Intramolecular Photocycloaddition Reactions in the 2-(4-Pentenyl)-5-aryl-Substituted Tetrazole System

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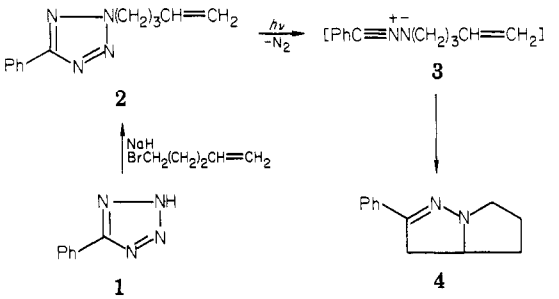
Received March 10, 1982

Irradiation of 2-(4-pentenyl)-5-aryl-substituted tetrazoles with UV light results in the loss of nitrogen and formation of a nitrile imine intermediate. This reactive 1,3-dipole undergoes an intramolecular 1,3-dipolar cycloaddition reaction to produce a bicyclopyrazoline ring. The primary photochemical process occurs from the n-π^* excited singlet state. The effect of substituents on the para position of the 5-phenyl group of the tetrazole ring was examined. A kinetic investigation, involving Stern-Volmer plots and relative reactivity studies, shows that there is a marked leveling of the rate profile associated with these internal cycloadditions when compared with their bimolecular counterparts. The high degree of order already present in the transition state for these intramolecular nitrile imine cycloadditions could account for the leveling of the rate profile.

The cycloaddition of 1,3-dipoles has become an important method for the preparation of five-membered heterocyclic rings[1,2] and has recently had a significant impact on the synthesis of natural products.[3-5] Numerous possibilities for variation are available by changing the structure of both the dipole and dipolarophile. Some of the more interesting members of the 1,3-dipole family are the nitrilium betaines. This class of 1,3-dipoles always contains nitrogen as the middle atom since only this element can supply an unshared electron pair while in the trivalent neutral state. 1,3-Dipolar cycloaddition of nitrilium betaines has been widely investigated[6,7] and in many cases has led to the synthesis of a variety of interesting heterocyclic compounds,[8] some of which would be tedious to synthesize by other routes. Our research groups have recently been concerned with the intramolecular 1,3-dipolar cycloaddition reactions of nitrilium betaines.[9-11] The internal cycloadditions of this class of 1,3-dipoles are of interest for a number of reasons. First, the reaction represents a general scheme for the synthesis of novel fused ring heterocycles. Secondly, among the possible forms of a nitrilium betaine, a carbene structure can be envisaged which makes conceivable an intramolecular 1,1-cycloaddition of this 1,3-dipole. Thirdly, the spatial relationship of the dipole and dipolarophile moieties would be expected to play an important role in controlling the rate and regioselectivity of the intramolecular cycloaddition reaction. The primary spatial requirement for 1,3-dipolar cycloaddition is that the distance between the two reacting centers should be sufficiently short so that effective three-center overlap of the dipole with the dipolarophile can occur. Moreover, the atoms of the dipolarophile should be arranged in such a way as to allow their p orbitals to lie in a plane parallel to the plane of the nitrilium betaine for internal 1,3-dipolar cycloaddition to occur. The technique of attaching two potentially interacting groups to a chain of methylene units was previously shown to be of considerable value in delineating the geometric features associated with the intramolecular dipolar cycloaddition reaction of nitrile ylides.[12,13] As part of a research program designed to uncover new cycloaddition reactions of nitrile imines,[14] we initiated a study dealing with the photochemistry of a series of *N*-alkenyl-substituted tetrazoles.[15] In this paper we report on the mechanistic features associated with the intramolecular 1,3-dipolar cycloaddition reaction of nitrile imines generated from tetrazole precursors.

Chart I



Results and Discussion

Nitrile imines can be obtained by the treatment of hydrazonyl halides with base,[16] the photolysis of sydnones,[17] the thermal elimination of carbon dioxide from 1,3,4-oxadiazolin-5-ones,[18,19] and the thermal or photochemical

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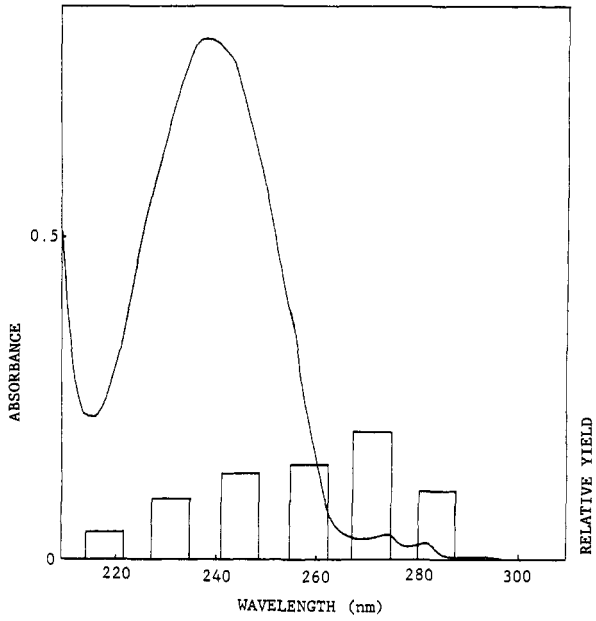


Figure 1. Ultraviolet spectrum of **2** and relative yield of **4**, depending on the wavelength.

