Photochemical Nitrogen Extrusion of 5-Amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles. Formation of Unusual Pyrroles[1)]

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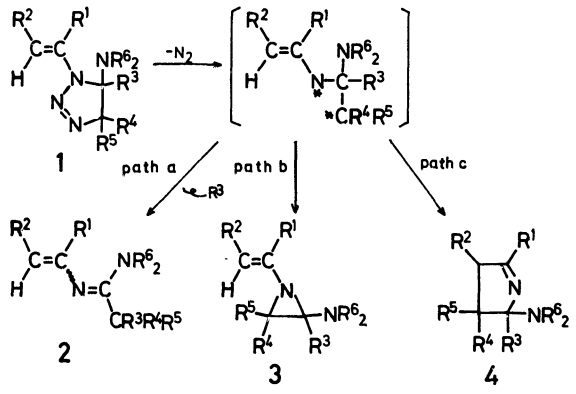
Photolysis of 4-alkyl-5-amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles gave not 3-alkylpyrroles, but unexpected 2-alkylpyrroles in 80—83% yields. 1-Vinylaziridines were assumed as a possible intermediate of this unusual pyrrole formation. In the photolysis of 7a-morpholino-1-styryl-3a,4,5,6,7,7a-hexahydro-1*H*-1,2,3-benzotriazole, however, nitrogen extrusion did not occur, but *trans-cis* isomerization took place.

Three reaction paths are expected in decomposition of 1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles (**1**) after elimination of nitrogen as shown in Scheme 1: The first is a 1,2-alkyl (or hydrogen) shift to N^2-vinylamidines (**2**) (path a), the second is a direct ring closure to form 1-vinylaziridines (**3**) (path b), and the third is formation of a C–C bond between C-4 of the dihydrotriazole and β-position of the vinyl group to give 1-pyrrolines (**4**) (path c). The N^2-vinylamidines have a 2-aza-1,3-butadiene skeleton, of which no general synthetic method has yet been developed, although its reactivity as a heterodiene has recently attracted attentions,[2-5)] and 1-vinylaziridines are only sparsely reported class of compounds.[6,7)]



Scheme 1. Expected paths for N_2 extrusion reactions of 1-vinyldihydrotriazoles (**1**).

Recently we reported that thermolysis[4)] or acid decomposition[8)] of **1** gave the corresponding N^2-vinylamidines (**2**) *via* path a, in accord with the general trends of 5-aminotriazolines.[9)] In order to elucidate the different reactivity of **1** in different conditions as well as the possibility of controlling reaction paths, we have examined the photo decomposition of the dihydrotriazoles (**1**).

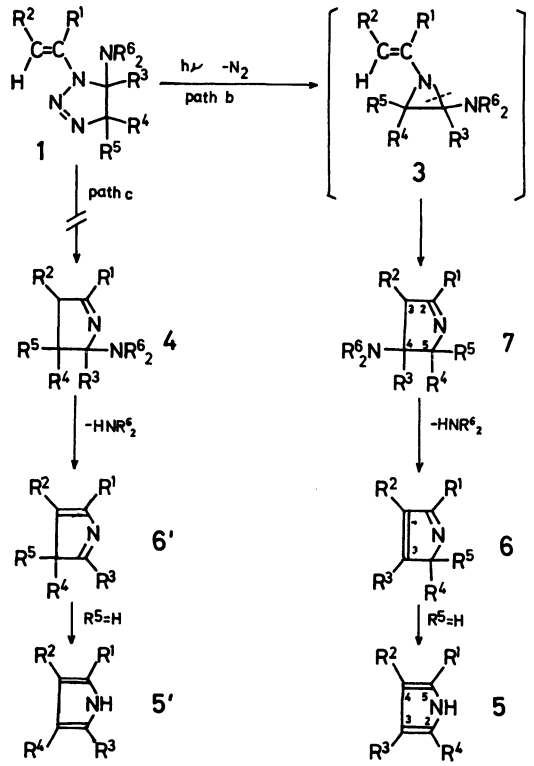
Results and Discussion

Formation of Unusual Pyrroles. The dihydrotriazoles (**1**) were irradiated in methanol at 0 °C with a 100 W high-pressure mercury lamp through a Pyrex filter. The results were shown in Table 1. In 45—140 min **1** was completely consumed, and chromatographic separation of the products gave the 1*H*-pyrroles (**5**) or 2*H*-pyrroles (**6**) in 19—83% yields (Runs 5—8). The pyrroles (**5** or **6**) were not detected among the initial products just after irradiation. This suggests that the pyrroles were formed by deamination during the chromatographic separation from certain initial products, possibly 1-pyrrolines (**7**).

