# SYNTHESIS AND PROPERTIES OF 2-ALKYL-5-ETHYNYLTETRAZOLES

S. R. Buzilova, V. M. Shul'gina,
G. A. Gareev, and L. I. Vereshchagin

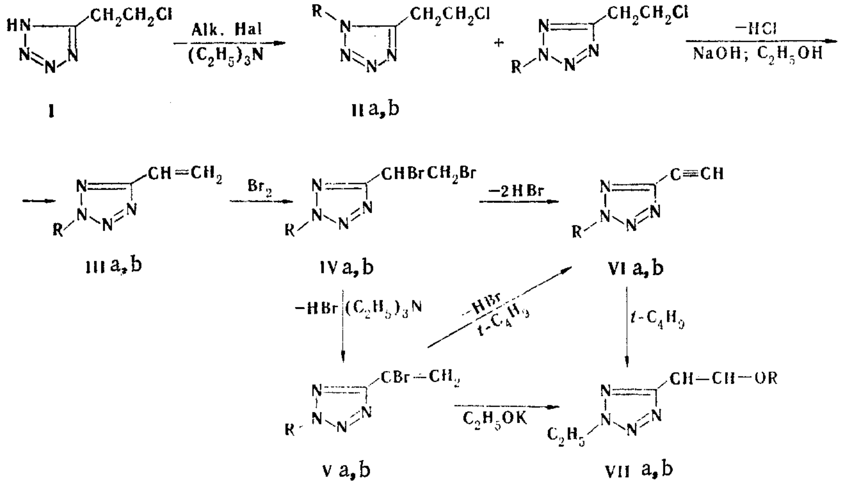
UDC 547.796.1.07

2-Alkyl-5-ethynyltetrazoles were synthesized. It is shown that ethynyltetrazoles have a triple bond with increased electrophilicity. They readily add aliphatic alcohols and amines and undergo aminomethylation, the Iotsich reaction, oxidative dimerization, and the cycloaddition of azides. 1-Phenyl-3-tetrazolyl-2-propyne, which has the properties of α-acetylenic ketones, was obtained by selective oxidation of tetrazolylethynylcarbinol.

In a continuation of our research on the chemistry of acetylenic compounds with activated triple bonds [1, 2] we searched for methods for the synthesis of tetrazolylacetylenes and studied some of their properties.

The presence of considerable positive charge on the carbon atom in the 5 position of the tetrazole ring has an electron-acceptor effect on the triple bond and increases its electrophilicity and consequently its reactivity.

Up until now, ethynyltetrazoles were unknown. There are several variants for introduction of a triple bond in nitrogen-containing heterocycles [3, 4]. We selected the halogenation and dehydrohalogenation of N-alkyl-5-vinyltetrazoles (II) for the introduction of an acetylenic fragment in the tetrazole ring.



II–VI a R–$CH_3$; b R–$C_2H_5$; VII a R–$C_2H_5$; b R=t-$C_4H_9$

A mixture of 1- and 2-alkyl-5-(2-chloroethyl)tetrazoles (IIa, b) is formed in the alkylation of 5-(2-chloroethyl)tetrazole (I) with alkyl halides. According to the PMR spectra, the isomer ratio is 1:4. For the subsequent steps in the synthesis we used the 2-alkyl isomer, since it was the predominant isomer and was readily isolated by rectification.

2-Alkyl-5-vinyltetrazoles III were obtained in good yields by dehydrohalogenation of tetrazoles II with alcoholic alkali. The products can be converted, without isolation, to dibromides IVa, b by the action of triethylamine in acetone through splitting out of one molecule of hydrogen bromide to give 2-alkyl-5-(1-bromovinyl)tetrazoles (Va, b), which can be dehydrobrominated to ethynyltetrazoles VI by the action of potassium tert-butoxide in tetrahydrofuran (THF) at 5°C [5]. A higher reaction temperature of prolonged standing of

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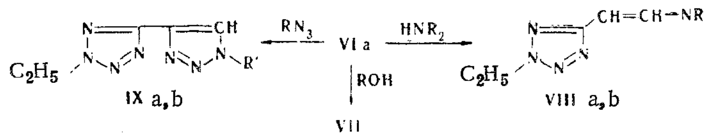
Institute of Petrochemical and Coal-Chemical Synthesis, Irkutsk State University, Angarsk 665813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 842-847, June, 1980. Original article submitted May 30, 1979; revision submitted January 3, 1980.