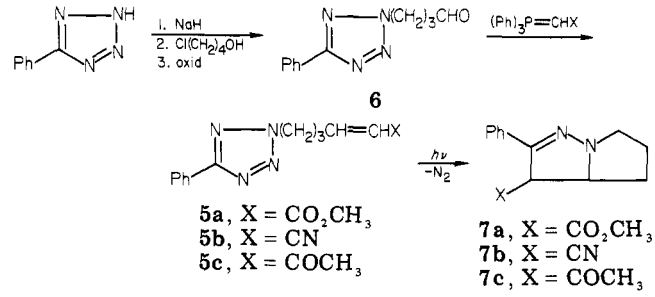
decomposition of tetrazoles.[20-22] The same products are generally obtained from cycloaddition reactions with the products of tetrazole photolysis as from nitrile imines generated by the standard procedure of treating hydrazonyl chloride with base. The synthesis of the 2-(4-pentenyl)-5-aryl-substituted tetrazole system was straightforward and involved the reaction of the appropriate 5-aryltetrazole with 5-bromo-1-pentene in the presence of base. Structural assignments were made on the basis of the spectroscopic and analytical data (see the Experimental Section).

Irradiation of 2-(4-pentenyl)-5-phenyltetrazole (**2**) in benzene with a light source of wavelength greater than 250 nm is known to give bicyclopyrazole derivative **4** in high yield (Chart I).[15] The formation of this product has been interpreted in terms of an initial loss of nitrogen to give nitrile imine **3**, which undergoes a rapid cycloaddition across the double bond present in the side chain.

The ultraviolet spectrum of tetrazole **2** shows maxima at 282, 275, 271, and 268 nm with characteristic fine structure and which is assumed to be due to an n–π^* transition. This conclusion is predicated on the fact that these bands have low extinction coefficients and are shifted to the blue on increasing the solvent polarity. We have now found that irradiation of **2** in this region is most effective for the formation of bicyclic pyrazoline **4** as shown in Figure 1. The elimination of nitrogen appears to proceed from the n–π^* singlet state. The involvement of the singlet state was attributed to the fact that a variety of triplet quenchers (i.e., piperylene, isoprene, etc.) and sensitizers (i.e., benzophenone, acetophenone, acetone, etc.) neither quenched nor sensitized the photolysis.

In order for the intramolecular 1,3-dipolar cycloaddition reaction of nitrile imines to proceed, two criteria must be met.[23,24] First, the distance between the two reacting

Chart II



centers should be sufficiently short so that effective three-center overlap of the nitrile imine with the dipolarophile can occur. Secondly, the atoms of the dipole and dipolarophile should be arranged in such a way as to allow attainment of the "two-plane orientation approach".[1,2] These criteria are readily satisfied with the nitrile imine (i.e., **3**) generated from the irradiation of tetrazole **2**. The intramolecular cyclization reaction of nitrile imine **3** is also of interest in that it involves cycloaddition with an unactivated olefin, a substrate that is generally unreactive toward nitrile imines.[25]

The cycloadditions of simple nitrile imines with electron-rich dipolarophiles are LU(1,3-dipole)–HO(dipolarophile) controlled.[25,26] For conjugated dipolarophiles, both HO and LU interactions are important, but the greater difference in LU coefficients leads to a preference for 5-substituted Δ^2-pyrazolines.[25,26] With electron-deficient dipolarophiles the regioselectivity is reversed since the cycloaddition becomes HO(1,3-dipole)–LU(dipolarophile) controlled. Since the intramolecular cycloaddition of **3** involves an alkyl-substituted double bond, one might inquire why the reaction occurs at all. Undoubtedly, the rate of internal cycloaddition reflects an extremely favorable entropy factor that offsets the unfavorable electronic factor.

In order to assess the importance of the entropy term, we decided to compare the rate of internal cycloaddition of **2** with that of a related system which possesses an electron-withdrawing substituent on the double bond. To this end we synthesized tetrazoles **5a**, **5b**, and **5c**. These compounds were readily prepared by treating the aldehyde **6** with carbomethoxy, cyanomethylene, and acetonyltriphenylphosphorane.

Irradiation of **5a** in benzene for 2 h led to the complete consumption of reactant. The only product obtained was pyrrolidino[1,2-*b*]-3-phenyl-4-(methoxycarbonyl)-2-pyrazoline (**7a**) in 88% yield (Chart II). Similar results were obtained on irradiation of tetrazoles **5b** and **5c**. Clearly, a nitrile imine related to **3** is an intermediate in these reactions and cycloadduct **7** arises by intramolecular 1,3-dipolar cycloaddition of the transient dipole with the neighboring double bond.

