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SYNTHESIS OF 1-(1,2,4-TRIAZOL-3-YL)-1,2,3-TRIAZOLES

G. I. Tsypin, T. F. Sharamet,
T. A. Kravchenko, and M. S. Pevzner

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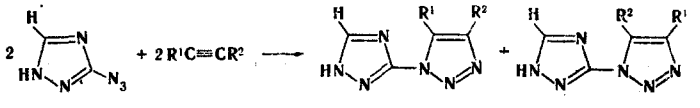
1-(1,2,4-Triazol-3-yl)-1,2,3-triazoles were obtained by 1,3-dipolar cycloaddition of 3-azido-1,2,4-triazole to acetylene derivatives.

1,3-Dipolar cycloaddition of organic azides to acetylene derivatives usually leads to the formation of substituted 1,2,3-triazoles. Aliphatic and aromatic azides have been investigated extensively as starting reagents in this reaction [1-6].

In the present research we have studied the possibility of subjecting heterocyclic azido compounds, particularly 3-azido-1,2,4-triazole, to this reaction. The reaction of the latter with a number of acetylene derivatives made it possible to obtain the corresponding 1-(1,2,4-triazol-3-yl)-1,2,3-triazoles (I-IV) (Table 1); the participation of monosubstituted acetylenes in the reaction led to the formation of two isomers, viz., Ia and Ib and IIIa,b-IVa,b.



I-V a I-V b

Ia,b $R^1=H$, $R^2=C_6H_5$; II $R^1=R^2=C_6H_5$; III a,b $R^1=H$, $R^2=HOCH_2$; IV a,b $R^1=H$, $R^2=CH_3OOC$; V $R^1=R^2=H$

In most cases we were able to separate the mixtures of isomers into individual compounds. Two-ring product V, which does not contain a substituent, was obtained by alkaline saponification of IVa and subsequent decarboxylation.

The structures of the isolated compounds were determined on the basis of the PMR spectra (Table 2). It is apparent from the spectral data presented in Table 2 that a change in the substituent in the ditriazolyl series has a slight effect on the chemical shift of the proton of the 1,2,4-triazole ring (δ_{CH} ranges from 8.90 to 9.08 ppm) because of the remoteness of this proton from the functional group in the 1,2,3-triazole ring.

The type of isomer (Ia or Ib) among the products of addition of the azide to phenylacetylene was easily established from the signal of the phenyl protons: in conformity with the data in [5-9], it is split in the case of 1,4-substituted 1,2,3-triazole Ia, whereas in the case of 1,5 isomer Ib it is recorded in the form of a singlet. Similar character of the signals of the phenyl groups is also observed in the spectrum of 1-(1,2,4-triazol-3-yl)-4,5-diphenyl-1,2,3-triazole (II).

The assignment of the chemical shifts in the PMR spectra of isomers IIIa,b and IVa,b was made on the basis of the general observation that the singlet of the proton bonded to the ring lies at weaker field in the spectra of 1,4-substituted 1,2,3-triazoles than in the spectrum of the corresponding 1,5 isomer [6]. This, as well as the data in [10], served as a basis for the interpretation of the spectrum of 1-(1,2,4-triazol-3-yl)-1,2,3-triazole (V).

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TABLE 1. Characteristics of 1-(1,2,4-Triazol-3-yl)-1,2,3-triazoles

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ia	255,5—256,5	56,5	3,9	39,8	$C_{10}H_8N_6$	56,6	3,8	39,6	28
Ib	162—163	56,5	3,7	39,5	$C_{10}H_8N_6$	56,6	3,8	39,6	15
II	257,5—258,5	66,4	3,8	29,4	$C_{16}H_{12}N_6$	66,6	4,2	29,2	17
IIIb	203—205	35,9	3,6	50,9	$C_5H_6N_6O$	36,2	3,6	50,6	40
IVa	214—215	37,3	2,9	43,6	$C_6H_6N_6O_2$	37,1	3,1	43,3	76
IV b	190—192	37,0	2,9	43,4	$C_6H_6N_6O_2$	37,1	3,1	43,3	3
V	237—238	35,1	2,7	61,5	$C_4H_4N_6$	35,3	3,0	61,7	43

