1,3-Dipolar Cycloaddition Reaction of Vinyl Azides with Enamines. Synthesis of Vinyltriazolines and Vinyltriazoles

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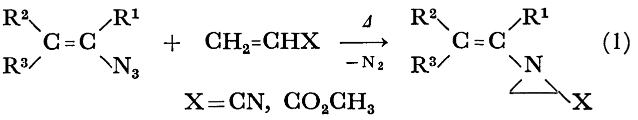
Reaction of α- and β-azidostyrene with enamines gave vinyltriazolines regioselectively in moderate yields. 1-Pyrrolidinyl enamines reacted with α-azidostyrene more readily than piperidino or morpholino enamines. β-Azidostyrene was as reactive as azidobenzene while α-azidostyrene was much less reactive. Vinyltriazolines formed from enamines of ketones were deaminated to yield the corresponding vinyltriazoles.

Although considerable amount of studies on vinyl azides has been cumulated[1] since Hassner and Fowler developed the general synthetic method for vinyl azides in 1968,[2] only few examples have hitherto been reported with regard to their reaction as 1,3-dipole: one with methyl propiolate or dimethyl acetylenedicarboxylate (DMAD)[3] and the other with 2-oxoalkylidenetriphenylphosphoranes.[4]

Extensive studies have been cumulated on 1,3-dipolar cycloaddition reaction of aryl azides.[5–10] Sustman and Trill have reported the correlation of the rate of cycloaddition reaction between azidobenzene and various dipolarophiles with the first ionization potentials (IP) of dipolarophiles, rationalizing the dual property of azides,[9] which are known to react readily with both electron-deficient dipolarophiles, such as DMAD, and electron-rich dipolarophiles, such as enamines. Munk and co-workers have examined the reaction of substituted azidobenzenes and enamines and demonstrated the electrophilic character of the azido group towards enamines.[10]

Previously we reported the thermal reaction of vinyl azides with electron-deficient olefins to give vinylaziridines with evolution of nitrogen (Eq. 1),[11] but

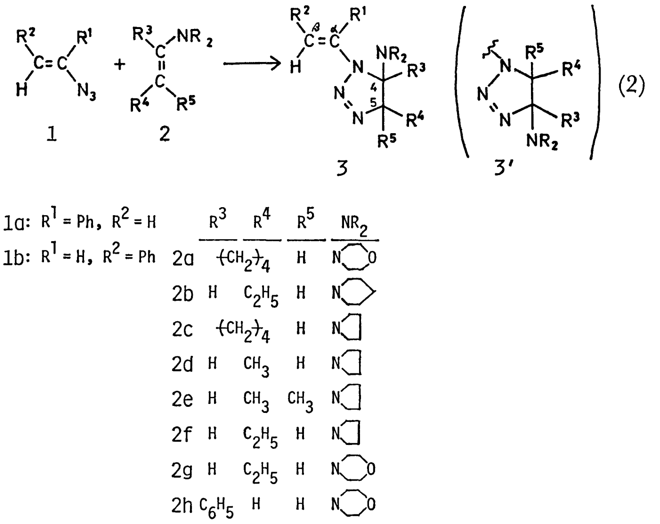

$$\begin{matrix}R^2\\R^3\end{matrix}{>}C{=}C{<}\begin{matrix}R^1\\N_3\end{matrix} + CH_2{=}CHX \xrightarrow[-N_2]{\Delta} \begin{matrix}R^2\\R^3\end{matrix}{>}C{=}C{<}\begin{matrix}R^1\\N{<}\triangle_X\end{matrix} \qquad (1)$$
$X{=}CN,\ CO_2CH_3$

1,3-dipolar adduct of azide was not isolated. In the course of our further study concerning the 1,3-dipolar reaction of vinyl azides, we have examined the reaction with electron rich olefins, and here we wish to report their reaction with enamines.

Results and Discussion

Reaction of Azidostyrenes with Enamines. Azidostyrenes (**1**) and enamines (**2**) were caused to react at 0 °C without solvent until **1** was completely consumed. The results are summarized in Table 1.

