Acid Decomposition of 5-Amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles. A Novel Formation of 1-Amino-2-azabutadienes

Masato M. Ito, Yujiro Nomura,* Yoshito Takeuchi, and Shuji Tomoda
Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
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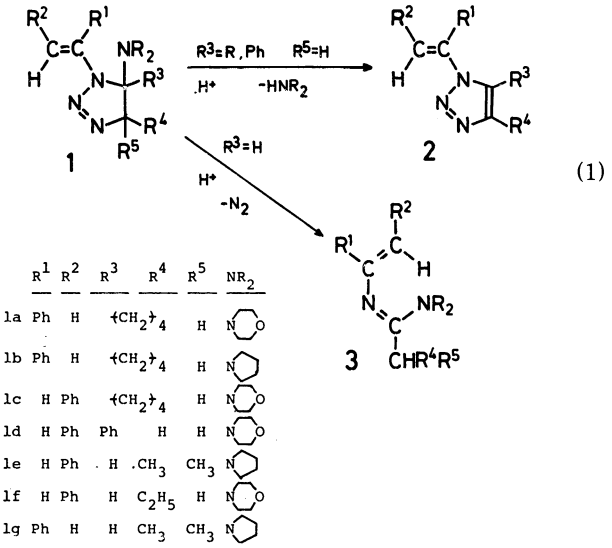
Synopsis. Acid decomposition of 4-alkyl-5-dialkylamino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles gave N^1,N^1-dialkyl-N^2-vinylalkanamidines, which have 2-aza-1,3-butadiene skeleton, in fair yields.

We have previously reported the deamination of 5-amino-1-vinyl-4,5-dihydro-1*H*-1,2,3-triazoles (**1a**—**d**, R^3 =alkyl or aryl) to give the corresponding triazoles (**2a**—**d**).[1] Dihydrotriazoles (**1e**—**g**, R^3=H), however, were not deaminated under similar conditions.



(1)

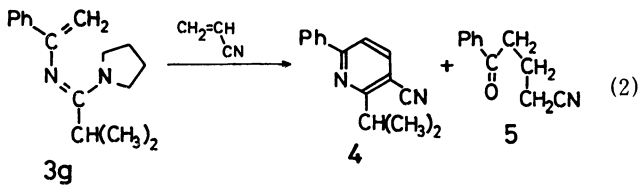
	R^1	R^2	R^3	R^4	R^5	NR_2
1a	Ph	H	$-(CH_2)_4-$		H	N⌒O
1b	Ph	H	$-(CH_2)_4-$		H	N⌒
1c	H	Ph	$-(CH_2)_4-$		H	N⌒O
1d	H	Ph	Ph		H	N⌒O
1e	H	Ph	H	CH_3	CH_3	N⌒
1f	H	Ph	H	C_2H_5	H	N⌒O
1g	Ph	H	H	CH_3	CH_3	N⌒

In the course of our study on nitrogen-extrusion reactions of the dihydrotriazoles (**1**), we noticed that acid decomposition of **1** (R^3=H) might give the corresponding N^2-vinylamidines (**3**) having a 2-aza-1,3 butadiene skeleton, so that the acid decomposition of **1e**—**g** was re-examined.

When the dihydrotriazoles (**1e**, **f**) were treated with 2 molar amounts of *p*-toluenesulfonic acid at 0 °C, **1** were decomposed with evolution of nitrogen to afford N^2-styrylamidines (**3e**, **f**) as slightly yellow oil in 46—64% yields.

Determination of the structure of **3e** and **3f** was based on the following spectral data. Mass spectra showed the existence of their molecular ion peak at *m/e* 242 and 258, respectively. In infrared spectra, no absorption corresponding to an N–H bond was observed, and absorption at about 1620 and 1600 cm^{-1} suggested the presence of C=C and C=N bonds. In ^1H and ^{13}C NMR, presence of a newly formed propyl or isopropyl group and an amidine carbon, in addition to a styryl and a 1-pyrrolidinyl or a morpholino group, was demonstrated by their characteristic signals (see Experimental).

