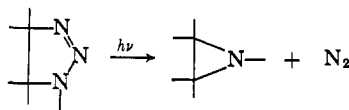# Triazoline Photodecomposition. Stereochemistry and Mechanism

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Abstract: Triazoline photodecomposition has been investigated. High photoefficiency, insensitivity to solvent, and predominant retention of initial geometry in the product characterize the direct photolysis. The results are interpreted in terms of a singlet excited state and a short-lived 1,3-diradical intermediate, although alternative, *e.g.*, concerted, mechanisms may not be definitively excluded. Photosensitized decomposition and structural effects on the product distribution accord with the postulated mechanism. The observed over-all success of triazoline photodecomposition as a synthetic route to aziridines is a consequence of the nature of the intermediates and their favorable geometry for aziridine formation.

Previous publications[1,2] have discussed the preparation of aziridines by the photodecomposition of Δ^2-1,2,3-triazolines. In view of the reaction's synthetic

potential, as well as its relationship to other photoprocesses, an investigation of triazoline photodecomposition was undertaken.

Results

Attempts to intercept photointermediates were unsuccessful. Photolysis of triazoline I in cyclopentene, for example, gave only aziridine II; none of the known aziridine III derived from cyclopentene was
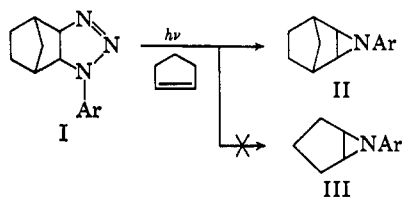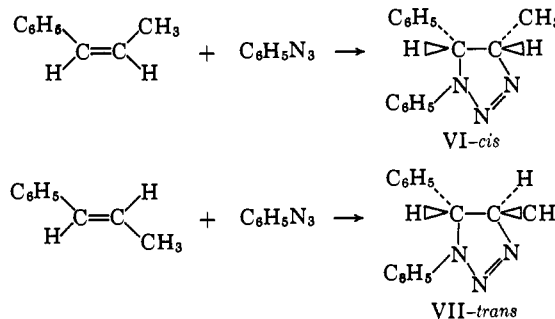

detected. Presumably, III might have resulted from dissociation to norbornene and azide, followed by photolysis to the nitrene and subsequent addition to cyclopentene.[3] However, the complete absence of III or nitrene insertion products argues against a dissociative mechanism.

Triazoline thermal decomposition intermediates have been intercepted.[4,5] Baldwin and coworkers have shown that V results from the pyrolysis of triazoline IV in the presence of phenyl isocyanate. Photolysis of IV in phenyl isocyanate, on the other hand, produced only the corresponding aziridine. Furthermore, V was not obtained when the aziridine was heated with phenyl isocyanate.[6] These results and the previously
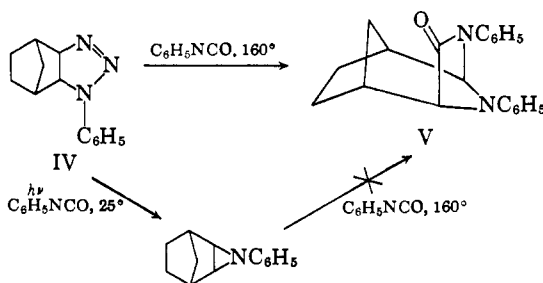
noted insensitivity to solvent[1] suggest that triazoline photodecomposition involves either extremely short-lived intermediates, or that it occurs by a one-step process involving no intermediate species.