The only product isolated proved to be a 1:1 adduct of azidostyrene and enamine. The structure of the adduct was determined from the spectroscopic inspection. In the case of Entry 4, for example, the two singlet signals at δ 4.85 and 5.36, together with the signals at δ 7.1—7.5, in ^{1}H NMR indicated the existence of 1-phenylvinyl group, the multiplet signals at δ 1.5—1.8 and 2.2—2.6 corresponded to 1-pyrrolidinyl group, and other signals (see experimental) demonstrated the existence of $CH_3\overset{|}{C}H\overset{|}{C}H$-moiety.



These results suggested the formation of 1,2,3-triazoline ring by the 1,3-dipolar cycloaddition between the azido group of **1a** and the carbon-carbon double bond of the enamine (**2d**). This was further supported by the ^{13}C NMR spectra of the adducts (Table 2): the two signals at δ 75.9 and 74.2 (both a doublet at off-resonance decoupling condition) corresponded to the two tertiary sp^3 carbons of the triazoline ring neighboring with the nitrogen atom.

The cycloadducts obtained are either 4-amino-Δ^1-1,2,3-triazolines (**3**) or their regioisomers, 5-amino derivatives (**3′**). The mass spectra of the triazolines **3d** and **3f** are summarized in Table 3. Molecular ions (M$^+$) were not detected in both cases. The peaks at *m/e* 228 and 242 corresponded to M-28 fragments (loss of nitrogen) of **3d** and **3f**, respectively. The peaks at *m/e* 199 corresponded to the further loss of C_2H_5 and C_3H_7 from **3d** and **3f**, respectively. This was rationalized from the β-cleavage of **3** (Fig. 1). The alternative structure **3′** was excluded by the existence of *m/e* 199 fragment becauce the cleavages expected from **3′** would not give this fragment.

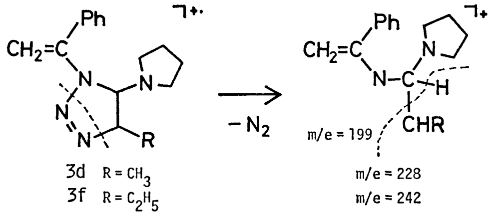
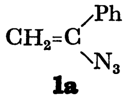
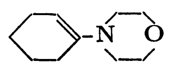
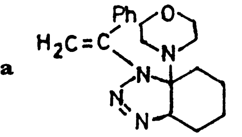
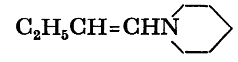
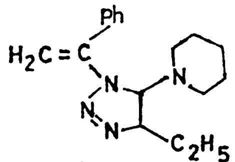
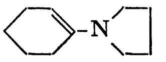
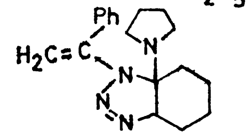
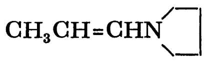
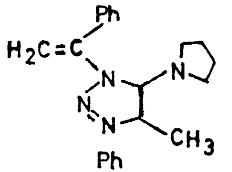
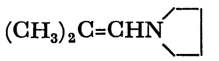
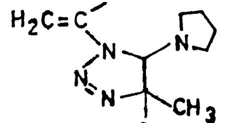
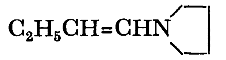
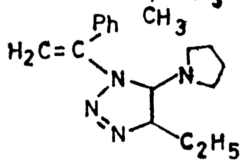
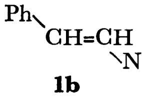
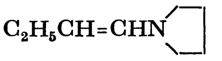
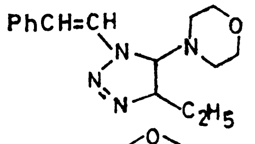
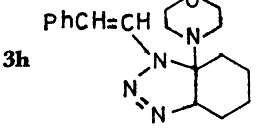
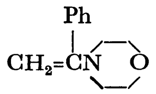
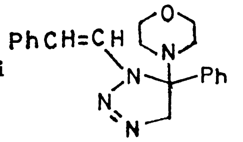
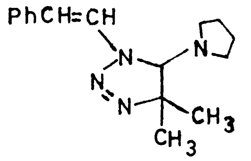


Fig. 1. β-Cleavage to give *m/e* = 199 fragment.