Irradiation of **1a** was carried out in various solvents, but no significant difference was observed either in time required for complete consumption of **1a** or in yields of the pyrrole (**5a**) (Runs 1—5).

Table 1. Photolysis of 5-amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles (**1**)

Run	Reactant	R^1	R^2	R^3	R^4	R^5	NR^6_2	Solvent	Irradiation time / min	Product (Yield/%)
1	**1a**	Ph	H	H	CH_3	H	N⟨ ⟩	*cyclo*-C_6H_{12}	60	**5a** (73)
2	**1a**							CH_2Cl_2	75	**5a** (83)
3	**1a**							Et_2O	75	**5a** (56)
4	**1a**							CH_3CN	60	**5a** (81)
5	**1a**							CH_3OH	45	**5a** (83)
6	**1b**	Ph	H	$(CH_2)_4$		H	N⟨ ⟩	CH_3OH	140	**5b** (73)
7	**1c**	Ph	H	H	C_2H_5	H	N⟨ ⟩	CH_3OH	45	**5c** (80)
8	**1d**	H	Ph	Ph	H	H	N⟨ ⟩O	CH_3OH	60	**5d** (19)
9	**1e**	Ph	H	H	CH_3	CH_3	N⟨ ⟩	CH_3OH	60	**6e** (70)
10	**1f**	H	Ph	H	CH_3	CH_3	N⟨ ⟩	CH_3OH	45	**6f** (74)



Scheme 2. A tentative route for the photolysis of 1-vinyldihydrotriazoles (**1**).

Table 2. ^{13}C NMR data of pyrroles (**5**) and 1-pyrrolines (**7**) (δ in $CDCl_3$)

	C-2[a]	C-3[a]	C-4[a]	C-5[a]
5a	128.0 s	(106.2 d	108.0 d)[b]	130.7 s
5b	128.4 s	118.8 s	105.2 d	130.1 s
5c	136.1 s	(106.5 d	106.6 d)[b]	131.0 s
5d	117.6 d	123.3 s	123.3 s	117.6 d
7a	170.1 s	40.2 t	69.5 d	72.2 d
7b	171.5 s	38.5 t	65.6 s	72.8 d
7e	167.8 s	40.7 t	73.1 d	73.5 s

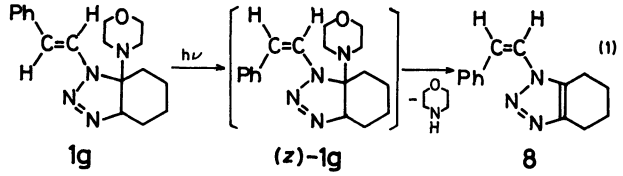
a) Numbers referred to Scheme 2. b) Or may be reversed.

The 2*H*-pyrroles (**6e, f**) formed from **1** (**e, f**) (Runs 9, 10) were the same as those formed by thermolysis of **1** (**e, f**).[4] Structure of 1*H*-pyrroles (**5**) was determined by spectral and analytical results. In the case of **5a**, for instance, existence of an N–H bonds was indicated by the absorption at 3290 cm^{-1} in its IR spectrum. In ^1H NMR, the singlet at δ 2.28 (3H) and the signals at δ 7.3—7.8 (5H) indicated the existence of methyl and phenyl groups, and it was unequivocally demonstrated by ^{13}C NMR that the product was a 2,5-disubstituted pyrrole (Table 2). The signals at δ 106.2 and 108.0 (both are doublet in off-resonance decoupling) are assigned to the methine carbons of the pyrrole ring by two reasons: a) The signal of 3- or 4-methine carbon of pyrrole appears at δ 108,[10] and b) alkyl and aryl substituents on a pyrrole ring have little influence upon chemical shift of its ring carbons which are not connected with these substituents.[11] Thus, it was demonstrated that the product was 2-methyl-5-phenylpyrrole (**5a**). ^{13}C NMR data pertinent to structural confirmation of other pyrroles (**5b—d**) were also listed in Table 2.

In the case of **1e**, 5,5-dimethyl-2-phenyl-4-(1-pyrrolidinyl)-1-pyrroline (**7e**) was isolated among the irradiation products. Mixtures of the 1-pyrrolines (**7a, b**) and the corresponding pyrroles (**5a, b**) could be afforded from the irradiation products of **1a, b**.