The photomechanism has been investigated by examining the stereochemical course of the reaction. Isomeric triazolines VI and VII were prepared by the addition of phenyl azide to *cis*- and *trans*-β-methyl-

styrenes. Although the yields were not high (~25%), only one triazoline product was obtained in each case. The addition of azides to olefins is a concerted cycloaddition,[7] and previous examples of its stereospecificity have been reported.[8] Similarly, the 1,5 disposition of the phenyl groups is in agreement with both mechanistic information concerning azide–olefin addition[7,9] and the structures of other aryl azide–styrene adducts.[10]

Adducts VI and VII exhibited complex ABX_3 nmr spectra. The experimental spectra, however, were

(1) P. Scheiner, *Tetrahedron*, in press.
(2) (a) P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965); (b) R. Huisgen, L. Mobius, G. Miller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965); (c) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabot, and R. L. Hale, *Chem. Ind.* (London), 1556 (1964).
(3) W. Lwowski and J. S. McConaghy, *J. Amer. Chem. Soc.*, **87**, 5490 (1965).
(4) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *ibid.*, **87**, 4114 (1965).
(5) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565, 633 (1963).

(6) Related additions to the aziridine ring have been reported. See H. W. Heine, R. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966).
(7) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, **87**, 306 (1965).
(8) R. Huisgen and G. Szeimies, *Chem. Ber.*, **98**, 1153 (1965).
(9) P. Scheiner, *Tetrahedron*, in press.
(10) G. D. Buckley, *J. Chem. Soc.*, 1850 (1954); P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **26**, 2331 (1961).

Table I. Chemical Shifts and Coupling Constants for VI and VII[a]

| | H₄[b] | H₅[b] | CH₃[b] | J, cps | |
				4,5	4,CH₃
VI-cis	5.64	5.57	9.14	12.0	7.3
VII-trans	5.89	5.82	8.84	8.8	7.1

[a] Degassed benzene solutions. Tetramethylsilane as internal standard. [b] In τ values.

reproduced in every detail by a standard computer program,[11] using the values given in Table I. Chemical shifts for hydrogen adjacent to the azo linkage (H₄) and for hydrogen adjacent to the N-aryl group (H₅) in several symmetrically 4,5-dialkyl-substituted triazolines show the following ranges: H₄, τ 5.3–5.9, and H₅, τ 6.0–6.4.[2b,9] Compounds VI and VII displayed complex multiplets (2 H's) in the H₄ region. Thus, as anticipated for structures VI and VII, the signals for the hydrogens at the 5 position have been displaced downfield, due to the presence of the adjacent phenyl group.

Irradiation of solutions of either VI or VII produced the same three products: cis-1,2-diphenyl-3-methyl-aziridine (VIII), trans-1,2-diphenyl-3-methylaziridine (IX), and propiophenone anil (X).[12] Control experiments demonstrated the photostability of the products under the conditions employed, and interrupted runs revealed no cis–trans triazoline interconversion prior to photolysis. Furthermore, the cis:trans aziridine ratio (determined by nmr) remained constant throughout the reactions. Synthetic product mixtures, prepared from authentic samples of VIII–X, displayed infrared and nmr spectra identical with those obtained by photodecomposition; additional products were not detected.
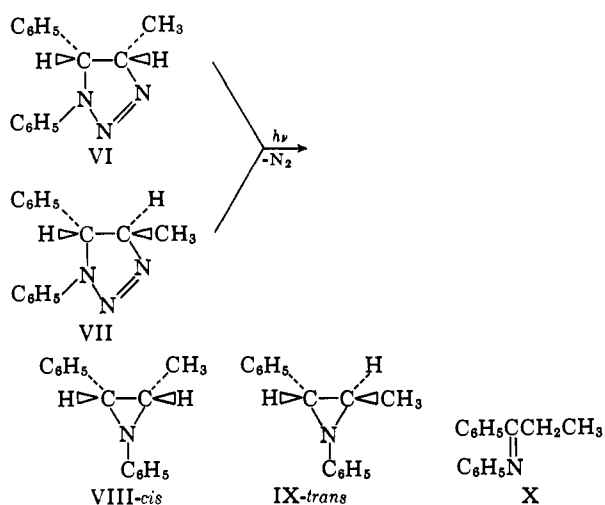

Table II summarizes the product distributions from direct photolysis. Predominant retention of the triazoline geometry in the aziridine products was ob-

(11) S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964).
(12) A preliminary report of this work has appeared: P. Scheiner, J. Amer. Chem. Soc., 88, 4759 (1966).