TABLE 1. REACTION OF VINYL AZIDES WITH ENAMINES

Entry	Azide	Enamine	Molar ratio (Enamine/Azide)	Reaction time/d[a]	Products	Isolated yield/%
1	 $CH_2{=}C(Ph)N_3$ **1a**	 **2a**	1.5	90[b]	**3a** 	40
2	**1a**	 **2b**	1.42	12	**3b** 	86
3	**1a**	 **2c**	1.06	2	**3c** 	66
4	**1a**	 **2d**	2.31	5	**3d** 	64
5	**1a**	 **2e**	1.0	1	**3e** 	95
6	**1a**	 **2f**	1.13	3	**3f** 	86
7	 $PhCH{=}CHN_3$ **1b**	 **2g**	1.03	8[b]	**3g** 	54[d]
8	**1b**	**2a**	1.03	3	**3h** 	62
9	**1b**	 **2h**	1.02	21	**3i** 	63
10	**1b**	**2e**	1.57	2[c]	**3j** 	78

a) Reaction time until **1** was completely consumed, unless otherwise noted. b) Some of **1** still remained unchanged. c) Carried out in diethyl ether to avoid uncontrolled reaction. d) Based on consumed **1b**.

The formation of the 4-amino isomers (**3**) is reasonable since the 1,3-dipolar cycloaddition reaction of azides and enamines unexceptionally gives 4-amino-Δ^1-1,2,3-triazolines.[6-10]

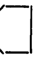
The reaction time necessary for the complete consumption of azides could be a measure of relative reactivity of azides and enamines qualitatively (Table 1). The reactivity of enamines towards azides decreased in the order of 1-pyrrolidinyl>piperidino>morpholino (Entry 1—6), which was the same order

Table 2. ^{13}C NMR spectral data of vinyltriazolines (**3**)[a] (δ)

	C-β[b]	C-α[b]	C-4[b]	C-5[b]	Others[c]
3a	97.5 t	144.8 s	80.3 s	73.4 d	15.8 t, 18.1 t, 21.0 t, 24.5 t
3b	98.9 t	146.5 s	79.0 d	78.7 d	10.4 q, 26.2 t
3c	100.5 t	145.6 s	79.8 s	75.3 d	17.7 t, 19.2 t, 25.2 t, 25.8 t
3d	100.2 t	146.2 s	75.9 d	74.2 d	16.9 q
3e	99.7 t	146.8 s	79.5 d	77.4 s	18.7 q, 24.8 q
3f	99.4 t	146.4 s	80.1 d	74.1 d	10.3 q, 24.9 t
3g	107.9 d	125.9 d	77.5 d	77.4 d	9.6 q, 25.4 t
3h	109.3 d	123.9 d	79.2 s	75.7 d	15.4 t, 17.2 t, 23.5 t
3i	110.3 d	125.2 d	84.1 s	76.7 t	
3j	108.3 d	125.8 d	78.5 d	78.2 s	18.5 q, 25.3 q

a) Splitting patterns obtained by off-resonance decoupling. b) See Eq. 2. c) Signals corresponding to phenyl and amino groups were omitted.

Table 3. Fragmentation of vinyltriazoline by electron impact (mass spectral data of **3d** and **3f**)

3d (R=CH_3)			**3f** (R=C_2H_5)		
m/e	Intensity/%	Fragment[a]	*m/e*	Intensity/%	Fragment[a]
228	13.6	(M)$-N_2$	242	5.6	(M)$-N_2$
			227	19.4	(242)$-CH_3$
213	12.0	(228)$-CH_3$	213	7.9	(242)$-C_2H_5$
199	10.3	(228)$-C_2H_5$	199	12.0	(242)$-C_3H_7$
159	43.9	(228)$-$N 	173	35.2	(242)$-$N 
111	81.4	C_3H_5N 	125	29.1	C_4H_7N 
98	Base	C_2H_4N 	112	Base	C_3H_6N 

a) See Fig. 1.

