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FORMATION OF UNUSUAL PYRROLES BY PHOTOLYSIS OF 1-VINYL-4,5-DIHYDRO-1*H*-1,2,3-TRIAZOLES

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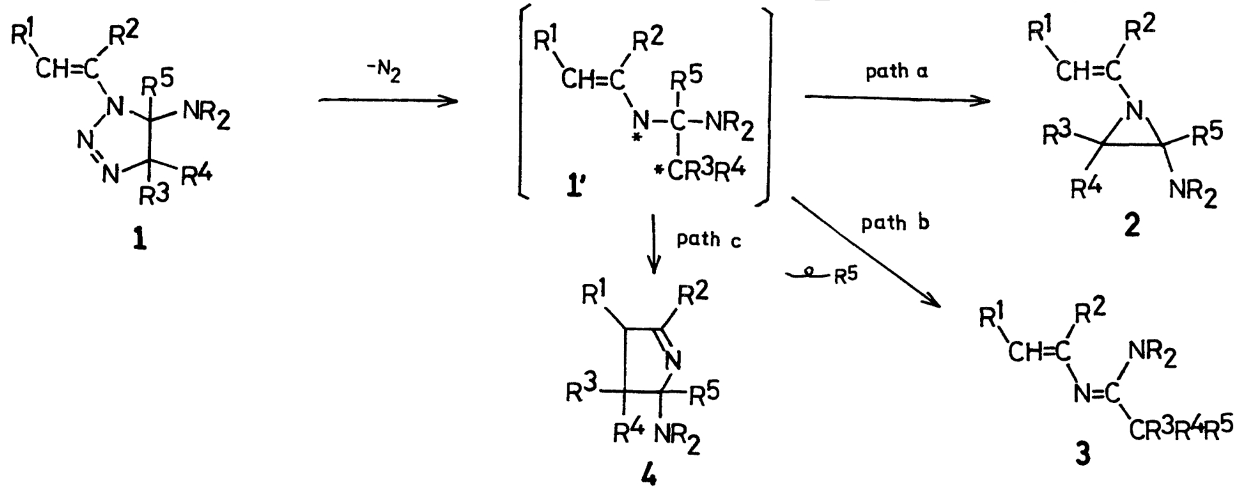
Photolysis of 4-alkyl-5-amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles gave not 3-alkylpyrroles but unexpected 2-alkylpyrroles in 80—83 % yields. Similarly 4,4-dimethyltriazole derivatives gave 2,2-dimethyl-2*H*-pyrroles in 70—74 % yields. 1-Vinylaziridines were assumed as a possible intermediate of this anomalous reaction.

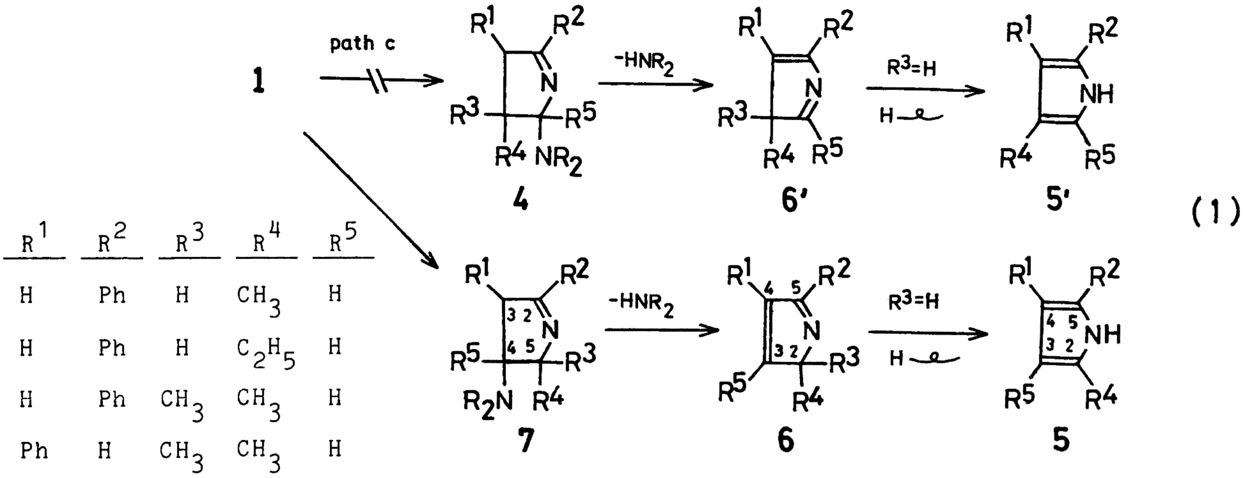
Three reaction paths are expected in the decomposition of 1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles (1) after the elimination of nitrogen as shown below: the first is direct ring closure to form 1-vinylaziridines (2) (path a), the second is 1,2-alkyl (hydrogen) shift to *N*-vinylimines (3) (path b), and 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).

Actually, thermolysis of 4,4-dimethyl-1-(1-phenylvinyl)-5-(1-pyrrolidinyl)-4,5-dihydro-1*H*-1,2,3-triazole (1c: $R^1=R^5=H$, $R^2=Ph$, $R^3=R^4=CH_3$, $NR_2=C_4H_8N$) in dimethyl sulfoxide is known to give the corresponding *N*^{2}-vinylamidine (3) via path



b,[1] in accord with the general trends of 5-aminotriazolines.[2]

In the present letter we wish to report the photolysis of the 1-vinyl-4,5-dihydro-1H-1,2,3-triazoles (1a–d),[3] which afforded unexpected pyrrolines and pyrroles.



