H, m)) led to their assignment as *endo*- and *exo*-2,4,5,6-tetraphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene. Both diazabicyclohexenes were found to undergo oxidative rearrangement to 2,4,6-triphenylpyrimidine (**9**) when treated with methanolic sodium methoxide.[14] Pyrimidine **9** was independently synthesized by treating 1,2-diphenylacrylophenone with benzamidine followed by oxidation over palladium on charcoal.

The formation of products **7a** and **7b** can be interpreted in terms of 1,3-dipolar addition of nitrile ylide **6** onto diphenylazirine. Other accounts describing the addition of 1,3 dipoles across the azirine double bond have appeared in the literature and provide good chem-

(11) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 3080 (1963).
(12) The choice of acetophenone as a sensitizer presupposes a diphenylazirine triplet energy of 74 kcal or less.
(13) Or possibly from a very short-lived triplet state.
(14) H. Heine, R. Weese, R. Cooper, and A. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967). These authors were the first to report the base-catalyzed oxidative rearrangement of 1,3-diazabicyclo[3.1.0]hex-3-enes to substituted pyrimidines.

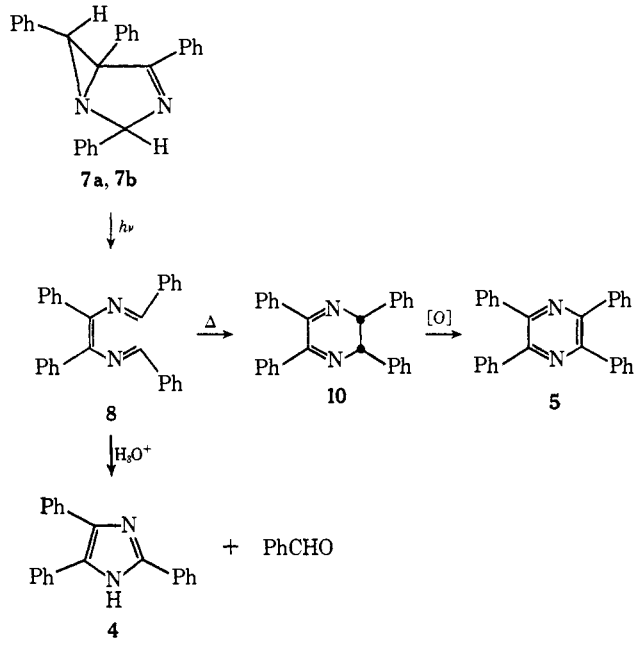


7a, 7b



9

ical analogy for the above reaction.[15-17] On further irradiation, dimers **7a** and **7b** are converted into compound **8**, mp 151–153°. From its absorption spectra (ir, 6.25 μ; uv λ_{max} 250 and 377 nm (ϵ 21,000 and 20,700); nmr τ 2.40–2.90 (20 H, m), 2.01 (2 H, s)), its thermal instability, and behavior on hydrolysis, this compound is most reasonably assigned as 1,3,4,6-tetraphenyl-2,5-diaza-1,3,5-hexatriene. Heating **8** at 50° results in the formation of *cis*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (**10**). Oxidation of **10** during work-up nicely rationalizes



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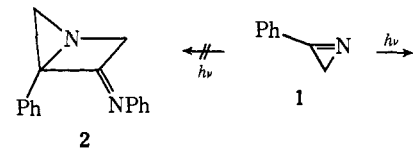
the formation of tetraphenylpyrazine (**5**). The photochemical ring openings of related 1,3-diazabicyclohexenes have appeared in the literature and provide precedent for the above transformations.[18,19] We also found that treatment of enediimine **8** with aqueous acid afforded triphenylimidazole (**4**) and benzaldehyde.[20] The above results allow us to arrive at a general mechanistic description of the photodimerization of diphenylazirine. This mechanism readily accommodates the formation of compounds **4** and **5** from the irradiation of **3**, as reported by Schmid[5,21] and Hassner.[6]

(15) A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).
(16) V. Nair, *ibid.*, **33**, 2121 (1968).
(17) V. Nair, *Tetrahedron Lett.*, 4831 (1971).
(18) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970); **94**, 7788 (1972).
(19) T. DoMinh and A. M. Trozzolo, *ibid.*, **92**, 6997 (1970); **94**, 4046 (1972).
(20) For related transformations of enediimines, see (a) P. Beak and J. L. Miesel, *ibid.*, **89**, 2375 (1967); (b) D. R. Arnold, V. Y. Abraitys, and D. McLeod, Jr., *Can. J. Chem.*, **49**, 923 (1971).