as was found for the reaction of azidobenzene with enamines.[8,10] From Entries 1 and 8, it seems that β-azidostyrene (**1b**) is much more reactive than the α-isomer (**1a**); indeed, the reactivity of **1b** towards enamines is comparable with that of azidobenzene.[6]

Frontier Molecular Orbital Treatment. Generally, in the case of 1,3-dipolar cycloaddition of electron-rich olefins, the interaction between LUMO of a dipole and HOMO of a dipolarophile is important.[9,12] The lower the energy of LUMO of azide is, and the higher the energy of HOMO of enamine is, the interaction between these orbitals would be greater so that the reaction should proceed faster.

The order of reactivity of enamines towards α-azidostyrene (**1a**), as was described, corresponded to the energy of HOMO of enamines, which is lowered in the order of 1-pyrrolidinyl, piperidino, and morpholino as was estimated by photoelectron spectra (Fig. 2).

The difference in reactivity between the azides (**1a**, **b**) would be rationalized by the difference in the energies of LUMO of **1a** and **1b**. β-Azidostyrene (**1b**), of which the phenyl group is more extensively conjugated with the azido group, would have a lower energy of LUMO than α-azidostyrene (**1a**). The energies of these orbitals estimated by CNDO/2 calculation supported the above trends (Fig. 2). The lower energy of LUMO of **1b** corresponds to its higher reactivity towards enamines.

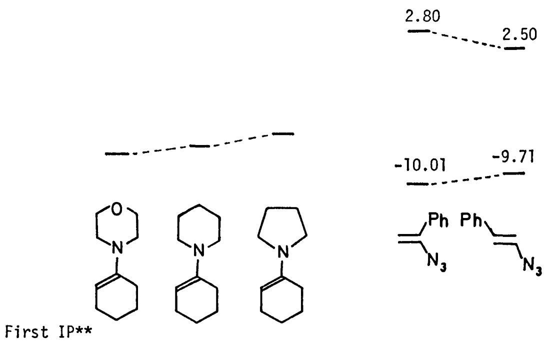


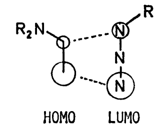
Fig. 2. Energies of frontier orbitals of azides* and enamines.

* Orbital energies (eV) of organic azides were estimated from CNDO/2 calculation.[14] ** Obtained from photoelectron spectroscopy by Domelsmith and Houk.[15]

A possible steric effect, interaction between phenyl group and the amino group in the transition state of the reaction, can also be responsible for the lower reactivity of **1a**.

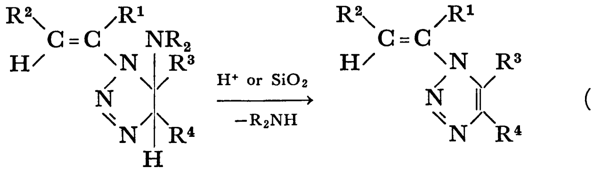
It is known that the reaction between azides and enamines is dipole-LUMO-controlled reaction, and the orientation should therefore be as shown in Table. 4,

Table 4. Coefficients of LUMO of azides estimated with CNDO/2 calculation[14]



R =	H[13]	Ph	CH_2=CH	CH_2=CPh	PhCH=CH
	0.37	0.263	0.298	0.169	0.165
	0.76	0.495	0.557	0.425	0.462

which is in fact the case.[12] We attempted the calculation of the coefficients of LUMO of various vinyl azides; it seems that the introduction of a vinyl group to the azide does not alter the relative magnitude of the coefficients of LUMO of simple azides such as hydrazoic acid. These results are consistent with the regioselective formation of the 4-aminotriazolines (**3**).