0009-3122/80/1606-0658$07.50

the reaction mixture at room temperature facilitates alkoxylation of the resulting triple bond and leads either to a mixture of 2-alkyl-5-ethynyltetrazole (VI) and 2-alkyl-5-(2-tert-butoxyvinyl)tetrazole (VIIb) or exclusively to vinyl ether VIIb. It must be noted that vinyl ether VIIa is obtained in quantitative yield in the dehydrohalogenation of monobromide Vb and dibromide IVb with alcoholic alkali. One can, in principle, exclude the step involving the preparation of monobromide V and dehalogenate dibromide IV with potassium tert-butoxide for the synthesis of tetrazolylacetylenes VI. The proposed method is a multistep process, but the accessibility of the starting 5-(2-chloroethyl)tetrazole, the high yields, and the reproducibility in all of the steps make it completely acceptable for the synthesis of 2-alkyl-5-ethynyltetrazoles.

As in the case of acetylenic ketones, nitriles, and acids, the triple bond of the ethynyltetrazoles has rather high electrophilicity and is capable of adding various nucleophilic agents under mild conditions. Thus, in the presence of an alcohol solution of potassium hydroxide ethynyltetrazoles readily add primary and even tertiary aliphatic alcohols to give mixtures of cis- and trans-alkoxyvinyltetrazoles. The PMR spectra contain signals of vinyl protons at 5.14 and 6.28 ppm for the cis and 5.58 and 7.39 ppm for the trans isomers. Bands of the vibrations of an ether bond (1260 $cm^{-1}$), of a disubstituted double bond (1670 $cm^{-1}$), and of a tetrazole ring (980 and 1090 $cm^{-1}$) [6] are present in the IR spectra of these compounds.

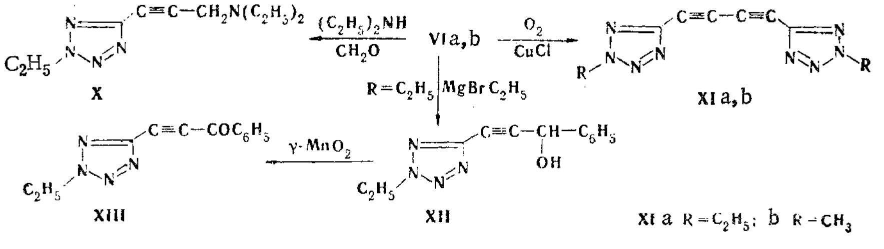


VII a R=$C_2H_5$; b R=$t$-$C_4H_9$; VIII a R=$C_2H_5$; b R= piperidyl IX a R′=$C_6H_5$; b R′=$CH_2$—$CH_2Cl$

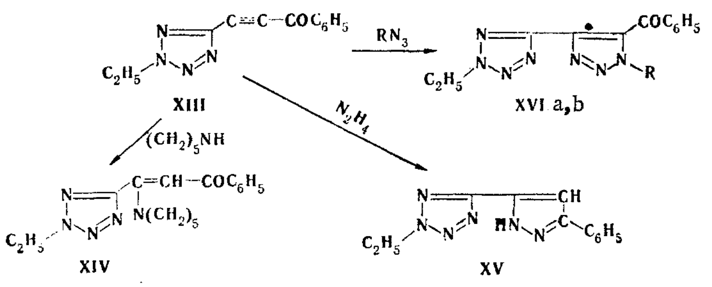
The reaction of ethynyltetrazoles VI with dialkylamines proceeds smoothly without a catalyst to give exclusively trans-vinylamines VIII. The PMR spectra contain signals of protons of a vinyl group at 5.12 and 7.14 ppm, which are characteristic for the trans isomer.