Photodimerization in the 2-Phenylazirine System. Woerner, Reimlinger, and Arnold[3] had previously reported that irradiation of 2-phenylazirine results in the formation of bicyclopentane **2**. We have also isolated, from the photolysis of **1**, a dimer consistent with that described by these workers to which we assign an alternate structure, 4,5-diphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (**11**), based on the data and an independent



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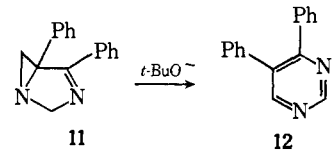
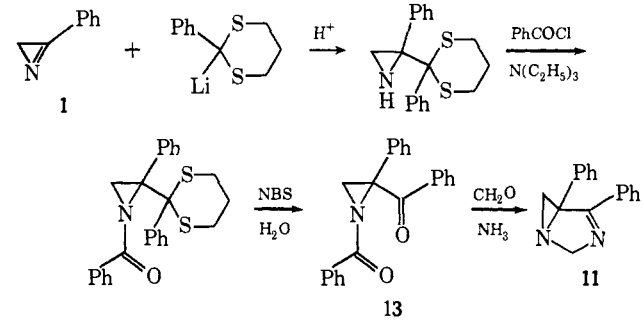


11 12

synthesis. The nmr peaks listed by these authors[3] (τ 8.38 (s), 7.20 (s), 4.90 (d), 5.20 (d)) are satisfactory for the 1,3-diazabicyclo[3.1.0]hexene system.[22] Similarly, the infrared and ultraviolet spectra are entirely consistent with this revised structure.[21] Chemical confirmation of structure **11** was obtained by the base-catalyzed rearrangement[14] of **11** to 4,5-diphenylpyrimidine (**12**): mp 130–131°; nmr τ 2.80 (10 H, m), 1.40 (1 H, s) and 0.80 (1 H, s). The structure of dimer **11** was further established by its unequivocal synthesis. Thus, cyclization of 1,2-dibenzoyl-2-phenylaziridine (**13**) with formaldehyde in an ethanolic solution saturated with ammonia led to **11** as shown in Scheme II.

Scheme II. Synthesis of 4,5-Diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene



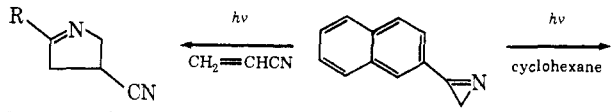
13

Diazabicyclohexene **11** was obtained in good yield and proved identical in all respects with the photochemically obtained material. Again, the formation of the dimer can be interpreted in terms of 1,3-dipolar addition of the initially generated nitrile ylide onto phenylazirine.

Photocycloaddition and Photodimerization in the 2-(β-Naphthyl)azirine System. Considerable information on the reactivity of singlet excited states of organic molecules can be obtained from a study of molecular fluorescence properties.[23] In order to secure additional information on the reactivity of the excited singlet state of the azirine system, we have studied the photo-

(21) Recently, Schmid and coworkers have reported that aryl-2*H*-azirines undergo photodimerization to give 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts; see N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972).
(22) The coupling constant of the geminal protons of phenylaziridine is less than 1.0 Hz; see S. J. Brois, *J. Org. Chem.*, **27**, 3532 (1962).
(23) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

chemistry of 2-(β-naphthyl)azirine (**14**). As was shown in the previous paper,[1] 2-(β-naphthyl)azirine (**14**) undergoes smooth cycloaddition with electron-deficient olefins. When **14** was irradiated in cyclohexane at room temperature, a single dimeric product **15** was obtained



R = β-naphthyl

14

15

R = β-naphthyl

in good yield. The 100-MHz nmr spectrum of this compound was essentially identical with that of **11**. On this basis, we have assigned the structure of **15** as 4,5-di-(β-naphthyl)-1,3-diazabicyclo[3.1.0]hex-3-ene, mp 166–167°.