3 **4** (3)

*Systhesis of Triazoles (**4**) by Deamination of the Aminotriazolines (**3**).* It is known that the 4-alkyl (or aryl)-4-amino-Δ^1-1,2,3-triazolines are easily deaminated by treatment with acid to give the corresponding 1*H*-1,2,3-triazoles.[6] When the aminotriazolines (**3a**,**c**,**h**,**i**) formed from the enamines of ketones were treated with acetic acid at room temperature or eluted through silica-gel column, deamination readily occurred, giving the corresponding triazoles (**4**) in 40—62% yields (Table 5).

Thus, a simple and useful method for the synthesis of vinyltriazoles from vinyl azides, under mild conditions, with high regioselectivity, and in moderate yields, was achieved. The vinyltriazoles like **4** were otherwise difficult to prepare. A known method with α-azidostyrene and 2-oxoalkylidinetriphenylphosphoranes requires much longer time (about a month) and affords the vinyltriazoles in no more than 54% yields.[4]

Experimental

General. Spectroscopic data were obtained with following apparatus: JEOL JNM-MH100 NMR Spectrometer, VARIAN FT-80A FT-NMR System, JEOL JNM-FX90Q FT-NMR System, JASCO DS-403G Grating Infrared Spectrophotometer, HITACHI EPS-3T Recording Spectrophotometer, and HITACHI RMU-6MG Mass Spectrometer.

α- and β-Azidostyrenes were prepared according to Hassner's method.[2] Enamines of ketones were prepared according to the method described in Organic Syntheses.[16] Enamines of aldehydes were prepared according to Mannich's method.[17]

Melting points were determined with microscopic apparatus and uncorrected.

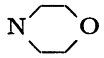
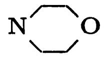
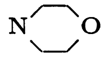
Reaction of Azidostyrenes with Enamines. The azide (**1**) and the enamine (**2**) were mixed and allowed to stand at 0 °C without solvent until the azide was completely consumed, unless otherwise described. The products were purified with alumina column chromatography (eluting with hexane–dichloromethane (1:1)) and/or with recrystallization from an appropriate solvent.[18]

*3a,4,5,6,7,7a-Hexahydro-7a-morpholino-1-(1-phenylvinyl)-1H-1,2,3-benzotriazole (**3a**):* The mixture of 4.4 g (30 mmol) of α-azidostyrene (**1a**) and 7.5 g (45 mmol) of 4-(1-cyclohexenyl)morpholine (**2a**) was allowed to stand at 0 °C for 90 d. Hexane (10 ml) was added and the precipitates formed were collected and recrystallized from ethanol to give 3.4 g of **3a** as colorless crystals (40% yield); mp 110—111.5 °C (dec); IR (KBr) 1615 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.1—2.3 (8H, m), 2.43 (4H, m), 4.61 (1H, t, *J*=5.5 Hz), 4.72 (1H, s), 5.58 (1H, s), and 7.44 (5H, m); UV_{max} (methanol) 246 nm (ε 7700). Found: C, 69.19; H, 8.01; N, 18.13%. Calcd for $C_{18}H_{24}N_4O$: C, 69.20; H, 7.74; N, 17.93%.

*5-Ethyl-3-(1-phenylvinyl)-4-piperidino-Δ^1-1,2,3-triazoline (**3b**):* The mixture of 2.0 g (14 mmol) of **1a** and 2.8 g (20 mmol) of 1-(1-butenyl)piperidine (**2b**) was allowed to stand at 0 °C for 12 d. Then the mixture was eluted through alumina column to give 3.9 g of **3b** as faint yellow oil (86% yield): IR (neat) 1615 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.06 (3H, t, *J*=7 Hz), 1.4—1.6 (6H, m), 1.7 (2H, q, *J*=7 Hz), 2.2—2.6 (4H, m), 4.2—4.4 (2H, m), 4.86 (1H, s), 5.42 (1H, s), and 7.5 (5H, m); UV_{max} (methanol) 240 nm (ε 13000).