The cycloaddition of organic azides to the triple bond to give tetrazolyl-1,2,3-triazoles IX takes place without complications. According to the PMR spectra, these two-ring systems are present in the reaction products in the form of two isomeric triazoles in a ratio of 3:2 with predominance of the 1,4-disubstituted 1,2,3-triazole. Two characteristic protons of isomeric triazoles (8.12 and 8.52 ppm) are recorded in the PMR spectrum. The signal at weaker field corresponds to the 1,4 isomer [6].

The 2-alkyl-5-ethynyltetrazoles undergo virtually all of the classical reactions that are characteristic for the terminal hydrogen atom of a triple bond. They are aminomethylated smoothly to give the corresponding aminomethylethynyltetrazoles X and give ditetrazolyldiacetylenes XI as a result of oxidative dimerization.



Acetylenes VI do not undergo the Iotsich reaction in ether; this is probably associated with the low solubility of the complex. Performance of the synthesis in tetrahydrofuran (THF) made it possible to obtain acetylenic carbinol XII in 34% yield. Selective oxidation of the carbinol with active manganese dioxide gave ketone XIII, which readily adds amines, hydrazine, and organic azides to give tetrazolylamino vinyl ketone XIV, pyrazole XV, and vicinal triazoles XVIa, b.



XVI a R=CH$_2$CH$_2$OH; b R=CH$_2$CH$_2$Cl

## EXPERIMENTAL

The IR spectra of the pure compounds and suspensions in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian LX-100 spectrometer with hexamethyldisiloxane as the internal standard.

2-Ethyl-5-(2-chloroethyl)tetrazole (IIb). 5-(2-Chloroethyl)tetrazole (I) was obtained by the method in [7]. A solution of 25 g (0.23 mole) of ethyl bromide in 30 ml of acetone was added to a solution of 24 g (0.18 mole) of tetrazole I and 23 g (0.23 mole) of triethylamine in 120 ml of acetone, and the mixture was refluxed with stirring for 3 h. It was then cooled, and the precipitated salt of triethylamine was removed by filtration. The filtrate was evaporated to 40 ml, and the concentrate was diluted with ether, washed with water until the wash water was neutral, and dried with magnesium sulfate. The solvent was removed by distillation, and the residue was distilled in vacuo to give 29.5 g of a mixture of two isomers consisting of 20% 1-ethyl-5-(2-chloroethyl)tetrazole [PMR spectrum: 4.32 (2H, CH$_2$), 1.46 (3H, CH$_3$), 3.90 (2H, CH$_2$), and 3.30 ppm (2H, CH$_2$Cl)] and 80% 2-ethyl-5-(-chloroethyl)tetrazole [PMR spectrum: 4.52 (2H, CH$_2$), 1.53 (3H, CH$_3$), 3.82 (2H, CH$_2$), and 3.24 ppm (2H, CH$_2$Cl)], from which 16.4 g (56%) of 2-ethyl-5-(2-chloroethyl)tetrazole, with bp 110-112°C (1 mm) and $n_D^{20}$ 1.4752, was isolated by rectification in vacuo. Found %: C 37.7; H 5.7; Cl 21.7; N 34.7. $C_5H_9ClN_4$. Calculated %: C 37.4; H 5.6; Cl 22.1; N 34.9.

Similarly, the reaction of 5 g of tetrazole I and 6 g of methyl iodide gave 2.8 g (48.0%) of 2-methyl-5-(2-chloroethyl)tetrazole (IIa) with bp 90-92°C (1 mm) and $n_D^{20}$ 1.4841. Found %: C 32.8; H 4.8; Cl 24.2; N 38.2. $C_4H_7ClN_4$. Calculated %: C 32.8; H 4.8; Cl 23.9; N 38.3.

2-Ethyl-5-vinyltetrazole (IIIb). A solution of 16.4 g (0.1 mole) of chloroethyltetrazole IIb in 10 ml of methanol was added dropwise at 35°C to a solution of 4.1 g of NaOH in 50 ml of methanol, and the mixture was stirred for 3 h. The precipitated sodium chloride was removed by filtration, and the filtrate was evaporated to 20 ml. The concentrate was diluted with ether and washed with water until the wash water was neutral. The solvent was removed in vacuo, and the residue was distilled to give 10 g (78%) of vinyltetrazole IIIb with bp 52-54°C (1 mm) and $n_D^{20}$ 1.4801. IR spectrum (thin layer): 1650 (C=C); 3040, 3110 cm$^{-1}$ (=CH). Found %: C 48.6; H 6.6; N 45.1. $C_5H_8N_4$. Calculated %: C 48.4; C 6.5; N 45.2.