Table II. Direct Photodecomposition of VI and VII[a]

| | Products, %[b] | | |
Triazoline	VIII-cis	IX-trans	X
VI-cis[c]	65	17	18
VI-cis + piperylene (4.9 M)	63	22	15
VI-cis; degassed[d]	61	20	19
VII-trans[c]	22	66	12
VII-trans + piperylene (4.9 M)	26	65	9
VII-trans; degassed[d]	25	61	14

[a] Pyrex filter, 25°. Initial concentrations: 0.042 M in benzene. [b] ±4%. [c] Average values for three runs. [d] Three freeze–thaw cycles at 0.1 mm.

served. Within experimental error, the same product distribution were obtained when the initial triazoline concentrations were raised to 0.068 and 0.135 M, and runs carried out at 45 and 60° with both triazolines gave identical results. (At higher temperatures, appreciable thermal decomposition occurred.) Photolyses in cyclohexane, o-dichlorobenzene, and acetonitrile showed no significant deviation from the results in Table II. Furthermore, the product distributions were found to be insensitive to the presence of either oxygen or piperylene, and quantum yields for nitrogen evolution (313 mμ) were unaffected by dissolved oxygen (Table III).

Table III. Quantum Yields for Nitrogen, 313 mμ[a,b]

Triazoline	Initial concn, M	% react.	Φ_N₂
VI-cis	0.042	43	1.03
	0.042	45	1.05[c]
	0.049	36	0.93
	0.071	27	1.10
		Av	1.03 ± 0.06
VII-trans	0.042	27	0.93
	0.042	31	1.06
	0.042	44	0.97[c]
		Av	0.99 ± 0.06

[a] 27 ± 1°, o-dichlorobenzene solvent. [b] At 313 mμ, the solvent absorbs 1% of the light with a 0.042 M solution of triazoline. Φ_N₂'s are uncorrected. [c] Degassed by three freeze–thaw cycles at 0.1 mm.

Although triplet energy transfer to azo compounds is well documented,[13] sensitized triazoline photodecomposition has not been reported. The occurrence of this process was clearly demonstrated when benzene solutions of XI were simultaneously irradiated (366 mμ) with and without added benzophenone. The ultraviolet spectrum of XI shows no detectable absorption at wavelengths greater than 335 mμ. After 10 hr, a quantitative evolution of nitrogen was observed from
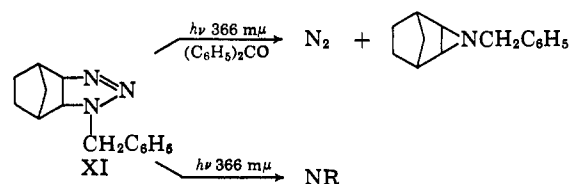
the photosensitized solution, while less than 1% reaction occurred in the directly irradiated solution.

(13) (a) J. R. Fox and G. S. Hammond, ibid., 86, 4031 (1964); (b) R. E. Rebbert and P. Ausloos, ibid., 87, 1847 (1965); (c) S. F. Nelsen and P. D. Bartlett, ibid., 88, 143 (1966).

Under conditions where benzophenone absorbed more than 90% of the incident radiation (366 mμ), triazolines VI and VII smoothly decomposed. The strikingly different product distributions obtained with benzophenone (cf. Tables II and IV) are indicative of a photosensitized process, although completely unambiguous photosensitization, as with XI, could not be demonstrated in these instances. Interrupted runs showed no triazoline isomerization prior to photolysis, and under the conditions employed, the products were photostable. Although a photosensitized interconversion (and perhaps other reactions) of the aziridine products[14] was observed on prolonged irradiation, this process was slow compared to triazoline photodecomposition (see Experimental Section). Additional products were not detected (infrared, vpc, and nmr), and runs with different sensitizer concentrations (0.138 and 0.286 M) gave essentially the same results. Thus, the data in Table IV appear to represent the primary reaction products.