Naphthylazirine (**14**) proved to be unreactive when irradiated in the presence of acetophenone. This observation identifies the excited singlet state of **14** as the reacting species. The fluorescence emission curve for β-naphthylazirine (**14**) was essentially identical in shape and wavelength with that of naphthalene. Most importantly, the fluorescence emission of **14** was not quenched with added quantities of dipolarophile. This observation is compatible with the mechanism shown in Scheme III, where A_0 = azirine **14**, NY =

Scheme III

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

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

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

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

$$NY + O \xrightarrow{k_3} \text{adduct}$$

$$NY + A_0 \xrightarrow{k_4} \text{dimer}$$

nitrile ylide, and O = dipolarophile. One can, in principle, obtain all the desired rate constants of the excited singlet state provided that Φ_r, Φ_f, and one of the rate constants are known. Here k_f is the rate constant of fluorescence, k_r is the rate of opening of the excited azirine ring, and k_d is the sum of all radiationless modes of excited singlet destruction (including any intersystem crossing).

$$\Phi_f = \frac{k_f}{k_f + k_r + k_d} \quad (1)$$

$$\Phi_r = \frac{k_r}{k_f + k_r + k_d} \quad (2)$$

The above two equations 1 and 2 may be combined to give eq 3. The excited singlet lifetime of **14** (τ_s =

$$\frac{\Phi_r}{k_r} = \frac{\Phi_f}{k_f} = \tau_s \quad (3)$$

Φ_f/k_f) was measured by single-photon counting and was shown to have a value of 1.5×10^{-9} sec.[24] Since the quantum yield for cycloaddition of **14** with methyl acrylate is high, we can estimate Φ_r as *ca.* 0.6 (*i.e.*, $\Phi_{\text{cycloaddition}} = 0.6 \sim \Phi_r$). A value of k_r can now be calculated using the measured singlet lifetime and Φ_r. The value obtained ($k_r = 4 \times 10^8$ sec) is compatible with a rapid opening of the excited azirine ring to give an electronically relaxed nitrile ylide intermediate. Future work will permit us to determine the effect of substituents on the rate of ring opening.

Relative Reactivity Studies. Recent results in the 1,3-dipolar cycloaddition reactions of pyridinium ylides have disclosed significant differences between the reactivity of the 1,3-dipole when it is generated in the ground state or in an excited state.[25,26] In order to determine whether an electronically relaxed or excited nitrile ylide intermediate is involved in the photocycloaddition reactions of diphenylazirine (**3**), we have studied the relative reactivity of various dipolarophiles toward nitrile ylide **6**. From the slope and intercept of the Stern–Volmer analysis for adduct formation with a given dipolarophile and at a fixed azirine concentration (see Figures 1 and 2), we find that

$$\text{slope/intercept} = k_{4'}/k_3$$

where $k_{4'} = k_4[A_0]$. For the case of methyl methacrylate, $k_4'/k_3 = 1/6$. This value indicates that the rate constant for cycloaddition of nitrile ylide **6** with methyl methacrylate is six times greater than the rate of its reaction with ground-state azirine. Since $k_{4'}$ is constant for the diphenylazirine series, we can estimate the relative reactivity of various dipolarophiles toward the photochemically generated nitrile ylide by determining the magnitude of their slopes and intercepts in a Stern–Volmer plot.

$$\frac{[k_{4'}/k_{3A}]_{\text{olefin A}}}{[k_{4'}/k_{3B}]_{\text{olefin B}}} = \frac{k_{3B}}{k_{3A}} = k_{\text{rel}}$$

Another approach was also used to secure a quantitative measure of the relative reactivity of various dipolarophiles toward nitrile ylide **6**. Generation of **6** by photolysis of diphenylazirine in the presence of a mixture of dipolarophiles creates a competitive system from which the ratio of relative rates, $k_{\text{rel}} = k_{3B}/k_{3A}$, may be obtained by standard treatment of the kinetic data. The required data for the calculation of k_{rel} are the initial concentration of each of the competing dipolarophiles and the concentration of each at a subsequent stage in the reaction. In principle, these data may be determined either directly by measuring the amount of dipolarophile remaining or indirectly from

$$k_{\text{rel}} = \frac{k_{\text{olefin B}}}{k_{\text{olefin A}}} = \frac{\log ([O_B]_i/[O_B]_f)}{\log ([O_A]_i/[O_A]_f)}$$

a knowledge of the concentration of reaction products. The agreement between the k_{rel} values determined by the Stern–Volmer technique and those determined by the direct competition method is excellent (see Table I).

Table II gives a list of the relative rate constants for the cycloaddition of various dipolarophiles with nitrile

(24) We thank Professor N. Turro for this measurement.
(25) T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Chem. Soc. C*, 481 (1970).
(26) T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, **36**, 813 (1971).