As was pointed out earlier, the dipole(HO)–dipolarophile(LU) orbitals control regioselectivity when nitrile imines react with electron-deficient alkenes. Recent calculations by Houk and Caramella[27] indicate that the ni-

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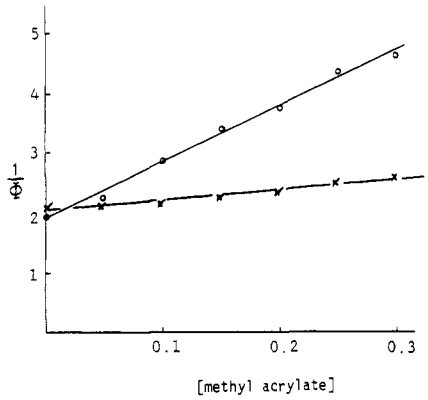


Figure 2. Plot of [quantum yield of cyclization]$^{-1}$ against [methyl acrylate] for 2-(4-pentenyl)-5-phenyltetrazole (**2**; O) and methyl (*E*)-6-(5-phenyltetrazol-2-yl)-2-hexenoate (**5a**; x).

Scheme I

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

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

$$A^* \xrightarrow[-N_2]{k_r} NI$$

$$NI \xrightarrow{k_1} P$$

$$NI + O \xrightarrow{k_2} \text{adduct}$$

trogen atom of the nitrile imine is the nucleophilic terminus in the HOMO. Alkyl-substituted olefins as well as electron-deficient alkenes have the largest coefficient on the substituted carbon in the LU orbital. The preferred regioisomeric transition state should be that in which the larger coefficients of the interacting orbitals are united. Thus, the formation of bicyclopyrazoline **7** rather than a criss-crossed cycloadduct is perfectly consistent with the principles of frontier MO theory.

In order to derive additional mechanistic information concerning the intramolecular dipolar cycloaddition reaction, a more quantitative investigation of these cycloadditions was undertaken. Quantum yields for product formation were determined with use of potassium ferrioxalate as a chemical actinometer.[28] Degassed and sealed quartz tubes containing hexane solutions of tetrazoles **2** and **5a** were irradiated along with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products. The quantum yield for product formation as a function of the concentration of added methyl acrylate was also studied. The data are presented graphically in Figure 2 for tetrazoles **2** and **5a**.

Several features become apparent upon examination of the data shown in Figure 2. Good linear relationships are observed between the inverse of the quantum yield for product formation and the concentration of added methyl acrylate. The slopes and intercepts of the plots depend on the structure of the tetrazole used. At zero dipolarophile concentration, the quantum yield for cycloaddition is 0.49 for tetrazole **2** and 0.48 for tetrazole **5a**. The high quantum efficiencies observed with these systems demonstrate that a significant path from the electronically excited state of the unsaturated tetrazole involves nitrogen extrusion and formation of a nitrile imine intermediate. The results obtained using these tetrazoles as nitrile imine precursors are consistent with the mechanism outlined in Scheme I. In this scheme, A_0 = tetrazole (**2** or **5a**), NI = nitrile imine, P = product, and O = dipolarophile (i.e., methyl acrylate). By making the usual steady-state assumption, we can write

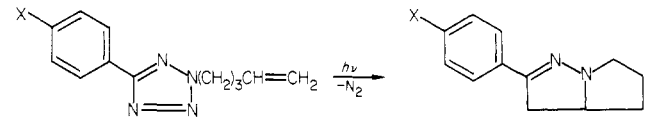
$$1/\Phi_p = [(k_d + k_r)/k_r][1 + (k_2[O]/k_1)] \quad (1)$$

where k_d represents the nonradiative decay of excited tetrazole, k_r is the rate of formation of nitrile imine, and Φ_p is the quantum yield of product formation.

The observation that the cyclization of the nitrile imine derived from tetrazole **5a** proceeds at a faster rate (6.3 times) than that of the dipole derived from **2** is unexceptional.[29] This is to be expected since nitrile imine cycloadditions are HO-controlled processes when electron-deficient olefins are used. What is surprising, however, is that the rate difference is so small. The rate constants associated with bimolecular cycloadditions of nitrile imines usually range over many powers of 10.[25,26] Ordinary olefins react so sluggishly with nitrile imines that their bimolecular rate constants cannot be measured. Clearly, there has been a marked leveling of the rate profile associated with the above intramolecular cycloadditions. The larger entropy term associated with the intramolecular cycloaddition will tend to compress the rate scale. Perhaps this is the reason for the "leveling-effect", since the smaller the steric requirements of the transition state, the less sensitive the system is to disturbance.