Table IV. Benzophenone-Photosensitized Decomposition of VI and VII[a]

Triazoline[c]	Products, %[b]		
	VIII-cis	IX-trans	X
VI-cis	60	36	4
VII-trans	54	42	4

[a] 366 mμ, 27 ± 1°; benzophenone, 0.028 M. [b] ±4% duplicate runs for each triazoline. [c] Initial concentrations: 0.042 M in benzene.

With 366-mμ light, naphthalene, triphenylene, and fluorene were ineffective as sensitizers. Runs with these materials inefficiently gave product mixtures identical with those from direct photolysis. On the other hand, photolysis in the presence of relatively high concentrations of acetophenone and triphenylamine afforded product mixtures similar to those obtained in the benzophenone-sensitized reaction. Due to analytical complications, imine analysis was not undertaken in these cases. The ratio of aziridines (retained geometry:rotated geometry) served to indicate the effectiveness of the sensitizer (Table V).

Table V. Effect of Photosensitizers on the Aziridine Ratio[a,b]

Sensitizer	E_T,[d] kcal/mol	Concn, M	VI-cis[c]: azir. ratio	VII-trans[c]: azir. ratio
...	...	...	3.8	3.0
Benzophenone	68.5	0.286	1.7	0.8
Triphenylamine	70.1	0.273	2.1	1.1
Acetophenone	73.6	0.420	2.4	1.9

[a] Aziridine ratio = retained geometry/rotated geometry, relative to the starting material. [b] 366 mμ, 27 ± 1°. [c] Initial concentration: 0.042 M in benzene. [d] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, J. Amer. Chem. Soc., **86**, 4537 (1964).

(14) The photosensitized isomerization of cis- and trans-1,2-diphenylcyclopropane has been reported by G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, J. Amer. Chem. Soc., **86**, 2532 (1964).

Discussion

Neither oxygen nor piperylene[15] (excited triplet state quenchers) altered the product distribution, and the quantum yield was unaffected by dissolved oxygen. Thus direct photolysis most probably occurs from an excited singlet state. The strikingly different product ratios observed in the photosensitized decompositions support this conclusion. As a basis for discussion, a mechanistic scheme consistent with the experimental results is presented (Scheme I, *S = excited singlet).

Scheme I
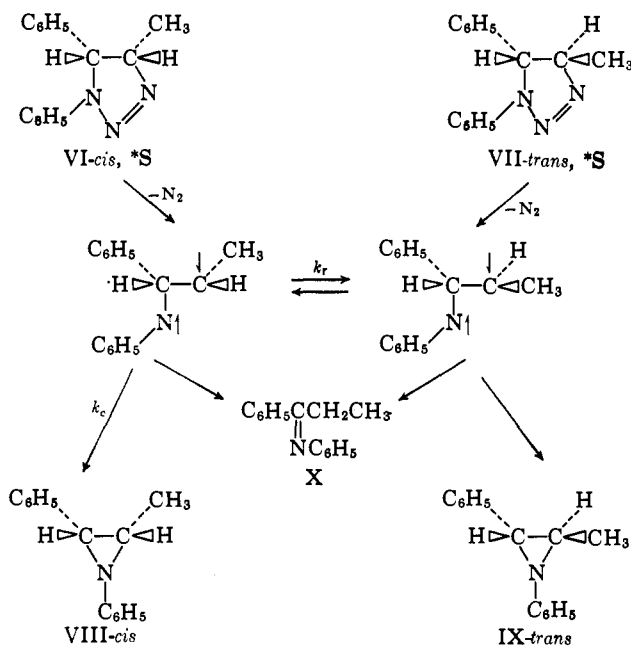
At the wavelengths of light employed, the departure of triplet nitrogen ($^3\Sigma_u^+$, 143 kcal/mol)[16] is energetically forbidden. Therefore, in agreement with the lack of effect of triplet quenchers, the excited singlet triazoline is pictured as giving rise to a 1,3 diradical possessing paired electron spins. This intermediate may then undergo (1) ring closure to the aziridine of retained geometry (k_c), (2) internal rotation to the isomeric diradical (k_r), or (3) H migration to the imine product. In terms of Scheme I and the product data (Table II), it has been calculated that starting from triazoline VI-cis, closure occurred 2.3 times more frequently than rotation ($k_c/k_r = 2.3$); from VII-trans, $k_c/k_r = 1.8$.[17] These values may be compared with those obtained by Bartlett and coworkers for 1,4 diradicals; $k_c/k_r = 0.10$.[18] In part, the difference (a factor of ~20) may arise from the more favorable geometry for bond formation in the present case. Larger k_c/k_r ratios than observed here, i.e., greater retention of geometry, have been reported for solution-phase photolyses of the analogous 1-pyrazoline system.[19]