Similarly, the reaction of 3.6 g of tetrazole IIa gave 1.4 g (51%) of 2-methyl-5-vinyltetrazole (IIIa) with bp 35-36°C (1 mm). IR spectrum (thin layer): 1650 cm$^{-1}$ (C=C). Found %: C 43.6; H 5.6; N 51.1. $C_4H_6N_4$. Calculated %: C 43.6; H 5.4; N 51.0.

2-Ethyl-5-(1,2-dibromoethyl)tetrazole (IVb). A solution of 16 g (0.1 mole) of bromine in 10 ml of chloroform was added dropwise to a solution of 10 g (0.08 mole) of vinyltetrazole IIIb in 30 ml of chloroform and the mixture was stirred for 1 h. The chloroform was removed by distillation, and the residue was distilled in vacuo to give 20.6 (90%) of a product with bp 126-127°C (1 mm) and $n_D^{20}$ 1.5490. Found %: C 21.0; H 2.9; Br 56.2; N 19.9. $C_5H_8Br_2N_4$. Calculated %: C 21.1; H 2.8; Br 56.2; N 19.7.

Similarly, the reaction of vinyltetrazole IIIa gave 2-methyl-5-(1,2-dibromoethyl)tetrazole (IVa) (90%) with mp 35-36°C (from alcohol). Found %: C 17.9; H 2.1; Br 59.5; N 21.1. $C_4H_6Br_2N_4$. Calculated %: C 17.7; H 2.2; Br 59.2; N 20.7.

2-Ethyl-5-(1-bromoethyl)tetrazole (Vb). A solution of 20 g (0.07 mole) of dibromide Vb in 15 ml of acetone was added dropwise to a solution of 10 g (0.1 mole) of triethylamine in 50 ml of acetone, and the mixture was refluxed gently with stirring for 2 h. The precipitated salt of triethylamine was removed by filtration, and the filtrate was evaporated to

20 ml. The concentrate was diluted with ether, and the ether solution was washed with water, dried, and distilled in vacuo to give 11.5 g (81%) of a product with bp 88-89°C (1 mm) and $n_D^{20}$ 1.5240. IR spectrum (thin layer): 1627 $cm^{-1}$ (C=C). PMR spectrum: 6.06, 6.85 (2H, J = 2.2 Hz, $C=CH_2$); 4.65 (2H, $CH_2$); 1.57 ppm (3H, $CH_3$). Found %: C 29.7; H 3.8; Br 39.1; N 27.0. $C_5H_7BrN_4$. Calculated %: C 29.6; H 3.4; Br 39.4; N 27.6.

Similarly, the reaction of 5 g of dibromide IVa gave 3 g (79%) of monobromide Va with mp 29-30°C (by freezing out from alcohol). PMR spectrum: 5.20, 5.80 (2H, J = 2.5 Hz, $C=CH_2$). Found %: C 25.6; H 2.7; Br 42.3; N 29.7. $C_4H_5BrN_4$. Calculated %: C 25.4; H 2.6; Br 42.3; N 29.6.

2-Ethyl-5-ethynyltetrazole (VIb). A) A solution of 50 ml of potassium tert-butoxide in tetrahydrofuran (THF) (from 1.7 g of potassium and 20 ml of tert-butyl alcohol) was added dropwise at 0-5°C in the course of 30 min to a solution of 6 g (0.03 mole) of monobromide Vb in 20 ml of THF, and the mixture was stirred for 1 h. The potassium bromide was removed by filtration, and the filtrate was evaporated rapidly in vacuo to 30 ml. Ether (50 ml) was added to the concentrate, and the mixture was washed with water, neutralized with dilute hydrochloric acid, dried with magnesium sulfate, and distilled in vacuo to give 3.1 g (86%) of a product with bp 70-72°C (1 mm) and $n_D^{20}$ 1.4910. IR spectum (thin layer): 2145 (C≡C) and 3380 $cm^{-1}$ (≡ C). PMR spectrum: 3.37 (1H, ≡CH), 4.55 (2H, $CH_2$), and 1.54 ppm (3H, $CH_3$). Found %: C 49.3; H 5.3; N 45.5. $C_5H_6N_4$. Calculated %: C 49.1; H 4.9; N 45.9.