*3a,4,5,6,7,7a-Hexahydro-1-(1-phenylvinyl)-7a-(1-pyrrolidinyl)-1H-1,2,3-benzotriazole (**3c**):* The mixture of 1.0 g (6.9 mmol) of **1a** and 1.1 g (7.3 mmol) of 1-(1-cyclohexenyl)pyrrolidine (**2c**) was allowed to stand at 0 °C for 2 d. Then the product was eluted through alumina column to give 1.35 g of **3c** as yellowish viscous oil (66% yield): IR (neat)

Table 5. Deamination of aminotriazolines (**3**) to triazoles (**4**)

Reactant	R^1	R^2	R^3	R^4	NR_2	Products	Method[a]	Yield/%
3a	Ph	H	$(CH_2)_4$			**4a**	B	40
3c	Ph	H	$(CH_2)_4$			**4a**	A	46
							B	40
3h	H	Ph	$(CH_2)_4$			**4b**	A	54
3i	H	Ph	Ph	H		**4c**	A	62

a) A: Treatment with acetic acid. B: Elution through silica-gel column.

1610 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.6—2.4 (8H, m), 2.6 (4H, m), 4.42 (1H, t, J=6 Hz), 4.89 (1H, s), 5.56 (1H, s), and 7.44 (5H, m); UV$_{\max}$ (methanol) 243 nm (ε 11000).

*5-Methyl-3-(1-phenylvinyl)-4-(1-pyrrolidinyl)-Δ^1-1,2,3-triazoline (**3d**)*: The mixture of 2.4 g (16 mmol) of **1a** and 4.2 g (37 mmol) of 1-(1-propenyl)pyrrolidine (**2d**) was allowed to stand at 0 °C for 5 d to give 2.73 g of **3d** as colorless crystals after chromatographic separation (64% yield). Recrystallization from methanol gave the analytically pure sample: mp 67—68.5 °C; IR (KBr) 1620 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.27 (3H, d, J=7 Hz), 1.5—1.8 (4H, m), 2.2—2.6 (4H, m), 4.27 (1H, dd, J=7 and 2.5 Hz), 4.48 (1H, d, J=2.5 Hz), 4.85 (1H, s), 5.36 (1H, s), and 7.42 (5H, m); UV$_{\max}$ (methanol) 240 nm (ε 16000). Found: C, 70.00; H, 8.06; N, 21.68%. Calcd for $C_{15}H_{20}N_4$: C, 70.28; H, 7.86; N, 21.86%.

*5,5-Dimethyl-3-(1-phenylvinyl)-4-(1-pyrrolidinyl)-Δ^1-1,2,3-triazoline (**3e**)*: The mixture of 3.25 g (22.4 mmol) of **1a** and 2.8 g (22.4 mmol) of 1-(2-methyl-1-propenyl)pyrrolidine (**2e**) was allowed to stand at 0 °C for 1 d to give 5.79 g of **3e** as faint yellow oil after chromatographic separation (95% yield): IR (neat) 1615 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.24 (3H, s), 1.40 (3H, s), 1.5—1.8 (4H, m), 2.2—2.6 (4H, m), 4.32 (1H, s), 4.81 (1H, s), 5.40 (1H, s), and 7.1—7.5 (5H, m); UV$_{\max}$ (methanol) 237 nm (ε 13000).

*5-Ethyl-3-(1-phenylvinyl)-4-(1-pyrrolidinyl)-Δ^1-1,2,3-triazoline (**3f**)*: The mixture of 4.7 g (32 mmol) of **1a** and 4.5 g (36 mmol) of 1-(1-butenyl)pyrrolidine (**2f**) was allowed to stand at 0 °C for 1 d. Purification with column chromatography gave 7.5 g of **3f** as colorless crystals (86% yield). Recrystallization from methanol gave the analytically pure sample: mp 31.5—32.5 °C; IR (KBr) 1615 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.08 (3H, t, J=8 Hz), 1.7 (6H, m), 2.5 (4H, m), 4.32 (1H, dt, J=2.5 and 6.5 Hz), 4.63 (1H, d, J=2.5 Hz), 4.95 (1H, s), 5.47 (1H, s), and 7.57 (5H, m); UV$_{\max}$ (methanol) 237 nm (ε 13000). Found: C, 70.94; H, 8.41; N, 20.50%. Calcd for $C_{16}H_{22}N_4$: C, 71.08; H, 8.20; N, 20.72%.