^{13}C NMR data corresponding to the pyrrolines (**7a, b, e**) were collected in Table 2. Both of two signals corresponding to C-4 and C-5 of the 1-pyrroline ring appeared at about δ 70, thus supporting the structure of 1-pyrrolines (**7**) in which C-4 and C-5 are connected with a pyrrolidine and a pyrroline nitrogen atoms, respectively. The 1-pyrrolines (**7**) were gradually deaminated into the corresponding 1*H*-pyrroles (**5**) or the 2*H*-pyrrole (**6e**) by repeated chromatographic separation or simply on standing at ambient temperature.

These results, together with the fact that no pyrroles were detected among the initial irradiation products, indicate that it was 1-pyrrolines (**7**) that were directly formed by photolysis of **1**.



trans-cis *Isomerization by Irradiation of 7a-Morpholino-1-styryl-3a,4,5,6,7,7a-hexahydro-1H-1,2,3-benzotriazole (**1g**).* Irradiation of 7a-morpholino-1-[(*E*)-styryl]-3a,4,5,6,7,7a-hexahydro-1*H*-1,2,3-benzotriazole (**1g**) took relatively long time (4.5 h) until **1g** was completely consumed, compared with other dihydrotriazoles (**1a—f**). Chromatographic separation of the products gave, accompanied by considerable amount of polymeric substances, 1-[(*Z*)-styryl]-4,5,6,7-tetrahydro-1*H*-1,2,3-benzotriazole (**8**) in 13% yield.

It is likely to consider that irradiation caused C=C bon isomerization into 1-(*Z*)-styryldihydrotriazole ((*Z*)-**1g**) and subsequent chromatographic separation resulted in deamination to give **8**. Although *trans-cis* photoisomerization of C=C bond is quite usual,[12] this is the only case, so far as examined, in which C=C bond isomerization of 1-vinyldihydrotriazole derivatives (**1**) actually occurred (and pyrrole ring (**5**) was not formed).

Mechanistic Consideration. It is unusual that photolysis of **1** gave 1-pyrrolines (**7**), 1*H*-pyrroles (**5**) or 2*H*-pyrroles (**6**) and that no pyrrolines (**4**), 1*H*-pyrroles (**5'**) or 3*H*-pyrroles (**6'**), which were expected from a direct 1,5-ring closure after loss of nitrogen from **1** (path c), were isolated from the irradiation products. The path including the 1-vinylaziridines (**3**) as an intermediate was tentatively assumed to rationalize most simply the formation of 1-pyrrolines (**7**) by photolysis of **1**: After removal of nitrogen, the 1-vinylaziridines (**3**) would be formed *via* path b. Then, selective ring cleavage of **3** at one of the C–N bonds under the reaction conditions followed by ring closure would give **7** as

depicted in Scheme 2. The amino group on the aziridine ring would play a crucial role for the selective C–N bond cleavage.

Photolysis of 4,5-dihydro-1*H*-1,2,3-triazoles is known to give aziridines.[13] Scheiner claims that this reaction proceeds *via* a singlet biradical intermediate.[14] Absence of solvent effect on consumption of **1** (Table 1, Runs 1—5) may indicate a similar radical path in the first stage of the present reaction.

De Poortere and De Schryver reported the formation of 2-dialkylamino-1-phenylaziridines by photolysis of 5-dialkylamino-1-phenyl-4,5-dihydro-1*H*-1,2,3-triazoles.[15] Some 1-vinylaziridines have been prepared from vinyl azides by thermal reactions.[7] Comparing the present results with the stability of 2-amino- and 1-vinylaziridines, if the present reaction really proceeds *via* the 1-vinylaziridines (**3**), the aziridines (**3**) must be unexpectedly unstable.

Both C–C and C–N bond fissions were reported for photolysis of aziridine derivatives, but C–C fission predominantly occurs.[16] The present reaction may add an example of photochemical selective C–N bond fission of an aziridine ring.

Experimental

General. Melting points were determined on a Mitamura Riken hot-stage melting point apparatus and were uncorrected. Infrared spectra were determined on JASCO DS-403G and A-202 grating infrared spectrophotometers. Nuclear magnetic resonance spectra were determined on JEOL MH-100, FX-90Q, Varian EM-390, and FT-80A spectrometers (splitting patterns in ^{13}C NMR data were obtained by off-resonance decoupling). Mass spectra were determined on a Hitachi RMU-6MG mass spectrometer.

