

Synthesis of *N*-Vinyl-1,2,3-triazole Derivatives

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Received June 27, 2001

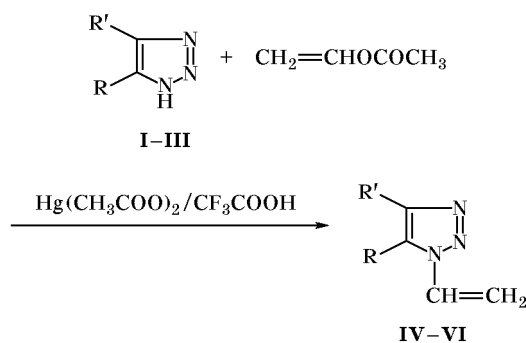
Abstract—Nitro-substituted *N*-vinyl-1,2,3-triazole derivatives were synthesized by the vinyl exchange reaction. The process was promoted by the catalytic system mercury(II) acetate–trifluoroacetic acid. This system is universal, and it can be used in the synthesis of vinylazoles having two, three, and four nitrogen atoms in the ring.

Vinyl derivatives of 1,2,3-triazoles attract interest as monomers for the synthesis of high-energy polymeric materials [1]. There are very limited published data on the methods of preparation of *N*-vinyl-1,2,3-triazoles and polymers based thereon [2–7]. Cycloaddition of vinyl azides to compounds having an activated methylene fragment [2] or α -ketophosphoranes [3] leads to formation of substituted *N*-vinyl-1,2,3-triazoles. The application of this procedure is limited because of risk of explosion and toxicity of the reagents. Moreover, unsubstituted vinyltriazole cannot be obtained in this way. We previously [4] synthesized vinyl derivatives of 1,2,3-triazoles by reaction of 2-chloroethyl azide with acetylenic compounds and subsequent dehydrochlorination of 1-(2-chloroethyl)-1,2,3-triazoles thus formed. In order to obtain unsubstituted 1-vinyl-1,2,3-triazole, the corresponding 1-chloroethyltriazolecarboxylic acids were preliminarily subjected to decarboxylation. *N*-Vinyl-1,2,3-triazole and some its derivatives were synthesized by direct vinylation of 1,2,3-triazoles with acetylene [5, 6]. However, experimental difficulties (high pressure and elevated temperature) together with the poor yield of the target product (<50%) strongly restrict the preparative potential of this procedure. *N*-Vinyl-1,2,3-triazole was obtained in a low yield in the synthesis of 1,2,3-triazole by reaction of hydrazoic acid

with acetylene (via vinylation of the preliminarily formed triazole (Scheme 1). The most appropriate procedure for the synthesis of *N*-vinyl-1,2,3-triazoles is based on the vinyl exchange reaction between triazoles and vinyl acetate. Shatalov *et al.* [6, 7] obtained alkyl 1-vinyl-1,2,3-triazole-5-carboxylates by reaction of the corresponding triazole derivatives with vinyl acetate in the presence of mercury(II) acetate and boron trifluoride–ether complex [6, 7]. The yield of the products did not exceed 40–50%. Furthermore, according to the authors, the use of the catalytic system mercury acetate/boron trifluoride–ether complex does not give reproducible results.

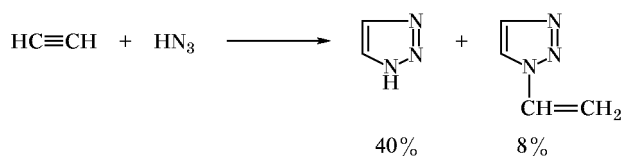
The present communication reports on the synthesis of 1-vinyl-1,2,3-triazole and its previously unknown nitro derivatives by vinyl exchange promoted by the catalytic system mercury(II) acetate–trifluoroacetic acid. (Scheme 2).

Scheme 2.

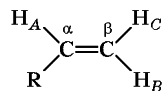


I, IV, R = R' = H; II, V, R = NO₂, R' = H; III, VI, R = Ph, R' = NO₂.

Scheme 1.



Yields, melting or boiling points, polarographic data, and UV and NMR spectra of vinyltriazoles **IV–VI**



Comp. no.	Yield, %	bp, °C (<i>p</i> , mm), or mp, °C	$E_{1/2}$, V	UV spectrum, λ_{\max} , nm (ϵ)	^1H and ^{13}C NMR spectra, δ (δ_{C}), ppm						
					H_A	H_B	H_C	H_{ring}	C^α	C^β	C_{ring}
IV ^a	88	68 (2)	−2.71 [8]	–	7.50	5.85	5.09	7.70 (5-H) 8.30 (4-H)	131.64	106.59	123.55 (C^4), 135.1 (C^5)
V	70	68–70	−1.76 −2.74	214 (8390) 238 (4920) 288 (8610)	7.50	6.18	5.49	8.60	132.70	109.14	133.9 (C^4), 155.0 (C^5)
VI	83	58–59	–	212 (13 650) 256 (15 030) 313 (4880)	7.50	6.20	5.45	7.50, 7.80 (H_{arom})	134.80	109.0	144.5 (C^4), 143.0 (C^5), 128.0–131.0 (C_{arom})

^a $n_{\text{D}}^{20} = 1.5130$.

