TETRAZOLE DERIVATIVES. XII.* SYNTHESIS AND SOME PROPERTIES

OF 5-TETRAZOLYLHYDRAZONES

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UDC 547.796.1.07

A number of 5-tetrazolylhydrazones were synthesized and their physicochemical characteristics were studied.

5-Tetrazolylhydrazones are of interest in connection with the possibility of the preparation from them of a number of valuable products: formazans [2], tetrazolium salts [2], and stable free radicals — verdazyls [1]. We have accomplished the synthesis of a series of 5-tetrazolylhydrazones, derivatives of aliphatic and aromatic aldehydes, for the investigation of their structures and properties.

The hydrazones were synthesized by the method in [3], which we modified somewhat. Diazotization of 5-aminotetrazole (I) in acetic acid proceeds smoothly to give 1,3-di(5tetrazolyl)triazene (II), the reduction of which with stannous chloride gives a solution of 5-hydrazinotetrazole (III). The isolation of III in pure form is an extremely laborious procedure involving the initial preparation of benzaldehyde 5-tetrazolylhydrazone (VIII) and subsequent prolonged hydrolysis [4]. The high reactivity of III enabled us to accomplish the synthesis of a series of aryl-containing hydrazones (VIII-XIV) by reaction of the corresponding aldehydes with the reaction mixture obtained after reduction of triazene II.

 $\begin{array}{c|cccc} \mathbf{N}\mathbf{H}_{2} & \mathbf{H}\mathbf{N} & \mathbf{N} \\ \mathbf{N} \\ \mathbf{N} & \mathbf{N} \\ \mathbf{N} \\$

IV $R = CH_3$; V $R = n - C_3H_7$; VI $R = i - C_3H_7$; VII $R = CH = CH - C_6H_5$; VIII $R = C_6H_5$: IX $R = -3 - NO_2C_6H_4$; X $R = 4 - NO_2C_6H_4$; XI $R = 2 - OHC_6H_4$; XII $R = 4 - N(CH_3)_2C_6H_4$; XIII $R = -3.4 - (OCH_3)_2C_6H_3$; XIV $R = 3 - OCH_34 - OHCH_6H_3$

This method is also applicable for the preparation of aliphatic hydrazones IV-VI, but their high solubility in water hinders the isolation of the latter from the reaction mixtures. The aliphatic hydrazones were therefore obtained by condensation of the appropriate aldehydes with 5-hydrazinotetrazole dihydrochloride isolated by the method in [4].

All of the hydrazones are readily soluble in aqueous alkali due to the acidic hydrogen atom of the tetrazole ring. The pK_{α} values determined in 72% ethanol are linearly related to the Hammett σ constants in the case of arylhydrazones VIII-X, XII, XIII. The correlation parameters are $\rho = 0.56$ and r = 0.998. The existence of the linear relationship indicates retention of the same reaction center within the limits of the investigated series [5], and this excludes the existence of a tautomeric equilibrium of the 1-H $\stackrel{>}{\downarrow}$ 2-H type: (See following page for scheme).

*See [1] for communication XI.

Tyumen Industrial Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 850-854, June, 1975. Original article submitted April 4, 1974; revision submitted September 23, 1974.

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The electronic spectra (Table 1) of alkyl derivatives IV-VI are characterized by an absorption maximum at 245-247 nm, which corresponds to a $\pi \rightarrow \pi^*$ transition and is due to a considerable contribution of p,π -conjugation in the system of -N-N=C- bonds of the hydrazone fragment [6, 7]. The transition to aryl derivatives VII-XVI is accompanied by an increase in the intensity and a bathochromic shift of the absorption band at 285-350 nm, which is caused by conjugation of the -N=C- group with the aromatic ring. The spectra of the hydrazones in alkaline solution differ little from the spectra in ethanol, and this constitutes evidence for the formation in alkaline media of the corresponding monoanion due to detachment of a proton of the tetrazole ring (detachment of hydrogen from the exocyclic nitrogen atom would be accompanied by a considerable bathochromic effect). Thus the absorption maximum of benzaldehyde 1-methyl-5-tetrazolylhydrazone (287 nm in ethanol), for which salt formation in alkaline media is possible only through the hydrogen of the exocyclic nitrogen atom, is shifted to the long-wave region by 60 nm in alkaline media $(\lambda_{\max} \text{ in } 0.1 \text{ N NaOH } 347 \text{ nm})$. A similar effect is observed in the UV spectra of other heterocyclic hydrazones containing only an exocyclic acid hydrogen atom [8]. A knowledge of the structure of tetrazolyl-containing hydrazones in alkaline media is valuable for an understanding of the mechanism of their diazo coupling, which proceeds only in alkaline media [2].