TABLE 2. PMR Spectra and pK_a Values of 1-(1,2,4-Triazol-3-yl)-1,2,3-triazoles

Compound	R^1	R^2	Chemical shifts, δ, ppm			pK_a
			CH	R^1	R^2	
Ia	H	C_6H_5	9,00 s	9,35 s	7,53—8,25 m	7,62
Ib	H	C_6H_5	8,90 s	8,25 s	7,45 s	7,86
II	C_6H_5	C_6H_5	8,95 s	7,57 s	7,20—7,90 m	7,82
IIIa	H	$HOCH_2$	8,92 s	8,63 s	4,70 s	—
IIIb	H	$HOCH_2$	9,00 s	8,00 s	4,90 s	7,89
IVa	H	CH_3OOC	9,08 s	9,48 s	4,03 s	7,63
IVb	H	CH_3OOC	9,00 s	8,70 s	3,95 s	—
V a	H	H	8,95 s	8,85 br.s	8,12 br.s	7,74

The pK_a values presented in Table 2 demonstrate the insignificant effect of the type and position of the substituent in the 1,2,3-triazole ring on the acidic properties of the compounds obtained.

Methyl propiolate, as a representative of acetylenes with an "activated" bond, may, in addition to undergoing 1,3-dipolar cycloaddition [11, 12], add one or two molecules of the nucleophilic agent such as, for example, a heterocycle that contains a labile proton attached to a nitrogen atom [13, 14]. However, this sort of possibility is not realized in this case.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Perkin—Elmer R-12 spectrometer with hexamethyldisiloxane as the internal standard. The pK_a values were measured by potentiometric titration in 50% aqueous ethanol.

3-Azido-1,2,4-triazole was obtained by the method in [15].

Ditriazolyls Ia,b-IVa,b were synthesized by the following method. A mixture of 2 g (18 mmole) of 3-azido-1,2,4-triazole and the acetylene dipolarophile (36 mmole) was refluxed in 15 ml of dioxane (the reaction times were 67 h with phenylacetylene, 84 h with diphenylacetylene, 13 h with propargyl alcohol, and 10 h with methyl propiolate). The reaction mixtures were worked up as indicated below.

1-(1,2,4-Triazol-3-yl)-4-phenyl-1,2,3-triazole (Ia) and 1-(1,2,4-Triazol-3-yl)-5-phenyl-1,2,3-triazole (Ib). The solution was evaporated, and the residue was refluxed in 100 ml of ethyl acetate. The insoluble material was removed by filtration and crystallized from ethanol to give 1.09 g of Ia. The filtrate was evaporated, and the residue was refluxed in 50 ml of chloroform. The insoluble material was removed by filtration and crystallized from a mixture of ethyl acetate with chloroform to give 0.56 g of Ib.

1-(1,2,4-Triazol-3-yl)-4,5-diphenyl-1,2,3-triazole (II). The precipitate was removed from the reaction mixture by filtration and crystallized from ethanol to give 0.9 g of II.

1-(1,2,4-Triazol-3-yl)-5-hydroxymethyl-1,2,3-triazole (IIIb). The precipitate was removed from the reaction mixture by filtration and crystallized from aqueous ethanol to give 1.2 g of IIIb. The filtrate from the crystallization was evaporated, and the residue was

crystallized from aqueous ethanol to give 0.6 g of a mixture of IIIb with the corresponding 1,4 isomer IIIa. We were unable to isolate the latter in pure form.

1-(1,2,4-Triazol-3-yl)-4-carbomethoxy-1,2,3-triazole (IVa) and 1-(1,2,4-Triazol-3-yl)-5-carbomethoxy-1,2,3-triazole (IVb). The precipitate was removed from the reaction mixture by filtration and crystallized from aqueous ethanol to give 2.7 g of IVa. The filtrate from the crystallization was evaporated, and the residue was crystallized from the aqueous ethanol to give 0.25 g of a mixture of IVa and IVb. The mixture was separated by preparative TLC on plates with a loose layer of Silpearl UV-254 silica gel in an ethyl acetate–carbon tetrachloride system (4:1). Isomer IVa had R_f 0.22, and isomer IVb had R_f 0.39. The chromatograms were developed in UV radiation. Isomer IVb was crystallized from a mixture of ethanol with carbon tetrachloride; the yield was 0.1 g.

1-(1,2,4-Triazol-3-yl)-1,2,3-triazole (V). A 1-g (5 mmole) sample of IVa was added to a solution of 0.4 g (0.01 mole) of sodium hydroxide in 10 ml of water, and the mixture was refluxed for 5 h. It was then acidified with concentrated HCl, and the precipitate was removed by filtration and refluxed in 10 ml of dioxane for 5 h. The precipitate was removed by filtration and crystallized from aqueous ethanol to give 0.3 g of V.

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