

SHORT
COMMUNICATIONS

Synthesis and Properties of 1-Nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one

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While studying the kinetics of nitration of 1,2,4-triazol-5-one in concentrated nitric acid by UV spectroscopy under the conditions leading to formation of 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one [1, 2], we found that in the first minutes 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one was formed and that the conversion attained 80% in 100% nitric acid. Simultaneously, the yield of 3-nitro-1,2,4-triazol-5-one considerably decreased in 98–100% nitric acid. However, we failed to isolate 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one from the reaction mixture. Although N-nitro derivatives of heterocyclic compounds are well known [3], we found no published data on derivatives having an =N–N(NO)₂–C(=O)– fragment.

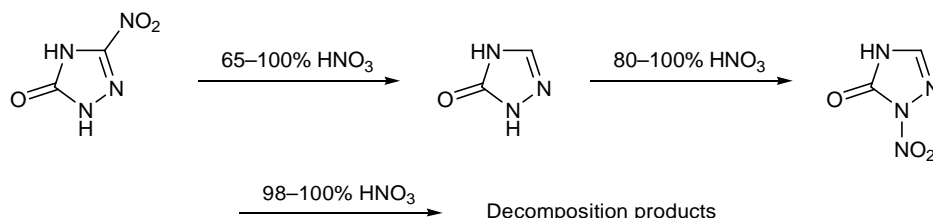
1-Nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one was synthesized by reaction of 4,5-dihydro-1*H*-1,2,4-triazol-5-one with nitric acid in acetic anhydride. Its structure was proved by ¹H NMR spectroscopy: the spectrum contained signals at δ 7.69 ppm (CH) and 9.80 ppm (NH). Splitting of the signal at δ 7.69 ppm ($J = 1$ Hz) indicates the presence of a hydrogen atom on the nitrogen neighboring to the CH group. In the IR spectrum of the product, absorption bands due to stretching vibrations of the nitro group (1326 and 1579 cm⁻¹) are displaced relative to the corresponding bands in the spectrum of 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one (1358 and 1548 cm⁻¹); an appreciable shift of the carbonyl absorption band was also ob-

served (1767 and 1719 cm⁻¹, respectively); and C–H stretching vibration band was present at 2840 cm⁻¹. The mass spectrum of 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one contained no molecular ion peak, but strong peaks with m/z 101 [$M + 1 - 30$]⁺ and 85 [$M + 1 - 46$]⁺ were present, which correspond to elimination of NO and NO₂ from the molecular ion.

1-Nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one is very readily hydrolyzed with water and aqueous bases, and the reaction is accompanied by vigorous gas evolution. The evolved gas consists of CO₂, N₂O, and N₂ at a molar ratio of 1.5:0.5:1, indicating cleavage of the triazole ring; no nitrogen(IV) oxide was detected. The product is more stable in dilute (1–3%) nitric acid where it undergoes slow hydrolysis to 4,5-dihydro-1*H*-1,2,4-triazol-5-one in several hours. The absorption band of 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one (λ_{\max} 278 nm) disappears almost instantaneously from the UV spectrum in concentrated sulfuric acid and trifluoroacetic acid, and 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one is then slowly formed (λ_{\max} 316 nm).

Thermal decomposition (70°C, $m/V = 5 \times 10^{-4}$ g/cm³) gives only 1.3 mol of gaseous products per mole of the initial compound, and nitrogen(IV) oxide is absent. The solid residue is characterized by an IR absorption band at 2165 cm⁻¹, which suggests the presence of a C≡N group.

Scheme 1.



1-Nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one acts as a nitrating agent. It reacts in ethyl acetate with *o*- and *p*-nitrophenols to give 2,4-dinitrophenol, and with *N,N'*-dimethylaniline, to give *N,N'*-dimethylnitroaniline.

The kinetic studies showed that 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one is formed from 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one via hydrolysis to 4,5-dihydro-1*H*-1,2,4-triazol-5-one and subsequent nitration of the latter rather than via rearrangement (as with the corresponding pyrazoles [3]). When the concentration of nitric acid is lower than 90%, the UV absorption band of 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one disappears from the spectrum in 1–2 min, the rate of accumulation of 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one approaches the rate of nitration of 4,5-dihydro-1*H*-1,2,4-triazol-5-one, and the maximal yield of 3-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one decreases. Our results led us to propose a mechanism of formation and disappearance of 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one in concentrated nitric acid, which is shown in Scheme 1.

1-Nitro-1,4-dihydro-1*H*-1,2,4-triazol-5-one. 4,5-Dihydro-1*H*-1,2,4-triazol-5-one, 5.1 g (0.06 mol), was added over a period of 30 min at –5 to –10°C to a mixture of 38 g of acetic anhydride and 12.6 g

(0.2 mol) of 100% nitric acid (freed from nitrogen oxides). The mixture was kept for 90 min at that temperature, and the light yellow precipitate was filtered off, washed with a mixture of acetic acid with acetic anhydride (10:1, by volume), and dried in a vacuum desiccator. Yield 1.9 g, mp 100.5–101.5°C.

The ¹H NMR spectra were recorded on a Varian Unity INOVA-400 spectrometer in acetonitrile-*d*₃. The IR spectra were measured in KBr on an Avatar-360 FTIR instrument. The mass spectra were run on a Waters 2690 mass spectrometer.

CAUTION! The sensitivity of 1-nitro-4,5-dihydro-1*H*-1,2,4-triazol-5-one to mechanical action and its rate of combustion approach the corresponding parameters of initiating explosives; a spontaneous explosion once occurred after prolonged storage at room temperature.

REFERENCES

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