Similarly, the reaction of 3 g of monobromide Va gave 1.2 g (70%) of 2-methyl-5-ethynyltetrazole (VIa) with bp 68-70°C (1 mm) and $n_D^{20}$ 1.4960. IR spectrum (thin layer): 2145 (C≡C) and 3300 $cm^{-1}$ (≡C). Found %: C 44.5; H 3.6; N 51.6. $C_4H_4N_4$. Calculated %: C 44.4; H 3.7; N 51.8.

B) A solution of potassium tert-butoxide in THF (from 3.5 g of potassium and 40 ml of tert-butyl alcohol in 70 ml of THF) was added dropwise at 0-5°C in the course of 30 min to a solution of 10 g (0.035 mole) of dibromide IVb in 25 ml of THF, and the mixture was stirred for 1.5 h. The precipitate was removed by filtration, and the reaction product was isolated from the filtrate as in experiment A to give 2.9 g (67%) of a product with bp 70-72°C (1 mm) and $n_D^{20}$ 1.4912. IR spectrum (thin layer): 2.45 (C≡C) and 3380 $cm^{-1}$ (≡CH).

2-Ethyl-5-(2-tert-butoxyvinyl)tetrazole (VIIb). The synthesis was carried out as in the preparation of 5-ethynyltetrazole (VIa) by method A. After the addition of the solution of potassium tert-butoxide, the mixture was maintained at room temperature for 10 h. The reaction of 6 g of monobromide Vb gave 3.8 g (58%) of VIIb with bp 123-125°C (1 mm) and $n_D^{20}$ 1.4923. IR spectrum (thin layer): 925, 980, and 1668 $cm^{-1}$ (C=C). PMR spectrum: 5.26, 6.48 (2H, J = 7.0 Hz, CH=CH); 4.43 (2H, $CH_2$); 1.47 (3H, $CH_3$); 1.27 ppm [9H, $C(CH_3)_3$]. Found %: C 55.7; H 8.0; N 28.7. $C_9H_{16}N_4O$. Calculated %: C 55.4; H 8.2; N 28.7.

2-Ethyl-5-(2-ethoxyvinyl)tetrazole (VIIa). A) A solution of 0.6 g of potassium hydroxide in 5 ml of ethanol was added to a solution of 1 g (0.005 mole) of monobromide Vb in 5 ml of ethanol, and the mixture was refluxed for 2 h. The precipitated salt was removed by filtration, and the filtrate was evaporated to 2 ml. Ether (10 ml) was added, and the mixture was washed with water, neutralized with dilute hydrochloric acid, and dried with magnesium sulfate. The solvent was removed by distillation, and the residue was distilled in vacuo to give 0.6 g (71%) of a product with bp 110-112°C (1 mm) and $n_D^{20}$ 1.4980. IR spectrum (thin layer): 1250 (C—O—C); 980, 1670 $cm^{-1}$ (CH=C). PMR spectrum, cis: 5.14 and 6.28 (2H, J = 6.5 Hz, CH=CH); trans: 5.58 and 7.39 ppm (2H, J = 13.0 Hz, CH=CH). Found %: C 50.3; H 7.2; N 33.1. $C_7H_{12}N_4O$. Calculated %: C 50.0; H 7.1; N 33.3.

B) A solution of sodium ethoxide (from 0.7 g of sodium in 3 ml of ethanol) was added to a solution of 0.4 g (0.003 mole) of 2-ethyl-5-ethynyltetrazole (VIb) in 6 ml of ethanol, and the mixture was refluxed for 1 h and worked up as in method A. The residue after removal of the solvent by distillation was chromatographed on activity II $Al_2O_3$ in an ether—petroleum ether system (4:1) to give 0.3 g (60%) of a product with $n_D^{20}$ 1.4960. IR spectrum (thin layer): 1250 (C—O—C); 980, 1670 $cm^{-1}$ (CH=CH).