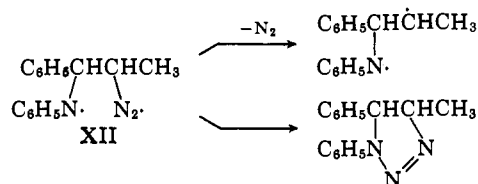(15) A. A. Lamola and G. S. Hammond, J. Chem. Phys., **43**, 2129 (1965).

(16) G. Hertzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950, p 449.

(17) Details of the calculation are available on request.

(18) L. K. Montgomery, K. Schueller, and P. D. Bartlett, J. Amer. Chem. Soc., **86**, 622 (1964).

(19) T. V. Van Auken and K. L. Rinehart, ibid., **84**, 3736 (1962); D. E. McGreer and W. S. Wu, Can. J. Chem., **45**, 461 (1967); C. G. Overberger, R. E. Zangaro, and J-P. Anselme, J. Org. Chem., **31**, 2046 (1966).
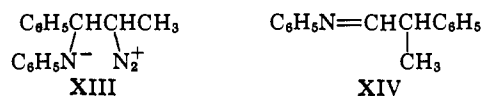
A one-step expulsion of nitrogen (Scheme I), rather than a path involving a 1,5 diradical (XII) with sufficient life time to undergo rotation, appears more consistent with the results. Apart from rotation or decomposition to the 1,3 diradical, an intermediate such as XII might

$$C_6H_5CHCHCH_3 \underset{XII}{\overset{C_6H_5N\cdot \quad N_2\cdot}{<}} \quad \xrightarrow{-N_2} \quad \begin{array}{l} C_6H_5\overset{\cdot}{C}HCHCH_3 \\ C_6H_5\overset{\cdot}{N}\cdot \\[6pt] C_6H_5CHCHCH_3 \\ C_6H_5N \quad N \\ \qquad N \end{array}$$

be expected to undergo recombination to the ground state starting material, but the latter would occur at the expense of a photon; it is therefore inconsistent with the observed quantum yield ($\Phi_{N_2} = 1.0$). Less easily dismissed is the recombination of XII to ground-state triazoline possessing vibrational energy sufficient for the quantitative thermal expulsion of nitrogen. However, thermal decompositions of VI and VII in xylene or toluene produced products not found in the photolysis. Among these, benzalaniline and 2-phenyl-propionaldehyde have been identified. Although not definitive, these results suggest that photodecomposition does not involve the vibrationally excited, ground-state triazoline.

Seltzer has estimated a lower limit for the decomposition rate constant of methyl azo radical ($CH_3N_2\cdot$): $>2.5 \times 10^{10}$ sec^{-1}.[20] If a 4-kcal/mol rotational barrier is assumed for XII, then rotation is estimated to have a rate constant of about 1.3×10^{10} sec^{-1}. Though quite crude, comparison of these estimates suggests that even if a 1,5-diradical intermediate were involved, the stereochemical outcome would be unaffected, since loss of nitrogen would be more rapid than rotation.

The imine product, propiophenone anil (X), results from hydrogen migration. Similar rearrangements have been reported for 1,3 diradicals.[21] On the other hand, a zwitterionic[4] precursor to X (or the aziridines) is unlikely. Only one azomethine was formed, but on the basis of migratory aptitudes to electron-de-

$$\underset{XIII}{\overset{C_6H_5CHCHCH_3}{\underset{C_6H_5N^- \quad N_2^+}{<}}} \qquad \underset{XIV}{\overset{\displaystyle C_6H_5N=CHCHC_6H_5}{\underset{\displaystyle CH_3}{|}}}$$

ficient centers ($C_6H_5 > H$), the formation of the anil of 2-phenylpropionaldehyde (XIV) would be anticipated from XIII (or polar species derived from it).