Table I. Relative Reactivity of Dipolarophiles toward Nitrile Ylide 6 Determined by the Stern–Volmer and Direct Competition Methods

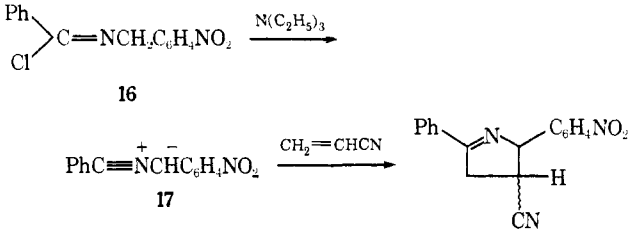
Dipolarophile	Stern–Volmer technique	Direct competition
Methyl methacrylate	8.5	9.0
Methylacrylonitrile	3.6	3.6
Methyl crotonate	1	1

Table II. Relative Reactivity of a Series of Olefins toward Nitrile Ylide 6

Dipolarophile	Rel rate
Methyl crotonate	1
Diphenylazirene	2.5
Methylacrylonitrile	3.6
Methyl methacrylate	9
Diethyl maleate	135
Methyl acrylate	160
Dimethyl maleate	166
Acrylonitrile	180
Dimethyl acetylenedicarboxylate	540
Maleonitrile	2,300
Diethyl fumarate	56,000
Dimethyl fumarate	84,000
Fumaronitrile	189,000

ylide 6. To facilitate comparison, all the k_3 values are related to that for methyl crotonate, which is taken as unity. The data presented in the table show that the rate of cycloaddition is dramatically affected by steric factors. Sterically congested dipolarophiles react so sluggishly that their very small rate constants cannot be measured satisfactorily. Introduction of a methyl group into the α or β position of the acrylic ester results in a significant diminution in rate. Also, trans-substituted dipolarophiles undergo cycloaddition at a much faster rate than the corresponding cis isomers. This same phenomenon has been reported by Huisgen for related 1,3-dipolar cycloaddition reactions.[27]

The above discussion has indicated that the photocycloaddition of diphenylazirine (**3**) with a variety of dipolarophiles proceeds by ring opening of **3** to form a nitrile ylide intermediate. The reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**16**) with trimethylamine in the presence of a dipolarophile has also been shown to proceed by way of a nitrile ylide intermediate (**17**).[28] In order to secure additional informa-



tion on whether an electronically relaxed nitrile ylide intermediate is involved in the photocycloaddition reaction, we have compared olefin reactivities of the same olefins toward nitrile ylide **17**. We expect that the *p*-nitro group present in **17** will not appreciably affect the reactivity of this species. The results are given in

(27) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 565, 633 (1963).
(28) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Chem. Ber.*, 105, 1258 (1972).

Table III. Relative Reactivities of Olefins toward the Nitrile Ylides Generated from Diphenylazirine (**3**) and *N*-(*p*-Nitrobenzyl)benzimidoyl Chloride (**16**)

Olefin	Diphenylazirine	Imidoyl chloride
Slow Set		
Methyl crotonate	1	1
Methyl methacrylate	9	10
Diethyl maleate	135	51
Dimethyl maleate	166	61
Fast Set		
Diethyl fumarate	1	1
Dimethyl fumarate	1.5	1.3
Fumaronitrile	3.3	3.1

Table III. Especially noteworthy is the near identity of the relative reactivities of all the olefins examined toward both nitrile ylides. These results would lead one to conclude that similar species are involved in the product forming step in both systems; the most reasonable intermediate common to both systems is a vibrationally and electronically relaxed nitrile ylide.

Conclusion

Our photochemical studies of arylazirines show that the electronically excited singlet state undergoes C–C bond cleavage to give a nitrile ylide intermediate. As a 1,3-dipole, this species can be intercepted with a variety of dipolarophiles to form five-membered rings. Kinetic studies show that the nitrile ylide is an electronically relaxed species. When the irradiation of the arylazirine is carried out with an olefin of low dipolarophilic activity, the nitrile ylide adds across the double bond of the azirine ring to give 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photodimers. These dimers undergo subsequent photoreaction. The products formed depend on the substituent groups, the time of irradiation, and the particular solvent employed.