2-Ethyl-5-(2-diethylaminovinyl)tetrazole (VIIIa). A mixture of 0.2 g of 2-ethyl-5-ethynyltetrazole (VIb) and 0.1 g of diethylamine in 2 ml of ethanol was refluxed until the disappearance of the spot of the starting acetylene on a thin layer of aluminum oxide. The alcohol was then evaporated, 3 ml of ether was added, and the solution was chromatographed on $Al_2O_3$ in an ether—petroleum ether system (4:1) to give 0.35 g (87%) of a product with $n_D^{20}$

1.5342. IR spectrum (thin layer): 962, 977, and 1648 cm$^{-1}$ (C=C). PMR spectrum: 4.98, 7.24 (2H, J = 14.0 Hz, CH=CH); 4.25 (2H, $CH_2$); 1.46 ppm (3H, $CH_3$). Found %: C 55.8; H 8.5; N 36.9. $C_9H_{17}N_5$. Calculated %: C 55.6; H 8.7; N 35.9.

2-Ethyl-5-(2-piperidinovinyl)tetrazole (VIIIb), with $n_D^{20}$ 1.5581, was similarly obtained in 75% yield. IR spectrum (thin layer): 960, 970, and 1645 cm$^{-1}$ (C=C). PMR spectrum: 5.12, 7.14 (2H, J = 14.0 Hz, CH=CH); 4.44 (2H, $CH_2$); 1.46 ppm (3H, $CH_3$). Found %: C 57.9; H 8.1; N 33.9. $C_{10}H_{17}N_5$. Calculated %: C 58.2; H 7.8; N 33.8.

1-Phenyl-4-(2-ethyltetrazolyl)-1,2,3-triazole (IXa). A solution of 0.6 g (0.005 mole) of ethynyltetrazole VIb and 0.7 g (0.006 mole) of phenyl azide in 2 ml of toluene was refluxed until the spot of the starting acetylene VIb disappeared on a thin layer of aluminum oxide, after which 3 ml of ether was added, and the precipitated IXa was separated by filtration to give 0.7 g (59%) of a product with mp 94-95°C (from alcohol). Found %: C 54.9; H 4.6; N 40.5. $C_{11}H_{11}N_7$. Calculated %: C 54.8; H 4.6; N 40.7.

1-(2-Chloroethyl)-4-(2-ethyltetrazolyl)-1,2,3-triazole (IXb), with mp 90-91°C (from alcohol), was similarly obtained in 60% yield. PMR spectrum in $d_6$-acetone: 8.52 (1H, CH); 4.08, 4.64 (4H, $CH_2CH_2$). Found %: C 36.8; H 4.5; Cl 15.6; N 43.4. $C_7H_{10}ClN_7$. Calculated %: C 36.9; H 4.4; Cl 15.6; N 43.0. The reaction of tetrazolylethynyl ketone XIII with hydroxyethyl and chloroethyl azides by the same method gave 1-(2-hydroxyethyl)-5-benzoyl-4-(2-ethyl-5-tetrazolyl)-1,2,3-triazole (XVIa) [in 62% yield as an undistillable viscous liquid. IR spectrum (thin layer): 1575 (C=C) and 1667 cm$^{-1}$ (C=O). Found %: C 54.4; H 5.0; N 30.2. $C_{14}H_{15}N_7O_2$. Calculated %: C 53.7; H 4.8; N 31.3] and 1-(2-chloroethyl)-5-benzoyl-4-(2-ethyl-5-tetrazolyl)-1,2,3-triazole (XVIb) [in 56% yield as an undistillable viscous liquid. IR spectum (thin layer): 1580 (C=C) and 1660 cm$^{-1}$ (C=O). Found %: C 51.2; H 4.5; Cl 11.4; N 28.9. $C_{14}H_{14}ClN_7O$. Calculated %: C 50.7; H 4.2; Cl 10.6; N 29.6].