The IR spectra of the hydrazones are characterized by strong absorption at $1630-1670 \text{ cm}^{-1}$ (C=N stretching vibrations of the hydrazone fragment [9] and vibrations of conjugated C=N and N=N bonds of the tetrazole ring [10]). In a number of cases these bands are resolved (IV, V, and VII), but more often they are overlapped. It may be assumed that the higher-frequency and more intense band belongs to the vibrations of the hydrazone C=N group. The characteristic absorption of the tetrazole ring appears at 1030-1100 cm⁻¹ which indicates the l-H structure of the hydrazones [10] (structure a).

Most of the hydrazones display a series of bands of medium intensity at 2850-3270 cm⁻¹ in the region of stretching vibrations of the NH group. The same absorption is also observed in the case of tetrazole-ring-methylated hydrazone XVI. In this connection, it may be assumed that the observed absorption in the spectra of the hydrazones is associated to a considerable degree with vibrations of the associated exocyclic NH group. However, the absorption of the ring NH group, which is usually observed in the spectra of tetrazole derivatives at 2500-2950 cm⁻¹ [10], does not appear in the spectra of most of the investigated hydrazones, and this may be a consequence of the formation of an intramolecular hydrogen bond (IHB) (it is known [11, 12] that weak absorption at 3030-3100 cm⁻¹ is observed when an IHB of the $\sum_{N=H=N^2}$ type is present) [11, 12].

HN - N = CH - R $N = \frac{V^{C} - N}{N}$

Unfortunately, the low solubility of the hydrazones in suitable solvents does not make it possible to investigate their IR spectra in solutions.

EXPERIMENTAL METHOD*

The IR spectra of KBr pellets (2 mg of the substance/800 of KBr) were recorded with a UR-20 spectrometer. The UV spectra of solutions in 95% ethanol were recorded with an SF-4A spectrophotometer. The pK_{α} values were determined in 72% (by weight) ethanol with an LPM-60M apparatus by the method described in [2].

Benzaldehyde Tetrazolylhydrazone (VIII). A solution of 13.8 g (0.2 mole) of sodium nitrite in 120 ml of water was added with vigorous stirring in the course of 2-2.5 h to a cooled (3-5°) suspension of 42.1 g (0.4 mole) of 5-aminotetrazole monohydrate in 120 ml of water and 80 ml of acetic acid. A copious yellow precipitate of 1,3-di(5-tetrazoly1)triazene (II) formed during the diazotization. The reaction mixture was maintained at

*With the participation of L. I. Korobotova and L. A. Loginova.

	Yield,		86	75	81	87	61	60	61
	рKa		7,40	7,36	7,48	7,12	7,10	6,76	6,65
trum. cm ⁻¹	$v_{N \text{ FI}}$ $v_{C=N}$, tetrazole $v_{C=N}$, ting $v_{N=N}$ vibra- tions		m 0901 1060 s	1095 m 1060 s	1110 m 1060 s	1105 m 1060 m	1054 s 1043 s	1110 m 1060 s 1040 m	1110 m 1050 m
			1660 s 1640m c	1670 s 1630 m	1640 s	1659 s c 1645 s c	1642 s	1640 s	1640 m
IR spec			270 w 3160 m 8045 s 2965 m 870 w	2975 s 2890 m	208 s 3120 m 6020 w 2980 w 890 w 2755 w 7700 w, 2660 w	6030 m 2975 m 870 m	1188 m 3095 w 1065 w 3018 m 1963 w 2856 m	2200 m 3090 s 030 m 2966 m 2865 m 2966 m	3310 m 3250 m 3040 m 2940 m 2880 m
	ethanol 0,1 N NaOH	lg e	3,95	4,06	4,20	4,76	4,63	4,50	4,47
ectrum		λ_{max} , nm	235	240	240	330	309	305	243 370
UV sp		lg e	3,86	4,09	3,97	4,13 4,66	4,29	4,21	4,15 4,33
		λ _{m a} x. nm	245	245	247	237 322	<220 295	<220 305	235 350
	% calc.		66,6	54,5	54,5	39,2	44.7	42,0	42,0
	ż	found	66,4	54,6	54,3	39,0	44,5	41,7	42,5
	Empirical formula		C ₃ H ₆ N ₆	C5H10N6	C5H10N6	$C_{10}H_{10}N_6$	C ₈ I1 ₈ N ₆	C ₈ H ₇ N ₇ O ₂	C ₈ H ₇ N ₇ O ₂
	mp, °C (dec.) ^a		180	167	173	209	232 (235 ⁴)	233 (250 ¹³)	231
	× .		CH ₃	n-C ₃ H ₇	i-C ₃ H ₇	CH=CHC ₆ H ₅	C ₆ H ₅	3-NO ₂ C ₆ H,	4-NO ₂ C ₆ H ₄
_	Com- pound		IV	>	N	ΝΛ	IIIV	X1	×