Under photosensitizing conditions, both the *cis*- and *trans*-triazolines gave similar product mixtures (Table IV). In these instances, the data indicate that during reaction rotational equilibrium is approached, if not actually attained. (The discrepancy between VI and VII could be due to partial direct photolysis.) If triplet-excited triazoline decomposes in the manner described above, then loss of singlet nitrogen would result in a 1,3 diradical possessing parallel electron spins. However, before ring closure to the aziridine products, the odd electron spins of the diradical must become paired,

(20) S. Seltzer and F. T. Dunne, *J. Amer. Chem. Soc.*, **87**, 2628 (1965).

(21) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); S. W. Benson, *ibid.*, **34**, 521 (1961); G. W. Griffin, J. Covall, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and G. S. Irving, *Tetrahedron Letters*, 2951 (1965.)

i.e., a spin inversion must occur. Since ring closure of the postulated diradicals possessing paired spins (direct photolysis) was sufficiently rapid to predominantly preserve the stereochemistry of the starting material, the loss of stereospecificity in the sensitized photolysis suggests that spin inversion is slower than σ-bond rotation. This interpretation agrees with Skell's hypothesis[22] concerning the nonstereospecific addition of triplet carbene to olefins, a process that also involves triplet 1,3 diradicals.

Although the results of the present study are accommodated by the description presented in Scheme I, alternative formulations are possible. Of interest in this regard is the character of the proposed (singlet) 1,3-diradical intermediate. As depicted, the odd electrons are confined to discrete orbitals, *i.e.*, negligible bonding between them. It is recognized, however, that this represents an extreme view; at the other extreme, aziridine formation might be considered concerted with the departure of nitrogen. Reaction *via* a transition state approximated by XV would completely

$$\underset{XV}{\overset{\displaystyle C_6H_5CH\text{---}CHCH_3}{\underset{\displaystyle C_6H_5N \diagup N \diagdown\!\!\diagup N}{}}}$$
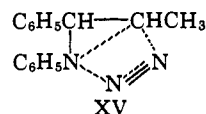
preserve triazoline geometry in the aziridine product, but from the rotation observed (Table II), it appears that at least 20% of the starting material did not decompose in this manner. A more realistic estimate (1.5 × rotated aziridine + imine) indicates that about 45% of the reaction could not have been concerted. Hence, pending additional experimentation, we prefer to view the photodecomposition as occurring through 1,3-diradical intermediates.

Data presented in a preceding paper[1] show that rotational freedom about the triazoline C_4–C_5 bond plays a role in the extent to which imine is produced. Increased flexibility about this bond resulted in greater yields of imine. Alkyl substitution at the 4 position also appeared to enhance imine formation.[1] In terms of the proposed mechanism (Scheme I), these effects are explicable, if stereoelectronic requirements for imine and aziridine formation are assumed. Expulsion of nitrogen from the excited triazoline was pictured as giving a 1,3 diradical, initially possessing (approximately) the indicated geometry. As formed, the odd-electron orbitals are favorably oriented for bonding;
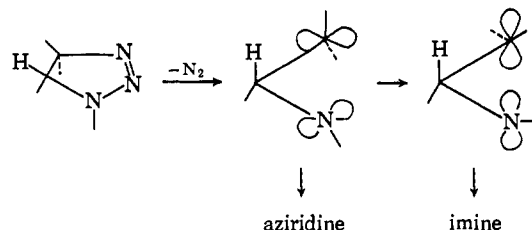
therefore, when severe rotational constraints are present, exclusive aziridine formation was observed,[1] but in the model system it was demonstrated that, in the absence of such restriction, appreciable rotation occurred. In the course of rotation a conformation suitable for

(22) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956); P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, Chapter 12.

hydrogen migration may be attained. Presumably, in this conformation the axis of the radical p orbital on carbon is parallel to the axis of the C–H bond, thereby maximizing overlap for hydrogen migration. (Involvement of the nitrogen radical may not, of course, be ruled out.) Alkyl substitution at C_4 might result in a somewhat increased lifetime for the more highly substituted intermediates. A longer lifetime could then allow a greater fraction of the intermediates to attain the conformation favorable for imine formation.