One final point worth mentioning concerns the efficiency associated with the photolysis of a series of aryl-substituted tetrazoles **8a–8g**. The results that we have obtained in-

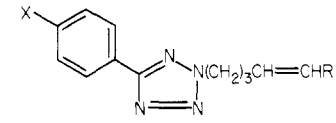
Chart III



8a, X = CH_3
8b, X = OCH_3
8c, X = $N(CH_3)_2$
8d, X = Cl
8e, X = CO_2CH_3
8f, X = CN
8g, X = NO_2

9

Table I. Time of Irradiation for Tetrazoles and Percent Yield of Photoproduct



compd	X	R	irrad time, h	product yield, %	recov starting material, %
2	H	H	2	90	
5a	H	CO_2CH_3	2	88	
5b	H	CN	2	71	
5c	H	$COCH_3$	2	48	
8a	CH_3	H	2	88	
8b	OCH_3	H	2	76	
8c	$N(CH_3)_2$	H	2	65	
8d	Cl	H	2	87	
8e	CO_2CH_3	H	20	17	51
8f	CN	H	20	28	33
8g	NO_2	H	20		79

(28) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 119.

(29) The slope/intercept values for tetrazole **2** (k_2/k_1 = 3.2) and **5a** (k_2/k_1 = 0.57) allows for the determination of the relative rate difference for internal cycloaddition of these two tetrazoles (i.e., k(**5a**)/k(**2**) = 6.3).

dicate that electron-donating substituents on the aromatic ring do not effect the course of the photolysis. In all cases, the expected bicyclopyrazoline **9** was formed in high yield (Chart III). The presence of electron-withdrawing substituents on the para position (i.e., nitro, cyano, and methoxycarbonyl), on the other hand, significantly retards the cycloaddition reaction (see Table I). The reason for this is not so obvious. One possibility is that the lone pair of nonbonding electrons on the nitrogen (N-2) atom is delocalized onto the aromatic ring when an electron-withdrawing substituent is present. Not only will this affect the energy of the n–π^* transition but it could also influence the ease with which nitrogen is extruded. Clearly, additional work is needed before this interesting substituent effect can be fully understood.

Experimental Section

General Procedure for the Synthesis of 5-(Para-substituted phenyl)tetrazoles (1a–9). These compounds were prepared by the procedure of Finnegan.[31] Physical constants of **1a–d,f,g** are in good agreement with the values reported in the literature.[31–33] 5-[*p*-(Methoxycarbonyl)phenyl]tetrazole (**1e**): colorless needles; mp 236–237 ° dec; recrystallized from MeOH–H_2O (82% yield); mass spectrum, *m/e* 204 (M^+), 176 (base), 145; NMR (Me_2SO-d_6) δ 3.95 (3 H, s), 7.60 (1 H, br s), 8.23 (4 H, s); IR (Nujol) 1705 cm^{-1}. Anal. Calcd for $C_9H_8N_4O_2$: C, 52.94; H, 13.95; N, 27.44. Found: C, 53.01; H, 13.90; N, 27.55.

General Procedure for the Synthesis of 2-(4-Pentenyl)-5-(para-substituted phenyl)tetrazoles (2, 8a–g). A 240-mg (5.0 mmol) sample of sodium hydride (50%) was washed with petroleum ether and was then suspended in 1.0 mL of anhydrous dimethylformamide. To the above stirred suspension at 0 °C was added dropwise a 5.0-mmol sample of tetrazole (**1**) in 10 mL of anhydrous dimethylformamide and the mixture was stirred for 30 min at room temperature. After the addition of 745 mg (5.0 mmol) of 5-bromo-1-pentene, the reaction mixture was stirred at room temperature for 20 h, poured into 50 mL of ice–water, and extracted with benzene. The extracts were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a thick-layer plate with methylene chloride. The product was purified by distillation under reduced pressure or by recrystallization.

2-(4-Pentenyl)-5-(*p*-methylphenyl)tetrazole (8a): colorless oil; bp 170 °C (bath temperature) (2 mmHg); 887 mg (78%); UV (EtOH) λ_{max} 282 nm (ϵ 368), 274 (ϵ 950), 247 (ϵ 17 800); NMR ($CDCl_3$) δ 2.04–2.24 (4 H, m), 2.37 (3 H, s), 4.57 (2 H, t, J = 7 Hz), 5.03 (1 H, d, J = 10 Hz), 5.05 (1 H, d, 17 Hz), 5.77 (1 H, ddt, J = 17, 10, 7 Hz), 7.25 (2 H, d, J = 9 Hz), 8.03 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 228 (M^+), 200 (base). Anal. Calcd for $C_{13}H_{16}N_4$: C, 68.39; H, 7.06; N, 24.54. Found: C, 68.58; H, 6.94; N, 24.43.

2-(4-Pentenyl)-5-(*p*-methoxyphenyl)tetrazole (8b): colorless oil; bp 180 °C (bath temperature) (2 mmHg); 1030 mg (84%); UV (EtOH) λ_{max} 256 nm (ϵ 18 800); NMR ($CDCl_3$) δ 2.04–2.22 (4 H, m), 3.80 (3 H, s), 4.58 (2 H, t, J = 7 Hz), 5.02 (1 H, d, 10 Hz), 5.04 (1 H, d, J = 17 Hz), 5.77 (1 H, ddt, J = 17, 10, 7 Hz), 6.96 (2 H, d, J = 9 Hz), 8.06 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 244 (M^+), 216 (base). Anal. Calcd for $C_{13}H_{16}N_4$: C, 63.91; H, 6.60; N, 22.94. Found: C, 63.66; H, 6.41; N, 22.68.