TABLE 1. 5-Tetrazolylhydrazones

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53	55	47	54	95	72
	7,35	7,23	I	I]
1090 m 1060 m	1110 m 1050 s	1105 m 1070 s 1030 s	1110 m 1060 m 1040 m	1070 m 1035 s	1096 s 1074 m
1640 s	1645	1645	1650 s	1635 s	1642 \$
3504 s (OH), 3220 m 3130 m 3030 s 2980 m 2880 m 2820 w	3210 m 3110 m 3025 s 2960 s 2860 m	3210 m 3110 m 3005 s 2970 s 2850	3510 m (OH), 3220 m 3130 s 3030 s 2980 m 2880 m	3250 s 3070 m 2875 m 2800 w 2760 w 2675 m	3262 w 3190 s 3068 w 3015, 2935 w 2878 m 2780 w
4,26	4,49	4,23	4,50	4,24	4,39
290 345	320	315	321	285	347
4,23	3,99 4,32	4,40	4,31 4,32	3,99	4,17
<220 300 325	225 330	<220 300 317	<220 296 320	285	287
33,6	42,4	33,8	35,9	41,6	41,6
33,6	42,9	33,4	36,0	41,7	41,5
C ₂ H ₅ N ₆ O · • C ₂ H ₅ OH b	C ₁₀ H ₁₃ N ₇	$C_{10}H_{12}N_6O_2$	C ₉ H ₁₀ N ₆ O ₂	C ₉ H ₁₀ N ₆	C ₉ H ₁₀ N ₆
215 (212 ¹³)	215	220 (217 ¹³)	210 (212 ¹³)	243 (235 ¹⁴)	206 (without decomposi- tion)(209 ¹⁵)
2-OHC ₆ H ₄	4-N (CH ₃) ₂ C ₆ H ₄	3,4- (OCH ₃) ₂ C ₆ H ₃	3-0CH ₃ , 4-0HC ₆ H ₃	Acetophenone 5- tetrazolylhy- drazone	Benzaldehyde 1- methyl-5-tetra- zolylhydrazone
IX	ШХ	IIIX	XIX	XV	IVX

a) Compounds IV and VI were recrystallized from isopropyl alcohol, V was recrystallized from 50% ethanol, IX was recrystallized from dimethylformamide water (2:1), and the remaining compounds were recrystallized from ethanol; b) Found: C 47.7; H 6.0%. Calculated: C 48.0; H 5.6%; c) Shoulder.

room temperature for 2 h, after which it was filtered. Crude II* was added in small portions to a solution of 90.4 g (0.4 mole) of $SnCl_2 \cdot 2H_2O$ in 500 ml of concentrated HCl, and the mixture was stirred at 35° for 2 h. It was then filtered, 20.3 ml (0.2 mole) of benzaldehyde was added to the filtrate, and the mixture was stirred for 1 h and filtered. The solid was washed successively with concentrated HCl, water, and alcohol, and dried. Hydrazones IX-XIV were similarly obtained. In the synthesis of IX, X, and XII-XIV the appropriate aldehyde was dissolved beforehand in alcohol.

<u>Acetaldehyde 5-Tetrazolylhydrazones (IV).</u> A 5.2-g (0.03 mole) sample of 5-tetrazolylhydrazone dihydrochloride, obtained by hydrolysis of hydrazone VIII by the method in [4], was dissolved by heating in 100 ml of water, after which 8.1 g (0.06 mole) of CH_3COONa · $3H_2O$ and 2.6 ml (0.45 mole) of freshly distilled acetaldehyde were added, and the mixture was maintained at 100° for 30 min. It was then concentrated to half its original volume, the concentrate was cooled, and the resulting IV was removed by filtration. Hydrazones V-VII and XV were similarly obtained (see Table 1).

<u>Benzaldehyde 1-Methyl-5-tetrazolylhydrazone (XVI)</u>. A 2.1-ml (0.022 mole) sample of dimethyl sulfate was added dropwise at $20-25^{\circ}$ to a solution of 3.76 g (0.02 mole) of hydrazone VIII in 60 ml of 5% Na₂CO₃, and the mixture was stirred for 30 min. The resulting precipitate was removed by filtration and recrystallized successively from chloroform and ethanol to give long rectangular plates.

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*Triazene II is an unstable product, and it is therefore better to use it immediately.