Experimental Section[23]

Photolysis of I in Cyclopentene. A sample of I[2a] (0.415 g, 1.42 mmol) in 50 ml of cyclopentene was irradiated (Hanovia Type A, Pyrex filter) at 16°. After evolution of the theoretical volume of nitrogen, the colorless solution was analyzed on a 3-ft column (10% Carbowax 20M on Chromosorb W, 215°). Comparison with authentic samples[2a] showed that no III was present. The single peak was isolated and found to be pure II (melting point and infrared).

trans-1,5-Diphenyl-4-methyl-Δ²-1,2,3-triazoline (VII). A mixture of 42.6 g (0.358 mol) of phenyl azide, 48.0 g (0.406 mol) of *trans*-β-methylstyrene, and 50 ml of ethyl acetate was refluxed for 7 hr. Evaporation under reduced pressure gave 43.0 g of viscous orange material. This was chromatographed over 350 g of alumina. Elution with petroleum ether–diethyl ether (1:1) afforded crude product, 20.8 g (24%), mp 80–90°. A sample recrystallized four times from *n*-hexane melted from 96.5 to 97.5°. The ultraviolet spectrum (ethanol) showed λmax 303 mμ (ε 8120) and λ 286 mμ (ε 7840).

Anal. Calcd for C₁₅H₁₅N₃: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.74; H, 6.34; N, 17.70.

cis-1,5-Diphenyl-4-methyl-Δ²-1,2,3-triazoline (VI). This compound was prepared from phenyl azide and *cis*-β-methylstyrene[24] as described for VII (22%). Recrystallizations from *n*-hexane gave the analytical sample, mp 129–130° dec. The ultraviolet spectrum (ethanol) showed λmax 307 mμ (ε 8320) and λ 287 mμ (ε 7430).

Anal. Calcd for C₁₅H₁₅N₃: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.71; H, 6.37; N, 18.0.

1-Phenylpropylideneaniline (X) A solution of 13.4 g (0.10 mol) of propiophenone, 9.3 g (0.10 mol) of aniline, and 0.5 ml of concentrated hydrochloric acid in 125 ml of toluene was refluxed for 24 hr. A Dean-Stark trap removed water during the reaction. Evaporation of volatile materials under reduced pressure gave 21.0 g of viscous oil which was distilled through a short Vigreux column. The product (13.3 g, 59%) distilled from 117 to 124° (0.8–1.0 mm) and solidified in the receiver, mp 47–49°. Two recrystallizations from methanol gave X, mp 50–51°.

Anal. Calcd for C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.93; H, 7.13; N, 6.62.

cis- and *trans*-1,2-Diphenyl-3-methylaziridines (VIII and IX). Equimolar portions (0.03 mol) of phenyl azide and either *cis*- or *trans*-β-methylstyrene were dissolved in 10 ml of ethyl acetate and refluxed (*ca.* 3 days) until the theoretical yield of nitrogen (gas buret) was observed. The crude product mixture was chromatographed on alumina. Elution with petroleum ether (bp 30–60°) gave a pale yellow oil consisting of VIII and IX. The aziridines were not adequately separated by fractional distillation, but essentially pure samples (>96%) were obtained by vapor phase chromatography, employing a 3-ft column packed with 10% Carbowax 20M on Chromosorb W at 230°. *trans*-Aziridine (IX) displayed the nmr spectrum previously described for the compound.[25] The benzylic hydrogen doublet (τ 7.13) showed J = 2.6 cps (lit.[26] J = 2.5 cps).