*5-Ethyl-4-morpholino-3-styryl-Δ^1-1,2,3-triazoline (**3g**)*: The mixture of 1.0 g (6.9 mmol) of β-azidostyrene (**1b**) and 1.0 g (7.1 mmol) of 4-(1-butenyl)morpholine (**2g**) was allowed to stand at 0 °C for 8 d. The resulting solid was recrystallized from methanol to give 0.37 g of **3g** as colorless crystals. Condensation of the filtrate followed by chromatographic separation of the residue gave additional 0.47 g of **3g** and 0.17 g of **1b** (17% recovery). Total yield of **3g** was 54% based on the consumed **1b**. Repeated recrystallization from methanol gave the analytically pure sample: mp 87—88 °C; IR (KBr) 1640 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.01 (3H, t, J=8 Hz), 1.4—2.0 (2H, m), 2.41 (4H, m), 3.67 (4H, m), 4.16 (2H, m), 6.22 (1H, d, J=14 Hz), 7.30 (5H, m), and 7.62 (1H, d, J=14 Hz); UV$_{\max}$ (methanol) 224 (ε 8600), 278 (ε 12000), and 317 nm (ε 18000). Found: C, 66.88; H, 7.82; N, 19.77%. Calcd for $C_{16}H_{22}N_4O$: C, 67.11; H, 7.84; N, 19.56%.

*3a,4,5,6,7,7a-Hexahydro-7a-morpholino-1-styryl-1*H*-1,2,3-benzotriazole (**3h**)*: The mixture of 1.0 g (6.9 mmol) of **1b** and 1.2 g (7.2 mmol) of **2a** was allowed to stand at 0 °C for 3 d. The resulting solid was recrystallized from methanol to give 1.33 g of **3h** as colorless crystals (62% yield): mp 111—112 °C; IR (KBr) 1640 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.0—1.2 (8H, m), 2.45 (4H, m), 3.7 (4H, m), 4.51 (1H, t, J=5 Hz), 6.71 (1H, d, J=15 Hz), 7.09 (1H, d, J=15 Hz), and 7.2—7.6 (5H, m); UV$_{\max}$ (methanol) 223 (ε 7300), 280 (ε 10000), and 309 nm (ε 9700). Found: C, 69.01; H, 8.00; N, 18.00%. Calcd for $C_{18}H_{24}N_4O$: C, 69.20; H, 7.74; N, 17.93%.

*4-Morpholino-4-phenyl-3-styryl-Δ^1-1,2,3-triazoline (**3i**)*: The mixture of 1.2 g (8.3 mmol) of **1b** and 1.6 g (8.5 mmol) of 4-(1-phenylvinyl)morpholine (**2h**) was allowed to stand at 0 °C for 21 d. The resulting solid was recrystallized from methanol to give 1.6 g (58% yield) of **3i** as colorless crystals. Condensation of the filtrate gave 0.13 g (5%) of second crop of **3i**. Repeated recrystallization gave the analytically pure sample: mp 125.5 °C (dec); IR (KBr) 1635 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 2.6 (4H, m), 3.7 (4H, m), 4.12 (1H, d, J=18 Hz), 4.62 (1H, d, J=18 Hz), 6.76 (1H, d, J=15 Hz), 7.02 (1H, d, J=15 Hz), and 7.1—7.7 (10H, m); UV$_{\max}$ (methanol) 273 (ε 11000) and 323 nm (ε 14000). Found: C, 71.80; H, 6.68; N, 16.53%. Calcd for $C_{20}H_{22}N_4$: C, 71.83; H, 6.63; N, 16.75%.