2-(4-Pentenyl)-5-[*p*-(dimethylamino)phenyl]tetrazole (8c): colorless oil; bp 200 °C (bath temperature) (2 mmHg); 670 mg (52%); UV (EtOH) λ_{max} 294 nm (ϵ 24 100); NMR ($CDCl_3$) δ 2.04–2.32 (4 H, m), 2.98 (6 H, s), 4.58 (2 H, t, J = 7 Hz), 5.02 (1 H, d, 10 Hz), 5.06 (1 H, d, J = 17 Hz), 5.78 (1 H, ddt, J = 17, 10, 7 Hz), 6.73 (2 H, d, J = 9 Hz), 8.00 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 257 (M^+), 229 (base). Anal. Calcd for $C_{14}H_{19}N_5$: C, 65.34; H, 7.44; N, 27.22. Found: C, 65.11; H, 7.30; N, 27.05.

2-(4-Pentenyl)-5-(*p*-chlorophenyl)tetrazole (8d): colorless oil; bp 160 °C (bath temperature) (2 mmHg); 925 mg (75%); UV (EtOH) λ_{max} 285 (ϵ 532), 244 (ϵ 18 200); NMR ($CDCl_3$) δ 2.03–2.18 (4 H, m), 4.63 (2 H, t, J = 7 Hz), 5.04 (1 H, d, J = 10 Hz), 5.06 (1 H, d, J = 17 Hz), 5.79 (1 H, ddt, J = 17.10, Hz), 7.42 (2 H, d, J = 9 Hz), 8.06 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 250, 248 (M^+), 222, 220 (base). Anal. Calcd for $C_{12}H_{13}ClN_4$: C, 57.95; H, 5.27; Cl, 14.25; N, 22.53. Found: C, 57.99; H, 5.38; Cl, 14.11; N, 22.43.

2-(4-Pentenyl)-5-[*p*-(methoxycarbonyl)phenyl]tetrazole (8e): colorless needles; mp 54–55 °C, recrystallized from ethyl ether–*n*-hexane; 857 mg (63%); IR (Nujol) 1710 cm^{-1}; UV (EtOH) λ_{max} 258 nm (ϵ 22 300); NMR ($CDCl_3$) δ 2.08–2.24 (4 H, m), 3.95 (3 H, s), 4.68 (2 H, t, J = 7 Hz), 5.06 (1 H, d, J = 10 Hz), 5.08 (1 H, d, 17 Hz), 5.80 (1 H, ddt, J= 17, 10, 7 Hz), 8.12 (2 H, d, J = 9 Hz), 8.24 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 272 (M^+), 244 (base). Anal. Calcd for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.84; H, 5.95; N, 20.45.

2-(4-Pentenyl)-5-(*p*-cyanophenyl)tetrazole (8f): colorless needles; mp 55–56 °C, recrystallized from ethyl ether–*n*-hexane; 639 mg (53%); IR (Nujol) 2220 cm^{-1}; UV (EtOH) λ_{max} 291 nm (ϵ 1290), 256 (ϵ 23 200); NMR ($CDCl_3$) δ 2.12–2.28 (4 H, m), 4.70 (2 H, t, J = 7 Hz), 5.08 (1 H, d, J = 10 Hz), 5.10 (1 H, d, J = 17 Hz), 5.82 (1 H, ddt, J = 17, 10, 7 Hz), 7.75 (2 H, d, J = 9 Hz), 8.26 (2 H, d, J = 9 Hz); mass spectrum, *m/e* 239 (M^+), 211 (base). Anal. Calcd for $C_{13}H_{13}N_4$: C, 65.25; H, 5.48; N, 29.27. Found: C, 65.42; H, 5.44; N, 29.34.

2-(4-Pentenyl)-5-(*p*-nitrophenyl)tetrazole (8g): colorless needles; mp 42–44 °C, recrystallized from ethyl ether–*n*-hexane; 730 mg (56%); UV (EtOH) λ_{max} (ϵ 15 700); NMR ($CDCl_3$) δ 2.12–2.28 (4 H, m), 4.72 (2 H, t, J = 7 Hz), 5.08 (1 H, d, J = 10 Hz), 5.11 (1 H, d, J = 17 Hz), 5.83 (1 H, ddt, J = 17, 10, 7 Hz), 8.32 (4 H, s); mass spectrum, *m/e* 259 (M^+), 231 (base). Anal. Calcd for $C_{12}H_{13}N_5O_2$: C, 55.59; H, 5.05; N, 27.02. Found: C, 55.69; H, 5.08; N, 27.07.