Anal. Calcd for C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.95; H, 7.11; N, 6.65.

The nmr spectrum of *cis*-aziridine (VIII) was also as described; the benzylic hydrogen doublet (τ 6.80) showed J = 6.2 cps (lit.[26] J = 6.0 cps).

Anal. Calcd for C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.12; H, 7.24; N, 6.89.

Photolyses. Direct photolyses were carried out by immersing cylindrical Pyrex tubes containing the reaction solutions in a temperature-controlled water bath, about 7 cm from the immersed light source (Hanovia Type A, 550-W, medium-pressure mercury arc). Irradiation was continued until the theoretical quantity of nitrogen was observed by means of a thermostated gas buret (∼4 hr).

For the quantum yield determinations and the photosensitized runs, the source was mounted in a ventilated box fitted with a shutter and aperture. In front of the aperture was placed a Pyrex cell (2 cm) through which cold water rapidly circulated. Filter combinations (313 mμ,[26] 366 mμ[27]) were interposed between the reaction vessel and the water cell. The photosensitized runs were purged with pure, dry nitrogen before irradiation, and magnetically stirred.

For quantum yields, the light flux was determined with a dual thermistor bolometer (YSI Model 65). Measurements were made with the probe inside the reaction cell, before and after each run. The radiometer output was graphically recorded, and the flux determined by integration over 10–15-min periods. Fluxes of 5.0–9.0 × 10⁵ ergs/cm² sec were employed. A completely blackened rectangular quartz cell with a 5.43-cm² window served as the reaction vessel. Measurements with an identical clear cell showed that in the concentration ranges used the solutions absorbed all incident light. The extent of reaction (evolved gas) was measured at atmospheric pressure with a thermostated gas buret connected to the reaction cell by capillary tubing. Before the final volume measurement, the contents of the reaction cell were vigorously stirred (shutter closed) for 0.5 hr. Quantum yields determined in benzene solution showed appreciable scatter (15%) and required a vapor pressure correction. More reliable results were obtained in *o*-dichlorobenzene.

Product Analysis. The photolyzed solution was evaporated thoroughly (40° 0.4 mm) to give the product mixture. Integration of the areas under the benzylic hydrogen signals in the nmr spectrum (100-cps sweep width) gave the ratio of *cis*- and *trans*-aziridines (VIII and IX). The infrared spectrum of an accurately prepared solution (CHCl₃) of the product mixture was recorded from 6.0 to 6.2 μ. Immediately prior to this measurement, the spectrophotometer was adjusted to zero absorbance in this range with solvent in the sample and reference cells. The intensity of the absorption at 6.11 μ was compared with the absorptions of a set of standard solutions containing known amounts of VIII–X. The amount of propiophenone anil present in the product was then determined by interpolation of the absorbance values. A similar procedure was used for the benzophenone-sensitized reactions, but benzophenone was included in the standards.

The accuracy of the analytical method (±4%) was established by analyzing prepared mixtures containing known amounts of VIII–X in approximately the same ratio as that from the photoproduct. On direct irradiation, such a mixture (or the photolysis solution) did not significantly change in composition after 10 hr. A benzene solution of the aziridines (0.040 *M*, 90% *trans*, 10% *cis*) and benzophenone (0.286 *M*) was irradiated (366 mμ) for 10 hr, then analyzed by nmr. The aziridine composition was found to be 82% *trans* and 18% *cis*, indicating that a slow isomerization (relative to triazoline photodecomposition) had occurred. Within experimental error, imine X was shown to be unaffected by irradiation (366 mμ) in the presence of benzophenone (0.040 *M* each, 20 hr).

(23) Nmr spectra were determined in deuteriochloroform with a Varian A-60 instrument, using tetramethylsilane as an internal reference. Melting points, uncorrected, were obtained with a Fisher-Johns melting point apparatus. Infrared spectra were determined for chloroform solutions with a Perkin-Elmer Model 237 instrument. Ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer. Vapor phase chromatography was carried out with an F & M Model 810, using a thermal conductivity detector and helium as the carrier gas.

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