(1)

	R^1	R^2	R^3	R^4	R^5
a	H	Ph	H	CH_3	H
b	H	Ph	H	C_2H_5	H
c	H	Ph	CH_3	CH_3	H
d	Ph	H	CH_3	CH_3	H

A solution of 4-methyl-1-(1-phenylvinyl)-5-(1-pyrrolidinyl)-4,5-dihydro-1H-1,2,3-triazole (1a) in methanol was irradiated with a 100 W high pressure mercury lamp through a pyrex vessel at 0 °C for 45 min, until 1a was completely consumed. After removal of the solvent in vacuo, the residue was purified through alumina column by eluting with dichloromethane to give 2-methyl-5-phenylpyrrole (5a) in 83 % yield. No 4-methyl-2-phenylpyrrole (5'a) was formed, strongly indicating that the product was not derived from direct 1,5-ring closure of possible intermediate 1' (path c).

The structure of the pyrrole 5a[4a] was determined by spectral and analytical results. In ^{1}H NMR, a singlet at δ 2.28 (3H) and the signals at δ 7.3–7.8 (5H)

Table 1. ^{13}C NMR data of the pyrroles 5, 6, and pyrrolines 7[a] (δ; $CDCl_3$).

Compound	C-2	C-3		C-4	C-5
5a	128.9	(106.2	and	108.0)	130.8
5b	136.1	(106.5	and	106.6)	131.0
6c	79.5	162.6		123.1	169.6
6d	80.3	153.6		138.1	161.3
7a[b]	170.1	40.2		72.2	69.5
7c	167.8	40.7		73.5	73.1

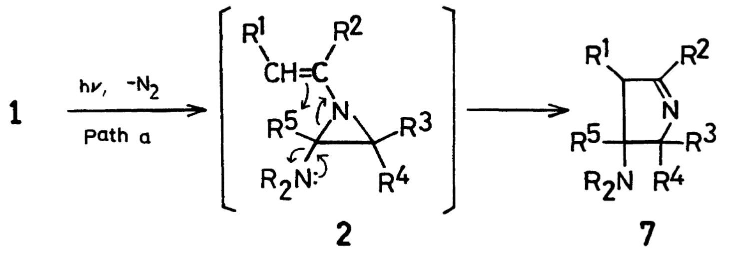
[a] Signals other than the pyrrole ring are omitted.

[b] Measured as a mixture with 5a.

indicated the existence of one methyl and one phenyl groups, and it was unequivocally demonstrated by ^{13}C NMR that the product was 2,5-disubstituted pyrrole (Table 1). There are two doublet signals[5)] at δ 106.2 and 108.0, corresponding to the methyne carbon of the pyrrole ring. These two signals are assigned to the β-carbon of the pyrrole ring by two reasons; a)the signal of β-carbon of pyrrole itself appears at δ 108,[6)] and b) alkyl and aryl substituents of pyrrole rings change little chemical shift values of its unsubstituted ring carbons.[7)] Thus, it was demonstrated that the product was 2-methyl-5-phenylpyrrole (5a).

Photolysis of the dihydrotriazoles (1b–d) were carried out in a similar manner as described above to give the corresponding pyrrole derivatives in 70–80 % yields. Spectral data of the products were compatible with the pyrrole (5b)[4b)] and 2H-pyrroles (6c,d).[2b)]

In the case of 1c, when the reaction product was purified through alumina column (Woelm N, 02084, Akt. II) by eluting with hexane-ethyl acetate (1:1), 5,5-dimethyl-2-phenyl-4-(1-pyrrolidinyl)-1-pyrroline (7c) was isolated. Its structure was determined by the spectroscopic results[8)] and from the fact that it was readily converted into 6c by elimination of pyrrolidine, although combustion analysis was impossible because of its lability. An attempt to isolate the pyrroline 7a from the reaction of 1a in a similar manner gave a 2:1 mixture of 7a and 5a. ^{13}C NMR spectra were measured as the mixture. The signals corresponding to the pyrroline were compatible with the structure 7a (Table 1). These results, together with the fact that no pyrroles were detected in the ^{1}H NMR of the crude products, suggests that 1-pyrrolines were formed by photolysis of 1, and they were converted into pyrroles (5,6) on elution through alumina column.



(2)

Formation of the 1-pyrroline 7 may be most simply rationalized by the following reaction path: after evolution of nitrogen, the vinylaziridine 2 would be formed via the path a (Scheme 1). Then, selective ring cleavage of 2 at one of the C-N bonds followed by ring closure would give 7 as depicted in Eq. 2.

Photolysis of 4,5-dihydro-1*H*-1,2,3-triazoles is known to give aziridines,[9)] but the above path contradicts the general trends in the ring cleavage of aziridines in two respects: first, both 1-vinylaziridines and 2-aminoaziridines are known to be rather stable under the similar reaction conditions,[9b,10] and second, thermal or photochemical ring cleavage of aziridines usually occurs at its C-C bond.[11]

Attempts to elucidate the actual path of the present unusual reaction as well as to detect the intermediate(s) are in progress.

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4) The new pyrroles gave satisfactory results in elemental analysis.
   a) 2-Methyl-5-phenylpyrrole (5a): Mp. 92.5—94 °C.
   b) 2-Ethyl-5-phenylpyrrole (5b): Mp. 47—48.5 °C.

5) Splitting patterns were obtained by off-resonance decoupling.

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8) 5,5-Dimethyl-2-phenyl-4-(1-pyrrolidinyl)-1-pyrroline (7c): MS: m/e 242 (M^+); IR (CH_2Cl_2): 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, m), 7.4 (3H, m), and 7.8 (2H, m).

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