4,5-Dihydro-1*H*-1,2,3-triazoles (**1**) were prepared according to the previously reported method.[17] Solvents were distilled under anhydrous conditions before use.

Photolysis of 5-Amino-1-vinyl-4,5-dihydro-1H-1,2,3-triazoles (1). General Procedure: The solution (150 ml) of **1** (3—3.7 mmol) in an appropriate solvent was irradiated with a high pressure mercury lamp (100 W) through a Pyrex filter at 0 °C under nitrogen atmosphere until **1** was completely consumed, as detected by high pressure liquid chromatography (through a Waters 7.8 mm × 30 mm μ-Bondapak C_{18} column eluting with methanol–water (7 : 3)). The solvent was removed *in vacuo* and the residue was separated with column chromatography.

When the neutral alumina (Akt. II) column eluting with hexane–ethyl acetate (2 : 1) was used, 5,5-dimethyl-4-(1-pyrrolidinyl)-1-pyrroline (**7e**) was isolated from the product from **1e**. Separation of the products from **1a**, **b** in a similar manner also gave the pyrrolines (**7a**, **b**), which were accompanied by the pyrroles (**5a**. **b**).

Photolysis of 1-(1-Phenylvinyl)-7a-(1-pyrrolidinyl)-3a,4,5,6,7,7a-hexahydro-1H-1,2,3-benzotriazole (1b): Photolysis of **1b** (1.30 g, 4.39 mmol) in methanol (150 ml) at 0 °C followed by chromatographic purification with neutral alumina (Woelm, Akt. II) eluting with diethyl ether gave 1.10 g of 80 : 20 mixture of 2-phenyl-3a-(1-pyrrolidinyl)-3a,4,5,6,7,7a-hexahydro-3*H*-indole (**7b**) and 2-phenyl-4,5,6,7-tetrahydroindole (**5b**). Elution of the mixture through a neutral alumina (Akt. I) column eluting with dichloromethane gave 480 mg (73% yield) of **5b** as colorless crystals.

2-Phenyl-4,5,6,7-tetrahydroindole (5b): Analytically pure sample was obtained by recrystallization from methanol: mp 105—106.5 °C; MS *m/e* 197 (M^+); IR (KBr) 3405 cm^{-1} (N–H); ^1H NMR ($CDCl_3$) δ 1.6—1.9 (4H, m), 2.3—2.7 (4H, m), 6.21 (1H, d, J=3 Hz), 7.0—7.4 (5H, m), and 7.75 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 22.8 (2C, t), 23.4 (t), 23.7 (t), 105.2 (d), 118.8 (s), 123.3 (*m*-2C, d), 125.4 (*p*-C, d), 128.4 (s), 128.7 (*o*-2C, d), 130.1 (s), and 133.2 (*ipso*-C, s).

Found: C, 85.08; H, 7.83; N, 7.12%. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10%.

2-Phenyl-3a-(1-pyrrolidinyl)-3a,4,5,6,7,7a-hexahydro-3H-indole (7b): MS *m/e* 268 (M^+); IR (neat) 1600 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.1—2.1 (12H, m), 2.4—2.8 (4H, m), 2.64 (1H, dd, J=17 and 1 Hz), 2.95 (1H, dd, J=17 and 1 Hz), 4.15 (1H, m), 7.3—7.7 (3H, m), and 7.8—8.1 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.8 (2C, t), 23.6 (2C, t), 28.4 (t), 31.6 (t), 38.5 (t), 47.1 (2C, t), 65.6 (s), 72.8 (d), 127.3 (*m*-2C, d), 128.3 (*o*-2C, d), 130.2 (*p*-C, d), 135.0 (*ipso*-C, s), and 171.5 (s, C=N).

2-Methyl-5-phenylpyrrole (5a): Sublimed at 80—90 °C/13 Pa; mp 92.5—94 °C; MS *m/e* 157 (M^+); IR (KBr) 3290 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 2.28 (3H, s), 5.95 (1H, m), 6.41 (1H, m), 7.3—7.8 (5H, m), and 8.4 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 13.2 (q), 106.2 (d), 108.0 (d), 123.4 (*m*-2C, d), 125.6 (*p*-C, d), 128.0 (s), 128.8 (*o*-2C, d), 130.7 (s), and 133.0 (*ipso*-C, s).

Found: C, 84.33; H, 7.05; N, 9.19%. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91%.