Experimental Section[29]

Photodimerization of 2,3-Diphenylazirine. A solution of 700 mg of diphenylazirine (**3**) in 500 ml of cyclohexane was irradiated with a 550-W Hanovia lamp using a Pyrex filter for 17 hr. The solvent was removed under reduced pressure to give a yellow oil which was subjected to scanning liquid–liquid partition chromatography.[1] The optical density trace revealed the presence of four components. The first peak contained 200 mg (30%) of a white solid, mp 250–251°. This component was identified as tetraphenylpyrazine (**5**) by comparison with an authentic sample.[30] The second peak in the chromatogram contained 70 mg (10%) of an intensely yellow colored solid, mp 151–153°, whose structure is assigned as 1,3,4,6-tetraphenyl-2,5-diaza-1,3,5-hexatriene (**8**) on the basis of the following data: ir (KBr) 6.25 μ; uv (95% ethanol) 250 and 377 nm (ϵ 21,000 and 20,700); nmr ($CDCl_3$, 100 MHz) τ 2.40–2.90 (20 H, m), 2.01 (2 H, s); *m/e* 386 (M^+), 179, 178, 103, and 81.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.88; H, 5.65; N, 7.16.

Further confirmation of the structure of **8** was obtained by its thermal conversion to *cis*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine (**10**). A 70-mg sample of **8** in benzene-d_6 was heated in a sealed

(29) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with a Varian Associates high-resolution spectrometer and at 100 MHz using a Jeol-MH-100 spectrometer.
(30) A. Rosenthal, *Can. J. Chem.*, 38, 2025 (1960).

degassed nmr tube at 50° for 2 hr. The product isolated in quantitative yield was identified as *cis*-dihydropyrazine **10** by comparison with an authentic sample.[31] If the thermolysis of **8** was carried out in an open vessel, the only product isolated was tetraphenylpyrazine **5**.

The third fraction isolated from the liquid–liquid partition chromatogram (245 mg, 35%) was a white crystalline solid, mp 125–127°, whose structure is assigned as *endo*-2,4,5,6-tetraphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**7a**): ir (KBr) 6.28, 6.95, 7.20, 7.90, 8.55, 10.80, 13.40, 14.50 μ; uv (95% ethanol) 238 nm (ε 18,300); nmr ($CDCl_3$, 100 MHz) τ 6.86 (1 H, s), 3.84 (1 H, s), and 2.20–3.20 (20 H, m); *m/e* 386 (M^+), 181, 102, and 79.

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.83; H, 5.78; N, 7.34.

The remaining fraction in the liquid–liquid partition chromatogram contained 190 mg (25%) of a pale yellow oil whose nmr spectrum showed it to be mainly *exo*-2,4,5,6-tetraphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**7b**): nmr ($CDCl_3$) τ 7.04 (1 H, s), 4.78 (1 H, s) and 2.2–3.20 (20 H, m). All attempts to separate the exo isomer **7b** from the small amount of the epimeric diazabicyclohexene **7a** present in the sample failed.

Treatment of *exo*- and *endo*-2,4,5,6-Tetraphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene with Sodium Methoxide. Further confirmation of the structures of **7a** and **7b** was obtained by their base-catalyzed rearrangement to 2,4,5,6-tetraphenylpyrimidine (**9**). A solution of 140 mg of *endo*- (or *exo*-) diazabicyclohexene (**7a** or **7b**) in 50 ml of a freshly prepared 0.13 *N* sodium methoxide–methanol solution was allowed to reflux for 12 hr. The reaction mixture was then diluted with water and extracted with ether. The ethereal layer was washed with water and dried over sodium sulfate. The yellow residue that remained was taken up in benzene and heated with excess palladium on charcoal for 1 hr. Filtration of the catalyst followed by removal of the solvent gave a yellow oil which was recrystallized from 95% ethanol to give 2,4,5,6-tetraphenylpyrimidine (**9**) as white crystals: mp 190–191°; ir (KBr) 6.60, 6.70, 6.95 μ; uv (95% ethanol) 258 nm (ε 31,700); nmr ($CDCl_3$) τ 1.40–3.20 (multiplet); *m/e* 384, 383 (base), 191, 178, 176, 103, and 77.

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.41; H, 5.24; N, 7.29. Found: C, 87.21; H, 5.39; N, 7.32.