This procedure is more advantageous from the preparative viewpoint than those known previously. The catalytic system mercury(II) acetate–trifluoroacetic acid makes it possible to carry out the reaction simultaneously charging all reactants. The reaction is not accompanied by side process leading to formation of tars and polymeric products. The yield of *N*-vinyl-1,2,3-triazoles attains 70–90% in 3–5 h. The yields, melting (or boiling) points, polarographic data, and spectral parameters of triazoles **IV–VI** are given in table.

The IR spectra of **IV–VI** contain absorption bands which are consistent with their structure. In the IR spectra of compounds **IV** and **V** stretching vibrations of the vinyl group on the nitrogen appear at 1645 and 1640 cm^{-1} ; stretching vibration bands of the vinyl C–H bond are located at 3100, 3130, and 3150 cm^{-1} , and out-of-plane bending vibrations of the =CH₂ moiety in compound **V** give rise to absorption at 824 cm^{-1} . Absorption bands at 1340 and 1530 cm^{-1} belong to symmetric and antisymmetric stretching vibrations of the nitro group, respectively; vibrations of the azole ring are characterized by absorption at 1520 and 1560 cm^{-1} (**IV**) and 1517 and 1558 cm^{-1} (**V**). Compound **VI** shows in the IR spectrum absorption bands belonging to the *N*-vinyl group (832, 1640, 3100, 3130 cm^{-1}), nitro group (1350, 1550 cm^{-1}), phenyl fragment (700, 780, 1600, 3050 cm^{-1}), and azole ring (1520 cm^{-1}).

Interaction between the nitro group, azole ring, and *N*-vinyl group gives rise to a strong long-wave

absorption band at λ 288 nm in the UV spectrum of nitro-substituted vinyltriazole **V**. The nitro group in molecule **VI** is forced out from the azole ring plane due to steric effect of the neighboring phenyl group; therefore, the corresponding band in the spectrum of **VI** is displaced toward shorter wavelengths (256 nm). On the other hand, conjugation between the triazole ring and phenyl substituent gives rise to an additional absorption band at λ 313 nm and increases the molar absorption coefficients of the other bands.

The ^1H NMR spectra of compounds **IV–VI** contain characteristic signals from the *N*-vinyl group in the following regions, δ , ppm: 7.50 q (H_A), 5.85–6.20 d (H_B), 5.09–5.49 d (H_C). The presence in the triazole ring of such a strong electron-acceptor substituent as nitro group induces downfield shift of the H_B and H_C signals by 0.35–0.4 ppm. Signals from the vinyl carbon atoms in the ^{13}C NMR spectra are also displaced to a weaker field (see table).

Vinyl exchange reaction with substituted triazoles could give isomeric products differing by the position of the vinyl group relative to the ring substituent. According to the ^1H and ^{13}C NMR data, the isolated products were individual isomers. The reaction with 4(5)-nitro-1,2,3-triazole gave 5-nitro-1-vinyl-1,2,3-triazole. The structure of the latter follows from much stronger downfield shift of the C^5 signal (from 135.1 to 155.0 ppm) relative to the corresponding signal of 5-unsubstituted 1-vinyltriazole, as compared with the shift of the C^4 signal (from 123.6 to 133.9 ppm). This is possible only when the nitro group occupies

position 5 of the heteroring. The vinyl exchange reaction with 4-nitro-5-phenyl-1,2,3-triazole (**III**) is likely to result in formation of 4-nitro-5-phenyl-1-vinyl-1,2,3-triazole (**VI**), for the largest downfield shift is observed for the C⁴ signal (from 123.55 ppm in the spectrum of **III** to 143.0 ppm).

Like other vinylazoles [8], the vinyl group in *N*-vinyl-1,2,3-triazoles can be reduced under polarographic conditions at a potential $E_{1/2}$ of about -2.7 V. 5-Nitro-1-vinyl-1,2,3-triazole gives rise to the second reduction wave in a less negative potential region due to reduction of the nitro group (see table). The relative ease of electrochemical reduction of the vinyl group in vinyltriazoles **IV–VI** indicates their ability to undergo polymerization.