1-Diethylamino-3-(2-ethyltetrazolyl)-2-propyne (X). A suspension of 0.6 g (0.005 mole) of acetylene VIb, 0.2 g of paraformaldehyde, 0.4 g of diethylamine, and 0.01 g of cuprous chloride in 5 ml of dioxane was heated on a water bath for 1 h, after which it was cooled and treated with 4 ml of 10% hydrochloric acid. The mixture was extracted with ether, and the acidic aqueous layer was neutralized with sodium bicarbonate and extracted with ether again. The ether solution was washed with water and dried, and the ether was removed. The residue was distilled in vacuo to give 0.8 g (80%) of a product with bp 120-122°C (1 mm) and $n_D^{20}$ 1.4943. Found %: C 58.0; H 8.2; N 33.8. $C_{10}H_{17}N_5$. Calculated %: C 57.9; H 8.2; N 33.9.

1,4-Bis(2-ethyltetrazolyl)-1,3-butadiyne (XIa). A 0.02-g sample of cuprous chloride in 0.5 ml of pyridine was added to a solution of 1.2 g (0.01 mole) of ethynyltetrazole VIb in 15 ml of alcohol, and the mixture was stirred in an atmosphere of oxygen until the spot of the starting acetylene on a thin layer of aluminum oxide vanished. Water (5 ml) was added, and the precipitated crystals were removed by filtration to give 0.8 g (67%) of diacetylene XIa with mp 77°C (from methanol). Found %: C 50.1; H 4.5; N 46.6. $C_{10}H_{10}N_8$. Calculated %: C 49.5; H 4.1; N 46.3.

Similarly, the reaction of 2-methyl-5-ethynyltetrazole gave 1,4-bis(2-methyltetrazolyl)-1,3-butadiyne (63%) with mp 161°C. Found %: C 45.2; H 2.9; N 52.0. $C_8H_6N_8$. Calculated %: C 44.9; H 2.8; N 52.3.

1-Phenyl-3-(2-ethyltetrazolyl)prop-2-yn-1-one (XIII). A solution of 2.4 g (0.02 mole) of 2-ethyl-5-ethynyltetrazole in 5 ml of THF was added dropwise at 10°C to a Grignard reagent prepared from 0.5 g (0.02 mole) of magnesium and 3.5 g (0.03 mole) of ethyl bromide in 20 ml of THF, and the mixture was stirred for 2 h. A solution of 2 g (0.02 mole) of benzaldehyde in 3 ml of THF was then added dropwise, and the mixture was heated until it began to reflux gently. It was refluxed for 3 h, after which it was decomposed with a solution of ammonium hydroxide. The resulting mixture was extracted with ether, the solvent was removed by distillation, and the resulting oil was dissolved in dry ether. A 15-g sample of active manganese dioxide was added in portions to the ether solution, and the mixture was stirred for 2 h. The manganese dioxide was removed by filtration, and the residue was recrystallized from ethanol to give 1.5 g (34%) of ketone XIII with mp 60°C (from alcohol). IR spectrum (mineral oil): 1645 (C=O) and 2220 cm$^{-1}$ (C≡C). Found %: C 64.3; H 4.67; N 24.8. $C_{12}H_{10}N_4O$. Calculated %: C 63.8; H 4.4; N 24.7.

1-Phenyl-3-piperidyl-3-(2-ethyltetrazolyl)propyn-2-one (XIV). A 0.1 g sample of piperidine was added to a solution of 0.2 g (0.001 mole) of ketone XIII in 3 ml of ethanol, and the mixture was refluxed for 20 min. The solvent was removed in vacuo, and the residue was chromatographed on $Al_2O_3$ (elution with ether) to give 0.2 g (67%) of a viscous yellow oil. IR spectrum ($CCl_4$): 1573 (C=C) and 1650 $cm^{-1}$ (C=O). Found %: C 66.0; H 6.6; N 22.5. $C_{17}H_{21}N_5O$. Calculated %: C 65.6; H 6.7; N 22.5.

Similarly, the reaction of 0.2 g of ketone XIII and 0.1 g of hydrazine hydrate gave 0.15 g (60%) of 2-ethyl-5-(3-phenyl-5-pyrazolyl)tetrazole (XV) with mp 172°C (from alcohol). Found %: C 60.8; H 4.2; N 35.1. $C_{12}H_{12}N_6$. Calculated %: C 60.2; H 4.6; N 35.1.

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