2-(4-Hydroxybutyl)-5-phenyltetrazole. A 1.42-g (0.03 mol) sample of sodium hydride (50%) was washed once with petroleum ether and was then suspended in 6 mL of anhydrous dimethylformamide. To the above stirred suspension cooled at 0 °C was added dropwise 4.38 g (0.03 mol) of 5-phenyltetrazole in 20 mL of anhydrous dimethylformamide. The mixture was stirred for an additional 30 min at room temperature. After the addition of 3.3 g (0.03 mol) of 4-chloro-1-butanol, the reaction mixture was stirred at 80 °C for 15 h and was then poured into 200 mL of ice–water and extracted with benzene. The extracts were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed, using 400 g of aluminum oxide and eluting with 1200 mL of CH_2Cl_2 and then with 500 mL of CH_2Cl_2–AcOEt (5:1). Removal of the solvent left an oil, which was distilled: bp 198–202 °C (1 mmHg); 2.85 g of colorless oil (44%); NMR ($CDCl_3$) δ 1.52 (2 H, quintet, J = 7 Hz), 2.10 (2 H, quintet, J = 7 Hz), 3.57 (2 H, t, J = 7 Hz), 4.61 (2 H, t, J = 7 Hz), 7.30–7.55 (3 H, m), 7.95–8.20 (2 H, m); mass spectrum, *m/e* 218 (M^+), 190 (base), 104, 77. Anal. Calcd for $C_{11}H_{14}N_4O$: C, 60.53; H, 6.47; N, 25.67. Found: C, 60.32; H, 6.65; N, 25.43.

4-(5-Phenyltetrazol-2-yl)butyraldehyde (6). To a stirred suspension of 4.31 g (0.02 mol) of pyridinium chlorochromate (Corey's reagent)[34] mL of anhydrous methylene chloride was added dropwise 2.85 g (0.013 mol) of the above alcohol in 10 mL of anhydrous methylene chloride. After the mixture was stirred for 2 h, 100 mL of anhydrous ether was added and the supernatant was decanted from the blackgum. The insoluble residue was washed throughly with four 50-mL portions of anhydrous ether. The combined organic solution was passed through a short pad

(30) All melting points are uncorrected. All irradiations were carried out with a 100-W Ushio high-pressure mercury arc. Mass spectra were determined with a JMS-D 300 mass spectrometer. The proton magnetic resonance spectra were determined with a Hitachi R-20B spectrometer and signals were reported in parts per million from tetramethylsilane as an internal standard. The ultraviolet absorption spectra were measured with a Shimazu UV-200 spectrometer. The infrared absorption spectra were determined on a JASCO IRA-1 infrared spectrophotometer. Preparative thick-layer chromatography was performed with use of silica gel (Wakogel B-5F).

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of silica gel (10 g). Removal of the solvent followed by distillation of the residue gave 1.40 g (50%) of aldehyde **6**: bp 160–165 °C (1 mmHg); IR (neat) 1715 cm^{-1}; NMR ($CDCl_3$) δ 2.1–2.7 (4 H, m), 4.65 (2 H, t, J = 7 Hz), 7.3–7.6 (3 H, m), 8.0–8.2 (2 H, m), 9.77 (1 H, s); mass spectrum, m/e 216 (M^+), 188 (base), 104. Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.06; H, 5.59; N, 25.91. Found: C, 60.98; H, 5.54; N, 25.83.

Methyl (*E*)-6-(5-Phenyltetrazol-2-yl)-2-hexenoate (5a). To a stirred solution containing 1.47 g (4.4 mmol) of [(carbomethoxy)methylene]triphenylphosphorane[35] in 10 mL of methylene chloride was added 860 mg (4.0 mmol) of aldehyde **6**. The mixture was stirred at room temperature for 16 h. Removal of the solvent under reduced pressure left an oil, which was chromatographed on a thick layer plate with methylene chloride as the eluent. The major fraction obtained was purified by distillation under reduced pressure: bp 240 °C (bath temperature) (1 mmHg); 947 mg (87%); IR (neat) 1715 cm^{-1}; UV (EtOH) λ_{max} 281 (ϵ 531), 274 (ϵ 858), 238 (ϵ 17 500); NMR ($CDCl_3$) δ 2.05–2.50 (4 H, m), 3.68 (3 H, s), 4.40–4.80 (2 H, m), 5.82 (1 H, d, J = 16 Hz), 6.65–7.20 (1 H, m), 7.30–7.60 (3 H, m), 7.95–8.25 (2 H, m); mass spectrum, m/e 272 (M^+), 244 (base), 185, 104. Anal. Calcd for $C_{14}H_{16}N_4O_2$: C, 61.72; H, 5.92; N, 20.58. Found: C, 61.63; H, 5.95; N, 20.59.