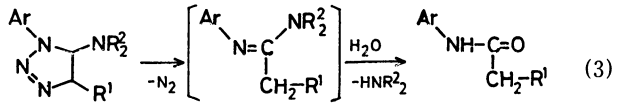
Treatment of the dihydrotriazole (**1g**) with *p*-toluenesulfonic acid was also shown to give the corresponding



(2)

N^2-vinylamidine (**3g**) according to the NMR spectra of the crude product,[2] but attempted isolation of **3g** failed due to its sensitivity to moisture. After the acid in the reaction mixture was removed by neutralization with anhydrous potassium carbonate, the crude product was treated with excess acrylonitrile. Chromatographic separation of the product gave 2-isopropyl-6-phenylnicotinonitrile (**4**) and 5-oxo-5-phenylpentanenitrile (**5**) in 13 and 11% yields, respectively.

Both **4** and **5** were formed by reaction of **3g** with acrylonitrile. It is known that the nicotinonitrile derivative (**4**) is formed by [4+2] cycloaddition reaction of **3g**, formed by thermolysis of **1g** with acrylonitrile, followed by deamination and air oxidation.[2] The oxo nitrile (**5**) would be formed by Michael addition of the enamine moiety of **3g** to acrylonitrile followed by hydrolysis. Thus the formation of **3g** by acid decomposition of **1g** was certified.



(3)

Fusco and coworkers reported that acid decomposition of 4-alkyl-1-aryl-5-dialkylamino-4,5-dihydro-1*H*-1,2,3-triazoles (**6**) gave *N*-arylamides (**7**).[3] They suggested the corresponding amidine (**7'**), which was not actually detected, as an intermediate (Eq. 3).

The present reaction demonstrated the formation of amidines by acid decomposition of 5-dialkylamino-4,5-dihydro-1*H*-1,2,3-triazoles, as well as gave a new route to 1-amino-2-aza-1,3-butadiene derivatives.

Experimental

General. Infrared spectra were determined on JASCO DS-403G and A-202 grating infrared spectrophotometers. Nuclear magnetic resonance spectra were determined on JEOL FX-90Q and Varian EM-390 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 from vinyl azides and enamines according to the previously reported method.[1] Solvents were distilled under anhydrous conditions before use.

*2-Methyl-1-(1-pyrrolidinyl)-*N*-styryl-1-propanimine (3e).* To a solution of 4,4-dimethyl-5-(1-pyrrolidinyl)-1-styryl-4,5-dihydro-1*H*-1,2,3-triazole (**1e**, 1.18 g, 4.4 mmol) in dry tetrahydrofuran (THF, 30 ml) was added a THF (30 ml) solution of anhydrous *p*-toluenesulfonic acid (1.57 g, 8.8 mmol) dropwise with stirring at 0 °C. Stirring was continued for further 30 min, until **1e** was completely consumed. Triethylamine (2 ml) was added and the solvent was removed *in vacuo*. After the residue was washed with diethyl ether (3×50 ml), it was alkalized with 5% aqueous solution (50 ml) of sodium hydrogencarbonate and was extracted with three portions (50 ml each) of diethyl ether. The ether layer was washed with saturated aqueous solution (50 ml) of sodium chloride and was dried over anhydrous magnesium sulfate. Removal of the ether *in vacuo* gave **3e** (243 mg, 46% yield) as slightly yellow oil: MS *m/e* 242 (M^+); IR (neat) 1620 and 1600 (C=C and C=N), and 940 cm^{-1} ($_H\rangle C=C\langle^H$); ^1H NMR ($CDCl_3$) δ 1.32 (6H, d, J=7 Hz), 1.83 (4H, m), 3.09 (1H, septet, J=7 Hz), 3.46 (4H, m), 6.14 (1H, d, J=13.5 Hz), 6.9—7.4 (5H, m), and 7.76 (1H, d, J=13.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.5 (q), 25.3 (t), 30.7 (d), 47.9 (t), 117.2 (d, PhCH=), 124.8 (d, *p*), 125.0 (d, *m*), 128.3 (d, *o*), 136.4 (d, =CHN), 139.3 (s, *ipso*), and 163.9 (s, C=N).

Found: *m/e* 242.1805. Calcd for $C_{16}H_{22}N_2$: M, 242.1783.

The amidine (**3e**) could not be induced to crystallize, and chromatographic separation caused decomposition; thus further purification was unsuccessful.