*5,5-Dimethyl-4-(1-pyrrolidinyl)-3-styryl-Δ^1-1,2,3-triazoline (**3j**)*: The solution of 4.35 g (30 mmol) of **1b** and 6.0 g (47 mmol) of 1-(2-methyl-1-propenyl)pyrrolidine (**2e**) in 50 ml of diethyl ether was stirred for 2 d.[19] After removal of the ether, the residue was purified with the alumina column to give 6.3 g (78% yield) of **3j** as slightly yellow oil: IR (neat) 1640 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.15 (3H, s), 1.43 (3H, s), 1.73 (4H, m), 2.7 (4H, m), 4.66 (1H, s), 6.07 (1H, d, J=15 Hz), 7.4 (5H, m), and 7.77 (1H, d, J=15 Hz).

Deamination of Aminotriazolines. *4,5,6,7-Tetrahydro-1-(1-phenylvinyl)-1*H*-1,2,3-benzotriazole (**4a**)*: The solution of 75 mg (0.25 mmol) of the triazoline **3c** in 1 ml of acetic acid was allowed to stand overnight at room temperature. Then the solution was poured into 50 ml of dichloromethane and the solution was washed with 5% aqueous sodium carbonate, water, and aqueous sodium chloride (saturated), successively. After drying the solution over anhydrous magnesium sulfate, the solvent was removed and the residue was purified with silica-gel column chromatography (eluting with dichloromethane) to give 26 mg (46% yield) of **4a** as faint yellow oil: IR (neat) 1640 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.5—2.0 (4H, m), 2.0—2.5 (2H, m), 2.5—2.9 (2H, m), 5.43 (1H, s), 5.68 (1H, s), and 7.0—7.4 (5H, m); UV$_{\max}$ (methanol) 241 nm (ε 11000). Picrate of **4a** was formed from **4a** with excess picric acid in ethanol and recrystallized from ethanol: mp 154—155 °C. Found: C, 52.99; H, 3.83; N, 18.71%. Calcd for $C_{20}H_{18}N_6O_4$: C, 52.87; H, 3.99; N, 18.49%.

Elution of **3c** or **3a** through silica-gel column with dichloromethane also afforded **4a** in 40% yield.

*4,5,6,7-Tetrahydro-1-styryl-1*H*-1,2,3-benzotriazole (**4b**)*: To the solution of 173 mg (0.55 mmol) of the triazoline **3h** in 3 ml of dichloromethane was added 0.5 ml of acetic acid and the solution was stirred for 3 d at room temperature. Then 40 ml of dichloromethane was added to the solution and it was washed with 5% aqueous sodium carbonate, water, and aqueous sodium chloride (saturated), successively, and dried over anhydrous magnesium sulfate. Removal of the solvent followed by chromatographic separation of the residue eluting through silica-gel column with diethyl ether gave 67 mg (54% yield) of **4b** as colorless crystals. Recrystallization from methanol gave the analytically pure sample: mp 117—117.5 °C; IR (KBr) 1650 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 1.8 (4H, m), 2.7 (4H, m), and 7.2—7.8 (7H, m); UV$_{\max}$ (methanol) 217 (sh, ε 13000) and 285 nm (ε 20000). Found: C, 74.35; H, 6.56; N, 18.60%. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65%.

*5-Phenyl-1-styryl-1*H*-1,2,3-triazole (**4c**)*: To the solution of 0.5 g (1.5 mmol) of the triazoline **3i** in 20 ml of dichloromethane was added 3 ml of acetic acid and stirred for 3 d at room temperature. The similar workup to the case of **4b** followed by recrystallization of the residue from methanol gave 229 mg (62% yield) of **4c** as colorless crystals:

mp 144.5—145.5 °C; IR (KBr) 1650 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 7.3—7.9 (m) and 7.85 (s); UV_{max} (methanol) 281 nm (ε 20000). Found: C, 77.97; H, 5.25; N, 17.16%. Calcd for $C_{16}H_{13}N_3$: C, 77.91; H, 5.30; N, 16.99%.

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18) The oily triazolines (**3b**, **c**, **e**, **j**) did not crystallize, and the distillation *in vacuo* caused decomposition.

19) Diethyl ether was used as solvent to avoid uncontrolled reaction.