(*E*)-6-(5-Phenyltetrazol-2-yl)-2-hexenenitrile (5b). This material was prepared by the same procedure used with **5a**. Thus, a sample containing 860 mg (4.0 mmol) of **6** and 1.32 g (4.4 mmol) of (cyanomethylene)triphenylphosphorane[36] gave 807 mg (83%) of **5b**: bp 230 °C (bath temperature)(1 mmHg); IR (neat) 2220 cm^{-1}; UV (EtOH) λ_{max} 281 (ϵ 553), 274 (ϵ 878), 238 (ϵ 16 800); NMR ($CDCl_3$) δ 2.05–2.80 (4 H, m), 4.50–4.80 (2 H, m), 5.40 (1 H, d, J = 16 Hz), 6.22–6.95 (1 H, m), 7.30–7.60 (3 H, m); mass spectrum, m/e 239 (M^+), 211 (base), 104. Anal. Calcd for $C_{13}H_{13}N_5$: C, 65.25; H, 5.48; N, 29.27. Found: C, 65.23; H, 5.61; N, 29.05.

Methyl 3-(5-Phenyltetrazol-2-yl)propyl Ketone (5c). This material was prepared in a similar fashion. Thus, 860 mg (4.0 mmol) of **6** and 1.40 g (4.4 mmol) of acetonylidenetriphenylphosphorane[37] gave 910 mg (89%) of **5c**: bp 230 °C (bath temperature)(1 mmHg); IR (neat) 1680 cm^{-1}; UV (EtOH) λ_{max} 281 (ϵ 622), 274 (ϵ 930), 230 (ϵ 21 200); NMR ($CDCl_3$) δ 2.00–2.50 (7 H, m), 4.55–4.83 (2 H, m), 6.13 (1 H, d, J = 16 Hz), 6.55–7.05 (1 H, m), 7.30–7.65 (3 H, m), 7.95–8.30 (2 H, m), 7.95–8.30 (2 H, m); mass spectrum, m/e 256 (M^+), 288 (base), 185, 104. Anal. Calcd for $C_{14}H_{16}N_4O$: C, 65.66; H, 6.29; N, 21.86. Found: C, 65.66; H, 6.28; N, 21.73.

General Procedure for the Photolysis of 2, 5, and 8. A solution containing tetrazole **2**, **5**, or **8** (1.0 mmol) in 250 mL of benzene was irradiated for 2 h or 20 h (**8e–g**) with a 100-W high-pressure mercury arc through a Vycor filter sleeve under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was purified by thick-layer PLC chromatography, using a CH_2Cl_2–AcOEt mixture (5:1, v/v; 2:1, v/v, for **8c**) followed by distillation or recrystallization.

3-Phenyl-4-(methoxycarbonyl)pyrrolidino[1,2-*b*]-2-pyrazoline (7a): colorless oil; bp 200 °C (bath temperature)(1 mmHg); 216 mg (88%); IR (neat) 1730 cm^{-1}; UV (EtOH) λ_{max} 291 nm (ϵ 11 900), 220 (ϵ 9370); NMR ($CDCl_3$) δ 1.25–2.25 (4 H, m), 3.00–3.85 (2 H, m), 3.65 (3 H, s), 4.15 (2 H, br s), 7.15–7.45 (3 H, m), 7.55–7.85 (2 H, m); mass spectrum, m/e 244 (M^+), 185 (base), 157. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.92; H, 6.62; N, 11.41.

3-Phenyl-4-cyanopyrrolidino[1,2-*b*]-2-pyrazoline (7b): colorless oil; bp 220 °C (bath temperature)(1 mmHg); 150 mg (71%); IR (neat) 2230 cm^{-1}; UV (EtOH) λ_{max} 292 nm (ϵ 11 700), 219 (ϵ 10 200); NMr ($CDCl_3$) δ 1.20–2.30 (4 H, m), 2.95–4.47 (4 H, m), 7.20–7.95 (5 H, m); mass spectrum, m/e 211 (M^+, base), 185, 157. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 74.08; H, 6.20; N, 19.84.

3-Phenyl-4-acetylpyrrolidino[1,2-*b*]-2-pyrazoline (7c): colorless oil; bp 180 °C (bath temperature)(1 mmHg); 110 mg (48%); IR (neat) 1705 cm^{-1}; UV (EtOH) λ_{max} 290 nm (ϵ 9750), 221 (ϵ 10 600); NMR ($CDCl_3$) δ 1.25–2.35 (4 H, m), 2.12 (3 H, s), 3.15–4.25 (4 H, m), 7.20–7.90 (5 H, m); mass spectrum, m/e 228 (M^+, base), 185, 157. Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.62; H, 7.03; N, 12.38.

3-(*p*-Tolyl)pyrrolidino[1,2-*b*]-2-pyrazoline (9a): colorless oil: bp 150 °C (bath temperature)(2 mmHg); 177 mg (88%); UV (EtOH) λ_{max} 293 nm (ϵ 11 200), 226 (ϵ 7900); NMR ($CDCl_3$) δ 1.20–2.10 (4 H, m), 2.35 (3 H, s), 3.05–4.20 (5 H, m), 7.17 (2 H, d, J = 9 Hz), 7.60 (2 H, d, J = 9 Hz); mass spectrum, m/e 200 (M^+, base), 172, 145. Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.31; H, 8.00; N, 13.91.