*1-Morpholino-*N*-styryl-1-butanimine (3f).* To a solution of 4-ethyl-5-morpholino-1-styryl-4,5-dihydro-1*H*-1,2,3-triazole (**1f**, 1.20 g, 4.20 mmol) in dry THF (40 ml) was added a THF (40 ml) solution of anhydrous *p*-toluenesulfonic acid (1.50 g, 8.40 mmol) dropwise with stirring at 0 °C. Stirring was continued for further 30 min, until **1f** was completely consumed. Then the solution was poured into 0.1 M hydrochloric acid (100 ml), and the solution was washed with diethyl ether (2×80 ml). After alkalization of the aqueous layer with excess sodium carbonate followed by extraction with diethyl ether (3×80 ml), the ether layer was washed with saturated aqueous solution (100 ml) of sodium chloride and was dried over anhydrous magnesium sulfate. Removal of the ether *in vacuo* gave **3f** (696 mg, 64% yield) as slightly yellow oil: MS *m/e* 258 (M^+); IR (neat) 1625 and 1600 (C=C and C=N), and 940 cm^{-1} ($_H\rangle C=C\langle^H$); ^1H NMR ($CDCl_3$) δ 0.96 (3H, t, J=7 Hz), 1.47 (2H, sextet, J=7 Hz), 2.21 (2H, t, J=7 Hz), 3.3—3.7 (8H, m), 6.30 (1H, d, J=13.5 Hz), 6.9—7.3 (5H, m), and 7.48 (1H, d, J=13.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 20.3 (t), 27.5 (t), 45.3 (t), 66.7 (t), 120.2 (d, PhCH=) 125.3 (d, *m*), 125.4 (d, *p*), 128.4 (d, *o*), 135.6 (d, =CHN), 138.6 (s, *ipso*), and 161.7 (s, C=N).

Found: *m/e* 258.1753. Calcd for $C_{16}H_{22}N_2O$: M, 258.1733.

The amidine (**3f**) could not be induced to crystallize, and attempted distillation *in vacuo* or chromatographic separation caused decomposition; thus further purification was unsuccesful.

*Decomposition of 4,4-Dimethyl-1-(1-phenylvinyl)-5-(1-pyrrolidinyl)-4,5-dihydro-1*H*-1,2,3-triazole (1g).* To a solution of **1g** (0.50 g, 1.9 mmol) in dry THF (30 ml) was added a THF (30 ml) solution of anhydrous *p*-toluenesulfonic acid (0.71 g, 4.0 mmol) dropwise with stirring at 0 °C. Stirring was continued for further 30 min until **1g** was completely consumed. Then anhydrous potassium carbonate (2.0 g) was added to the solution and stirring was continued overnight. After solid materials had been filtered off and the solvent had been removed *in vacuo*, acrylonitrile (3 ml) was added to the residue and the mixture was stirred for 2 d at room temperature. Excess acrylonitrile was removed and the silica gel preparative thin layer chromatography of the residue gave previously reported 2-isopropyl-6-phenylnicotinonitrile (**4**,[2] 54 mg, 13% yield) and 5-oxo-5-phenylpentanenitrile (**5**, 34 mg, 11% yield).

2-Isopropyl-6-phenylnicotinonitrile (4): Colorless crystals; mp 73.5—75.0 °C, lit, 75.5—76.5 °C.[2] Mixed melting point test with the authentic sample; mp 74.5—76.0 °C.

5-Oxo-5-phenylpentanenitrile (5): Colorless oil; MS *m/e* 173 (M^+); IR (neat) 2220 (C≡N) and 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.09 (2H, quintet, J=6.5 Hz), 2.56 (2H, t, J=6.5 Hz), 3.17 (2H, t, J=6.5 Hz), 7.4—7.7 (3H, m), and 7.9—8.1 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.6 (t), 19.9 (t), 36.4 (t), 119.3 (s, C≡N), 128.0 (d), 128.7 (d), 133.4 (d), 136.6 (s), and 198.2 (s, C=O).

References

1) Y. Nomura, Y. Takeuchi, S. Tomoda, and M. M. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 261 (1981).

2) Y. Nomura, Y. Takeuchi, S. Tomoda, and M. M. Ito, *Chem. Lett.*, **1979**, 187; *Bull. Chem. Soc. Jpn.*, **54**, 2779 (1981).

3) R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 933 (1961).