To conclude, it should be noted that the catalytic system mercury(II) acetate–trifluoroacetic acid is universal, i.e., it can be used in the synthesis of *N*-vinylazole derivatives having two, three, and four nitrogen atoms in the ring. This system is the most advantageous in the synthesis of 1-vinyltetrazole. With the other, previously known catalytic systems, such as $\text{Hg}(\text{CH}_3\text{COO})_2/\text{H}_2\text{SO}_4$ [9], $\text{Hg}(\text{CH}_3\text{COO})_2/\text{CH}_3\text{COOH}$ [10], and $\text{Hg}(\text{CH}_3\text{COO})_2/\text{BF}_3\text{–Et}_2\text{O}$ [11], the reactions were characterized by poor reproducibility, and the yields were low. The use of the $\text{Hg}(\text{CH}_3\text{COO})_2/\text{CF}_3\text{COOH}$ system ensures considerable increase in the yield of 1-vinyltetrazole, simplifies the experimental procedure, and makes the process safer.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument from samples prepared as thin films or suspensions in mineral oil. The UV spectra were measured on a Specord UV-Vis spectrophotometer from solutions in acetonitrile. The ¹H and ¹³C NMR spectra were obtained on a Varian 500 spectrometer at 500 and 125.6 MHz, respectively, using (CD₃)₂CO as solvent. Polarographic measurements were performed on an LP-7 polarograph with a dropping mercury electrode; a solution of tetrabutylammonium perchlorate in dimethylformamide was used as supporting electrolyte.

1-Vinyl-1,2,3-triazole (IV). A mixture of 17.6 g (0.26 mol) of 1,2,3-triazole, 4.75 g of mercury(II) acetate, 4.8 ml of trifluoroacetic acid, and 0.1 g of hydroquinone in 75 ml of vinyl acetate was stirred for 3 h at 70°C. Excess vinyl acetate was removed by distillation under reduced pressure, and the residue was neutralized with a concentrated aqueous solution

of sodium hydrogen carbonate. The product was extracted into diethyl ether, the extract was dried over anhydrous magnesium sulfate and evaporated, and the residue was distilled under reduced pressure.

1-Vinyl-1,2,4-triazole was synthesized in a similar way using 1,2,4-triazole as initial compound. Yield 90%, bp 103°C (15 mm), $n_{\text{D}}^{20} = 1.5092$.

1-Vinylimidazole was synthesized as described above using imidazole as initial compound. Yield 71%, bp 80°C (10 mm), $n_{\text{D}}^{20} = 1.5332$.

5-Nitro-1-vinyl-1,2,3-triazole (V). A mixture of 16.5 g (0.14 mol) of 4-nitro-1,2,3-triazole, 4 g of mercury(II) acetate, 4.5 ml of trifluoroacetic acid, 0.1 g of hydroquinone, and 200 ml of vinyl acetate was stirred for 5 h at 70°C. The mixture was cooled and treated with a concentrated aqueous solution of sodium hydrogen carbonate. The organic layer was separated, the aqueous layer was extracted with diethyl ether, the extracts were combined with the organic phase, and the solvent and excess vinyl acetate were distilled off. The dry residue was recrystallized from acetone.

4-Nitro-5-phenyl-1-vinyl-1,2,3-triazole (VI) was synthesized in a similar way from 4-nitro-5-phenyl-1,2,3-triazole.

1-Vinyltetrazole. A mixture of 40 g (0.57 mol) of tetrazole, 10.8 g of mercury(II) acetate, 11 ml of trifluoroacetic acid, 0.5 g of hydroquinone, and 200 ml of vinyl acetate was stirred for 2 h at 73°C. Excess vinyl acetate was distilled off under reduced pressure, the residue was poured into water, and the product was extracted into methylene chloride. The extract was dried over MgSO₄, the solvent was distilled off, and the residue was distilled in a vacuum. Yield 46 g (85%), bp 70°C (0.01 mm), $n_{\text{D}}^{20} = 1.5010$.

Reaction of hydrazoic acid with acetylene. A vertical 500-ml high-pressure reactor was charged with a suspension of 65 g (1 mol) of sodium azide in 25 ml of water and 200 ml of benzene, and an open ampule containing 50 ml of 65% sulfuric acid was placed thereto. Acetylene was supplied to the reactor to a pressure of 15–16 atm, and the mixture was stirred for 60 h at 100°C. The reactor was opened, the mixture was neutralized to pH 5 with sodium hydrogen carbonate, the aqueous layer was separated and treated with diethyl ether, and the extract was combined with the organic phase, dried over magnesium sulfate, and distilled. We thus isolated 43 g (40%) of 1,2,3-triazole, bp 80–81°C (4 mm), $n_{\text{D}}^{20} = 1.4985$, and 12 g (8%) of 1-vinyl-1,2,3-triazole (**IV**), bp 59°C (1 mm), $n_{\text{D}}^{20} = 1.5130$.

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