3-(*p*-Methoxyphenyl)pyrrolidino[1,2-*b*]-2-pyrazoline (9b): colorless oil; bp 150 °C (bath temperature)(1 mmHg); 164 mg (76%); UV (EtOH) λ_{max} 287 nm (ϵ 15 900), 200 (ϵ 8130); NMR ($CDCl_3$) δ 1.20–2.10 (4 H, m), 3.82 (3 H, s), 3.00–4.20 (5 H, m), 6.88 (2 H, d, J = 9 Hz), 7.63 (2 H, d, J = 9 Hz); mass spectrum, m/e 216 (M^+, base), 188, 161. Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.16; H, 7.65; N, 12.65.

3-[*p*-(Dimethylamino)phenyl]pyrrolidino[1,2-*b*]-2-pyrazoline (9c): colorless oil; bp 145 °C (bath temperature)(1 mmHg); 149 mg (65%); UV (EtoH) λ_{max} 3.17 nm (ϵ 24 900), 222 (ϵ 8480); NMR ($CDCl_3$) δ 1.20–2.10 (4 H, m), 2.96 (6 H, s), 3.00–4.15 (5 H, m), 6.68 (2 H, d, J = 9 Hz), 7.57 (2 H, d, J = 9 Hz); mass spectrum, m/e 229 (M^+, base), 215, 200, 174, 146. Anal. Calcd for $C_{14}H_{19}N_3$: C, 73.32; H, 8.35; N, 18.33. Found: C, 73.31; H, 8.45; N, 18.32.

3-(*p*-Chlorophenyl)pyrrolidino[1,2-*b*]-2-pyrazoline (9d): colorless oil; bp 140 °C (bath temperature)(2 mmHg); 191 mg (87%); UV (EtOH) λ_{max} 285 nm (ϵ 4600), 221 (ϵ 10 400); NMR ($CDCl_3$) δ 1.20–2.15 (4, H, m), 3.00–4.15 (5 H, m), 7.35 (2 H, d, J = 9 Hz), 7.63 (2 H, d, J = 9 Hz); mass spectrum, m/e 222, 220 (M^+, base), 194, 192, 167, 165. Anal. Calcd for $C_{12}H_{13}ClN_2$: C, 65.31; H, 5.94; Cl, 16.06; N, 12.69. Found: C, 65.41; H, 5.90; Cl, 15.86; N, 12.53.

3-[*p*-(Methoxycarbonyl)phenyl]pyrrolidino[1,2-*b*]-2-pyrazoline (9e): colorless solid; mp 74–46 °C, sublimed at 90 °C (1 mmHg); 42 mg (17%); IR (Nujol) 1710 cm^{-1}; UV (EtOH) λ_{max} 317 nm (ϵ 13 600), 232 (ϵ 10 300); NMR ($CDCl_3$) δ 1.20–2.15 (4 H, m), 3.92 (3 H, s), 3.05–4.20 (5 H, m), 7.73 (2 H, d, J = 9 Hz), 8.07 (2 H, d, J = 9 Hz); mass spectrum, m/e 244 (M^+, base) 216, 189. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.99; H, 6.69; N, 11.24.

3-(*p*-Cyanophenyl)pyrrolidino[1,2-*b*]-2-pyrazoline (9f): colorless needles; mp 96–98 °C, recrystallized from methylchloride–ethyl ether; 60 mg (28%); IR (Nujol) 2220 cm^{-1}; UV (EtOH) λ_{max} 321 nm (ϵ 13 800), 231 (ϵ 11 600); NMR ($CDCl_3$) δ 1.15–2.15 (4 H, m), 3.00–4.25 (5 H, m), 7.62 (2 H, d, J = 9 Hz), 7.80 (2 H, d, J = 9 Hz); mass spectrum, m/e 211 (M^+, base), 183, 156. Anal. Calcd for $C_{13}H_{13}N_2$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.84; H, 6.24; N, 19.73.

Acknowledgment. A.P. acknowledges the National Cancer Institute for generous support of this research.

Registry No. 1, 18039-42-4; **1e**, 82544-82-9; **2**, 65103-33-5; **4**, 65103-38-0; **5a**, 82544-83-0; **5b**, 82544-84-1; **5c**, 73670-69-6; **6**, 82544-85-2; **7a**, 73670-78-7; **7b**, 73670-79-8; **7c**, 73670-80-1; **8a**, 73670-62-9; **8b**, 73670-61-8; **8c**, 73670-60-7; **8d**, 73670-63-0; **8e**, 73670-64-1; **8f**, 73670-65-2; **8g**, 73670-66-3; **9a**, 73670-72-1; **9b**, 73670-71-0; **9c**, 73670-70-9; **9d**, 73670-73-2; **9e**, 82544-86-3; **9f**, 73670-75-4; 5-bromo-1-pentene, 1119-51-3; 2-(4-hydroxybutyl)-5-phenyltetrazole, 82544-87-4; 4-chloro-1-butanol, 928-51-8; [(carbomethoxy)methylene]triphenylphosphorane, 2605-67-6; (cyanomethylene)triphenylphosphorane, 16640-68-9; (acetonylidene)triphenylphosphorane, 1439-36-7.

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