The structure of pyrimidine **9** was confirmed by an unequivocal synthesis. A mixture of 0.71 g of benzamidine hydrochloride and 2.56 g of 1,2-diphenylacrylophenone[32] in 25 ml of 95% ethanol was stirred at room temperature. To the above mixture was added a solution of 0.51 g of potassium hydroxide in 25 ml of 95% ethanol. The resulting solution was heated under reflux for 1.5 hr. The oil which remained on removal of the solvent was taken up in benzene and heated in the presence of palladium on charcoal (100 mg) for 1 hr. Recrystallization of the solid from 95% ethanol gave white crystals, mp 190–191°. The infrared spectrum of this material was identical in all respects with that of a sample of **9** obtained from the base-catalyzed rearrangement of **7a** (or **7b**). A mixture melting point of the two samples was undepressed at 190–191°.

Irradiation of *endo*- and/or *exo*-2,4,5,6-Tetraphenyldiazabicyclo-[3.1.0]hex-3-ene. A solution containing 25 mg of *endo*- and/or *exo*-diazabicyclohexene **7a** (or **7b**) in 1 ml of benzene-d_6 was irradiated for 12 hr using a 450-W Hanovia lamp equipped with a Pyrex filter. The solution turned deep yellow after several hours of irradiation. Removal of the solvent left a yellow oil which gave white crystals (90%) on crystallization from 95% ethanol, mp 250–251°. This material was identical in all respects with an authentic sample of tetraphenylpyrazine **5**.

Photodimerization of Phenylazirine (1). A solution containing 500 mg of phenylazirine (**1**) in 400 ml of benzene was irradiated for 5 hr using a 450-W Hanovia lamp equipped with a Vycor filter. Removal of the solvent under reduced pressure left an oil which was subjected to liquid–liquid partition chromatography. The major component (425 mg, 85%) was a solid, mp 136–138°, whose properties are consistent with that described by Woerner, Reimlinger, and Arnold:[3] ir (KBr) 6.20, 9.98, 10.16 μ; uv (95% ethanol) 244 nm (ε 12,200); nmr ($CDCl_3$, 100 MHz) τ 8.38 (1 H, s) 7.20 (1 H, s), 5.20 (1 H, d, J = 16 Hz), 4.90 (1 H, d, J = 16 Hz), 2.4–2.8 (10 H, m). The structure of this material is assigned as 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**) on the basis of its chemical behavior and by an independent synthesis.

Chemical confirmation of the structure of the photodimer was obtained by the base-catalyzed rearrangement of **11**. A mixture of 100 mg of 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**) and 50 mg of potassium *tert*-butoxide in 50 ml of xylene was heated at reflux for 15 hr. At the end of this time, the solvent was removed under reduced pressure and the residue was dissolved in chloroform and washed several times with water to remove all the base. The chloroform solution was dried over sodium sulfate and evaporated to give 90 mg (90%) of 4,5-diphenylpyrimidine (**12**): mp 130–131°; ir (KBr) 6.61, 7.0, 7.21, 7.70, 7.90, 8.82, 9.40, 9.81, 10.14, 10.90, 12.41, 13.20, 14.40 μ; nmr ($CDCl_3$, 60 MHz) τ 2.80 (10 H, m), 1.40 (1 H, s), 0.89 (1 H, s); *m/e* 232 (M^+), 205, 178, and 77.

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.20; N, 12.06. Found: C, 82.71; H, 5.23; N, 12.00.

Synthesis of 4,5-Diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (11). An authentic sample of photodimer **11** was prepared by the reaction of 1,3-dibenzoyl-2-phenylaziridine (**13**) with formaldehyde in an ethanolic solution saturated with ammonia. The desired aziridine **13** was synthesized by treating the anion of 2-phenyl-1,3-dithiane with 2-phenylazirine in the following fashion. A solution of 46.2 g of 2-phenyl-1,3-dithiane[33] in 500 ml of dry tetrahydrofuran was cooled to −78° in a Dry Ice–acetone bath, and 0.25 mol of *n*-butyllithium in hexane (2.5 *M* solution) was added dropwise with efficient stirring over a 1-hr period. After the mixture was stirred for an additional 45 min at −78°, a solution of 28 g of 2-phenylazirine in 100 ml of tetrahydrofuran was added. The mixture was stirred for 2 hr at −78°, warmed to room temperature, and quenched with 100 ml of water. The organic phase was dried over magnesium sulfate. Removal of the solvent left an orange solid which was crystallized from acetonitrile to give 2-phenyl-2-(2′-phenyl-1,3-dithianyl)aziridine (38 g, 54%): mp 143–146°; ir (KBr) 6.80, 6.95, 7.10, 13.15, 13.90, 14.35 μ; nmr ($CDCl_3$, 100 MHz) τ 8.76 (1 H, broad s), 8.22 (1 H, s), 8.20 (2 H, m), 7.48 (1 H, s), 7.40 (4 H, m), 2.2–3.1 (10 H, m); *m/e* 284 (base), 210, 178, 105, and 77.