5-Methyl-2-phenyl-4-(1-pyrrolidinyl)-1-pyrroline (7a): Obtained by elution of the photolysis product from **1a** (220 mg, 0.86 mmol) through neutral alumina (Woelm Akt. II) with hexane–ethyl acetate (2 : 1) as a 65 : 35 mixture (150 mg) with **5a**. ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 23.3 (2C, t), 40.2 (t), 52.0 (2C, t), 69.5 (d), 72.2 (d), 127.5 (*m*-2C, d), 128.4 (*o*-2C, d), 130.4 (*p*-C, d), 134.5 (*ipso*-C, s), and 170.1 (s, C=N).

5,5-Dimethyl-2-phenyl-4-(1-pyrrolidinyl)-1-pyrroline (7e): MS *m/e* 242 (M^+); IR (KBr) 1615 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.22 (3H, s), 1.49 (3H, s), 1.8 (4H, m), 2.6 (5H, m), 3.0 (2H, d, J=8 Hz), 7.4 (3H, m), and 7.8 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 23.3 (2C, t), 29.4 (q), 40.7 (t), 54.2 (2C, t), 73.1 (s), 73.6 (d), 127.3 (*m*-2C, d), 128.2 (*o*-2C, d), 130.1 (*p*-C, d), 134.8 (*ipso*-C, s), 167.8 (s, C=N).

2-Ethyl-5-phenylpyrrole (5c): Sublimed at 45 °C/130 Pa; mp 47—48.5 °C; MS *m/e* 171 (M^+); IR (KBr) 3390 cm^{-1} (N–H); ^1H NMR ($CDCl_3$) δ 1.17 (3H, t, J=7.5 Hz), 2.42 (2H, q, J=7.5 Hz), 5.95 (1H, m), 6.40 (1H, m), 7.1—7.6 (5H, m), 7.9—8.3 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 21.4 (t), 106.5 (d), 106.6 (d), 123.8 (*m*-2C, d), 126.0 (*p*-C, d), 129.2 (*o*-2C, d), 131.0 (s), 133.4 (*ipso*-C, s), 136.1 (s).

Found: C, 84.46; H, 7.78; N, 8.04%. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18%.

3,4-Diphenylpyrrole (5d): Distilled with the Kugelrohr apparatus at 115 °C/13 Pa; mp 94.5—95.5 °C (lit, 99 °C[18]); MS *m/e* 219 (M^+); IR (KBr) 3420 cm^{-1} (N–H); ^1H NMR ($CDCl_3$) δ 6.79 (2H, d, J=3 Hz), 7.2—7.4 (10H, m), 8.18 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 117.6 (2C, d), 123.3 (2C, s), 125.7 (*p*-2C, d), 128.2 (*m*-4C, d), 128.5 (*o*-4C, d), and 136.0 (*ipso*-2C, s).

Found: C, 87.81; H, 5.75; N, 6.35%. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39%.

Photolysis of 7a-Morpholino-1-[(E)-styryl]-3a,4,5,6,7,7a-hexahydro-1H-1,2,3-benzotriazole (1g): Methanol (150 ml) solution of **1g** (824 mg, 2.64 mmol) was irradiated with a high pressure mercury lamp (100 W) through a Pyrex filter at 0 °C for 4.5 h, until **1g** was completely consumed. The methanol was removed *in vacuo* and the residue was separated with alumina column chromatography to give 1-[(*Z*)-styryl]-4,5,6,7-tetrahydro-1*H*-1,2,3-benzotriazole (**8**) in 13% yield (73 mg). Recrystallized from methanol: mp 91.5—92.5 °C; MS *m/e*

225 (M^+); IR (KBr) 1650 (C=C) and 940 cm^{-1} ($^{H}\!>\!C=C<^{H}$); ^1H NMR ($CDCl_3$) δ 1.5—1.8 (4H, m), 2.0—2.2 (2H, m), 2.6—2.8 (2H, m), 6.63 (1H, d, J=9.5 Hz), 6.85 (1H, d, J=9.5 Hz), 6.8—7.0 (2H, m), and 7.1—7.3 (3H, m); ^{13}C NMR ($CDCl_3$) δ 20.3 (t), 21.8 (t), 22.3 (t), 22.5 (t), 121.5 (d, PhCH=) 128.6 (d, *o* and *m*), 128.8 (d), 129.6 (d), 132.7 (s), 133.1 (s), 143.4 (s).

Found: C, 74.17; H, 6.60; N, 18.36%. Calcd for $C_{14}H_{15}N_3$; C, 74.64; H, 6.71; N, 18.65%.

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