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SYNTHESIS OF 1-ALKYL-4(5)-HYDROXYMETHYL-1,2,3-TRIAZOLES

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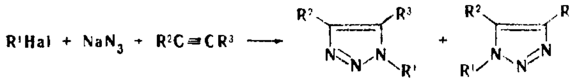
An in situ method for the synthesis of 1-alkyl-4(5)-hydroxymethyl-1,2,3-triazoles by the action of acetylenic alcohols with alkyl azides as the latter are formed from sodium azide and alkyl halides in dimethylformamide is proposed.

1-Alkyl-4(5)-hydroxymethyl-1,2,3-triazoles (I) are usually obtained by the reaction of acetylenic carbinols with various alkyl azides [1-4]. However, this reaction does not always give satisfactory results, particularly when lower alkyl azides are used. The cycloaddition of alkyl azides generally takes place during prolonged heating of the reaction mixture at 100-120°C, which is unacceptable for low-boiling azides. When the synthesis is carried out in an autoclave, the yields of lower N-alkyl-substituted triazoles do not exceed 20% [5]. The use of dimethylformamide (DMF) as the solvent markedly reduces the reaction time, but a diffucult-to-separate azeotropic mixture of alkyl azide and solvent is formed in this case.

In the present paper we present an in situ method for the synthesis of 1-alkyl-4(5)-hydroxymethyl-1,2,3-triazoles by the reaction of acetylenic alcohols with alkyl azides as the latter are formed from sodium azide and alkyl halides.



I a-j

I a $R^1=CH_3$, $R^2=H$, $R^3=CH_2OH$; b $R^1=C_2H_5$, $R^2=H$, $R^3=CH_2OH$; c $R^1=C_4H_9$, $R^2=H$, $R^3=CH_2OH$; d $R^1=C_7H_{15}$, $R^2=H$, $R^3=CH_2OH$; e $R^1=CH_2C_6H_5$, $R^2=H$, $R^3=CH_2OH$; f $R^1=C_7H_{15}$, $R^2=H$, $R^3=C(OH)(CH_3)_2$; g $R^1=C_7H_{15}$, $R^2=H$, $R^3=C(OH)(CH_3)_2$; h $R^1=C_4H_9$, $R^2=R^3=CH_2OH$; i $R^1=C_7H_{15}$, $R^2=R^3=CH_2OH$; j $R^1=CH_2C_6H_5$, $R^2=R^3=CH_2OH$

This method excludes the step involving the isolation and purification of the alkyl azides. The most effective solvents in this reaction are DMF and Carbitol [2-(2-ethoxyethoxy)ethanol]. Various alkyl halides react equally successfully, but alkyl chlorides are to be preferred, since the resulting sodium chloride precipitates. Sodium bromide and iodide are partially soluble in DMF and hinder the isolation of the desired reaction products. The yields of the triazoles depend to a considerable extent on the length of the alkyl substituent in the alkyl halide. The higher alkyl halides give higher yields of triazoles (see Table 1). Of all of the examined acetylenic alcohols, propargyl alcohol reacts more readily. Prolonged heating of the reaction mixture at high temperatures is required for the synthesis with butynediol.

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TABLE 1. 1-Alkyl-4(5)-hydroxymethyl-1,2,3-triazoles (Ia-j)

Compound	RHal:NaN$_3$:acetylenic alcohol molar ratio	Temp., °C	Time, h	bp, °C (mm)	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
Ia	2,5 : 1,2 : 1	50—60	18	160—182 (18)	41,7	6,6	37,0	$C_4H_7N_3O$	42,4	6,2	37,1	14
Ib	2 : 1,2 : 1	60—70	12	170—180 (3)	47,1	7,2	33,0	$C_5H_9N_3O$	47,2	7,0	33,0	29
Ic*	2 : 1,2 : 1	90—105	10	150—170 (3)	54,3	8,5	26,8	$C_7H_{13}N_3O$	54,1	8,3	27,0	76
Id	1,3 : 1,2 : 1	100—120	5	172—175 (3)	60,5	9,3	21,1	$C_{10}H_{19}N_3O$	60,9	9,6	21,3	90
Ie	1,3 : 1,2 : 1	110—120	3	192—207 (3)	63,6	5,5	22,8	$C_{10}H_{11}N_3O$	63,4	5,8	22,2	93
If	1,3 : 1,2 : 1	110—120	10	165—167 (1)	63,8	10,1	18,6	$C_{12}H_{25}N_3O$	64,0	10,2	18,6	53
Ig	1,3 : 1,2 : 1	110—120	12	180—184 (1)	66,7	6,8	19,5	$C_{12}H_{25}N_3O$	66,3	6,9	19,3	62
Ih	2 : 1,2 : 1	120—140	11	225—226 (4)	51,7	8,2	22,4	$C_8H_{15}N_3O_2$	51,8	8,1	22,7	66
Ii	1,3 : 1,2 : 1	120—130	8	240—245 (1)	57,9	9,3	18,5	$C_{11}H_{21}N_3O_2$	58,1	9,2	18,5	56
Ij*	1,3 : 1,2 : 1	120—130	9	240 (4)	60.2	5,9	19,1	$C_{11}H_{13}N_3O_2$	60,5	6,2	19,2	59

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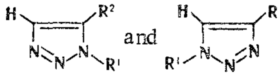
*The constants of the compounds obtained are in agreement with the literature data.

TABLE 2. PMR and IR Spectra of 1-Alkyl-4(5)-hydroxymethyl-1,2,3-triazoles (I)



Compound	PMR spectrum, δ, ppm			IR spectrum, ν, cm^{-1}	
	4-H	5-H	1,4:1,5 isomer ratio	triazole ring	OH
I a	7,78	7,42	65 : 35	910, 1060, 1450, 1570	3360
I b	7,89	7,58	55 : 45	910, 1070, 1480, 1580	3365
I c	7,98	7,68	62 : 38	908, 1070, 1470, 1570	3360
I d	7,96	7,62	60 : 40	910, 1070, 1450, 1580	3400
I e	7,98	7,68	55 : 45	910, 1070, 1460, 1580	3400

As in the case of the direct cycloaddition of alkyl azides to acetylenic alcohols, a virtually inseparable mixture of two regioisomers is formed as a result of the in situ synthesis. According to the data from the PMR spectra, the ratio of these products is close to unity (Table 2).

EXPERIMENTAL

The IR spectra presented in this paper were obtained with a UR-20 two-beam spectrometer. The PMR spectra were recorded with a Varian H-100 spectrometer with hexamethyldisiloxane as the internal standard.

1-Alkyl-4(5)-hydroxymethyl-1,2,3-triazoles. A 0.13-mole sample of the alkyl halide was added dropwise to a suspension of 0.12 mole of sodium azide and 0.1 mole of the acetylenic alcohol in 50 ml of DMF, and the mixture was stirred at 60-130°C for 3 to 18 h, depending on the starting reagents. It was then cooled and treated with 70 ml of absolute ether, and the precipitate was removed by filtration. The solvent was removed, and the residue was distilled in vacuo. The principal reaction conditions, constants, and analytical data for the triazoles obtained are presented in Tables 1 and 2.

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