Anal. Calcd for $C_{18}H_{19}NS_2$: C, 68.99; H, 6.11; N, 4.47; S, 20.43. Found: C, 69.10; H, 6.22; N, 4.53; S, 20.28

To a mixture of 0.78 g of the above aziridine and 0.25 g of triethylamine in 50 ml of dry benzene at 0° was added a solution of 0.35 g of benzoyl chloride in 30 ml of anhydrous ether. The reaction mixture was stirred at 25° for 3 hr and then filtered to remove triethylamine hydrochloride. The filtrate was concentrated to an oil which was then recrystallized from acetone to give 0.85 g (82%) of *N*-benzoyl-2-phenyl-2-(2′-phenyl-1,3-dithianyl)aziridine as white crystals: mp 150–152°; ir (KBr) 6.12 μ; uv (95% ethanol) 232 nm (ε 11,600); nmr ($CDCl_3$, 100 MHz) τ 8.20 (2 H, m), 7.40 (4 H, m), 7.12 (1 H, s), 6.90 (1 H, s), 1.80–3.60 (15 H, m); *m/e* 286 (M^+), 223, 195 (base), 178, 165, 121, 119, 105, 91, and 77.

Anal. Calcd for $C_{23}H_{23}NOS_2$: C, 71.90; H, 5.55; N, 3.35; S, 15,37. Found: C, 71.77; H, 5.59; N, 3.25; S, 15.39.

A solution of the above *N*-benzoylaziridine (3.15 g) in tetrahydrofuran (75 ml) was added dropwise at 0° to a solution of *N*-bromosuccinimide (10.7 g) and 2,6-dimethylpyridine (19.2 g) in 200 ml of 95% tetrahydrofuran. After 15 min the mixture was washed with a saturated sodium sulfite solution. The organic phase was diluted with 300 ml of methylene chloride and then washed with several portions of a 5 *M* cupric nitrate solution. The solvent was removed, after drying over sodium sulfate, and the residual oil was crystallized from methanol to give 1,2-dibenzoyl-2-phenylaziridine (**13**) (1.8 g, 73%) as white crystals: mp 118–119°; ir (KBr) 6.05, 6.25, 6.35, 6.90 μ; uv (95% ethanol) 247 nm (ε 21,300); nmr ($CDCl_3$, 100 MHz) τ 6.88 (1 H, s), 6.58 (1 H, s), 1.90–2.80 (15 H, m); *m/e* 327 (M^+), 297, 222, 165, 119, 105, 91 (base), and 77.

Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.52; H, 5.29; N, 4.32.

A solution of 500 mg of the above aziridine **13** in 10 ml of absolute ethanol containing 60 mg of ammonium bromide was saturated with formaldehyde. After standing for 10 min, the mixture was resaturated with ammonia at 0°. The resulting solution was allowed to stand at room temperature for 24 hr. Removal of the solvent under reduced pressure gave 322 mg (91%) of 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**), mp 137–139°. The infrared and nmr spectra of this material were identical in every detail with those of the dimer obtained from irradiation of 2-phenylazirine. A mixture melting point was undepressed at 137–139°.

Photodimerization of 2-(β-Naphthyl)azirine (14). A solution of 500 mg of 2-(β-naphthyl)azirine (**14**) in 125 ml of cyclohexane was irradiated under a nitrogen atmosphere for 1.25 hr using a 450-W

(31) A. Padwa and E. Glazer, *J. Amer. Chem. Soc.*, **94**, 7788 (1972).
(32) J. Parrick, *Can. J. Chem.*, **42**, 190 (1964).
(33) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965).

Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a crude solid which was purified by thick layer chromatography using ethyl acetate as the eluent. Recrystallization of the white solid from acetone gave 4,5-di(β-naphthyl)-1,3-diazabicyclo-[3.1.0]hex-3-ene (**15**) (37%) as a crystalline solid: mp 166–167°; ir (KBr) 6.20, 7.38, 7.52, 9.95, 11.48, 12.01, 13.29 μ; uv (cyclohexane) 226 nm (ε 107,000), 245 (53,200), 253 (48,600), 273 (15,300), 283 (16,100), 292 (12,200), 341 (1,100); nmr ($CDCl_3$, 100 MHz) τ 8.12 (1 H, s), 6.84 (1 H, s), 5.00 (1 H, d, J = 16 Hz), 4.64 (1 H, d, J = 16 Hz), 1.80–2.80 (14 H, m); m/e 334 (M^+), 332 (base), 331, 304, 276, 153, 127.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.27; H, 5.42; N, 8.29.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate/100 ml of water through the inner jacket.[34] All studies were made at room temperature. Samples were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol[8] or cyclopentanone[35] solutions were used as the chemical actinometer. For cyclopentanone, an actinometer quantum yield of 0.38 was used[35] which gave a reproducible lamp output of 2.01×10^{16} quanta sec^{-1}. After irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions in the arylazirine series were run to 15% or less. The mass balance in these runs was generally better than 95%.

Competitive studies were carried out photochemically on mixtures of an arylazirine, an internal standard, and two different dipolarophiles in sealed, degassed tubes. The relative reactivities were determined by gas chromatography using the relation

$$k_{rel} = (\log A/A_0)/(\log B/B_0)$$

where A_0 and B_0 are the areas of the two dipolarophiles relative to the internal standard prior to the reaction, and A and B the same quantities after reaction. Relative reactivities of dipolarophiles toward the nitrile ylide generated from *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**16**) were determined in a similar fashion. In a small test tube was added a benzene solution of the two dipolarophiles, an internal standard, and triethylamine. After measuring the area of the peaks corresponding to the dipolarophiles, the solution was allowed to react with *N*-(*p*-nitrobenzyl)benzimidoyl chloride (**16**). Since cycloaddition rates varied considerably between systems, tubes were removed periodically and analyzed by glc until optimum conversion times for analysis had been determined. The final peak areas were determined by glc after *ca.* 40% of the dipolarophiles had been consumed. The results are summarized in Table III.

Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure Xenon lamp, as supplied by the manufacturer. The fluorescence spectra of naphthalene and 2-(β-naphthyl)azirine (**14**) were determined in cyclohexane solution at 25°. The concentration of the substrate was 5×10^{-3} *M*. The solvent was checked for emission each time a spectrum was run. No interference due to solvent was found at any time. All slits were set at 3 mm and excitation was at 335 nm. The naphthylazirine showed a fluorescence maximum at 375 nm and the shape of the emission envelope was essentially identical with that of naphthalene. The singlet lifetime (τ_s) of 2-(β-naphthyl)azirine was measured by single-photon counting and was determined to be 1.5×10^{-9} sec.[24]

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Photochemical Reactions of 1-Cyclopentenyl and 1-Cyclohexenyl Ketones

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Abstract: Photolysis of several 1-acylcycloalkenes has been investigated and found to lead to three types of rearrangement. Simple ketones **1**–**5**, as well as **22**, undergo hydrogen transfer with formation of spiroketones **7**–**11** and **23** plus some minor products. Cyclohexenyl ketones **25** and **29** give the hexahydrofluorenones **27** and **28** in an electrocyclic reaction, and the doubly unsaturated **35** is isomerized to ketene **43** which can be isolated as esters **36** and **37**. All three processes occur on both direct irradiation and triplet sensitization in preparatively attractive yields.

In a previous report,[1] we described photochemical reactions of cyclopentenones in which a key step is intramolecular transfer of hydrogen to the β carbon atom of the enone system. These findings suggested that related processes might occur in other types of α,β-unsaturated ketones. This has indeed proved to be the case, and we describe below our experience with photolysis of a number of 1-acylcycloalkenes. Apart from hydrogen transfer reactions, two other processes occur in some of these ketones. In several cases the various transformations observed provide synthetically worthwhile routes to useful systems.

The simple alkyl 1-cyclopentenyl ketones **1**–**5** are all available through Friedel–Crafts acylation[2] of cyclopentene with the appropriate carboxylic acid chloride. If irradiation of these compounds leads to the hydrogen abstraction observed in cyclopentenones, the result expected is that shown in eq 1. Abstraction by the β

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(2) N. Jones and H. T. Taylor, *J. Chem. Soc.*, 4017 (1959), and references cited therein.