cm^{-1} (amide NH). UV spectrum, λ_{max} (log ε): 200 (4.15), 225 (4.53), 250 (4.34), and 310 nm (4.06). Found: C 62.4; H 5.3; N 8.4; S 9.9%. $C_{17}H_{16}N_2O_3S$. Calculated: C 62.2; H 4.9; N 8.5; S 9.8%.

8-Acetyl-1,2-dihydroindolo[3,2-b]indolo[1,7a,7-ab][1,5]diazepin-3(4H)-one (IIIc). This compound was obtained from 1-nitroso-2,3-dihydro[1,5]benzodiazepin-4-one and N-acetylindoxyl by a method similar to that used to prepare IIc. Workup gave a product with mp > 300°C (from acetic acid) in 12% yield. IR spectrum: 1650, 1685 (C=O); 3100, 3200 cm^{-1} (amide NH). Found: C 71.8; H 4.5; N 13.3%. $C_{19}H_{13}H_3O$. Calculated: C 71.9; H 4.8; N 13.2%.

2,3-Dihydroindolo[3,2-b]indolo[1,7a,7-ab]pyridine (IVa). Compound IIIa was obtained from 1-amino-1,2,3,4-tetrahydroquinoline and N-acetylindoxyl by a method similar to that used to prepare IIIa. The precipitated IIIa (1.33 g) was treated with 2.28 g (0.04 mole) of potassium hydroxide in 10 ml of methanol, and the mixture was refluxed for 10 min. It was then cooled and diluted with 30 ml of water to give 0.8 g (71%) of a product with mp 167-169°C (from dioxane). IR spectrum: 3380 cm^{-1} (indole ring NH). UV spectrum, λ_{max} (log ε): 213 (4.22), 240 (4.24), 264 (4.66), and 327 nm (4.33). Found: C 83.3; H 5.7; N 11.3%. $C_{17}H_{14}N_2$. Calculated: C 82.9; H 5.7; N 11.4%.

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INVESTIGATION OF THE REACTIVITIES AND TAUTOMERISM OF AZOLIDINES. 41.* "ANOMALOUS" PRODUCTS OF AMINOMETHYLATION OF 2-IMINOTHIAZOLIDIN-4-ONE WITH AQUEOUS FORMALDEHYDE AND PRIMARY AMINES

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The corresponding thiazolo[3,2-a]-1,3,5-triazines, which are substituted in the $C_{(7)}$ position of the condensed heterocyclic system, are formed as a result of aminomethylation of 2-iminothiazolidin-4-one with aqueous formaldehyde and several primary aliphatic amines. A 2,3-bis(aminomethyl)derivatives is formed when o-iodoaniline is used as the amino component.

In [1] we showed that the aminomethylation of 2-iminothiazolidin-4-one (Ia) and several of its 5-substituted derivatives with primary amines in the presence of an approximately threefold excess of formaldehyde leads to the formation of the corresponding 6-oxo-2,3,4,5,6,-7-hexahydrothiazolo[3,2-a]-1,3,5-triazines (II, R^3 = Alk, Ar; $R^1 = R^2 = H$, $R^1 = R^2 = CHAr$). Continuing our study of this reaction, we established that, in addition to the expected

*See [1] for Communication 40.

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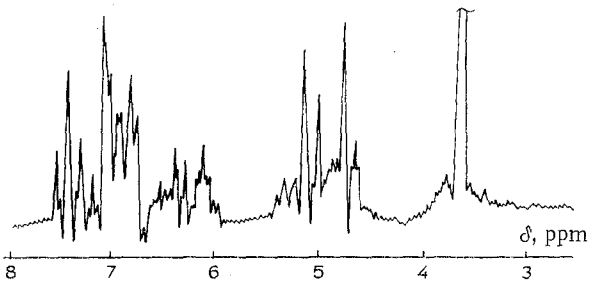


Fig. 1. PMR spectrum of III in $CDCl_3$ (100 MHz).

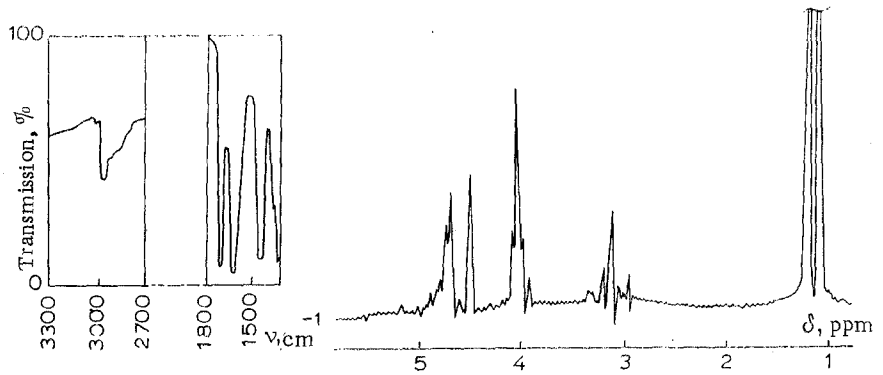
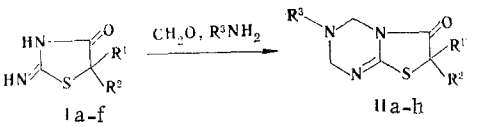


Fig. 2. IR spectrum (in perfluorinated mineral oil) and PMR spectrum (in $CDCl_3$, 100 MHz) of IIi.

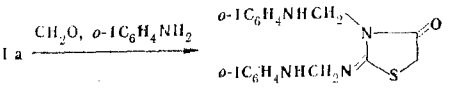
thiazolo[3,2-a]triazines (IIa-e), "anomalous" aminomethylation products are formed in some cases.



I a-f II a-h

I a $R^1=R^2=H$; b $R^1=H$, $R^2=CH_3$; c $R^1=H$, $R^2=C_2H_5$; d $R^1—R^2=CHC_6H_4Cl$-*p*; e $R^1—R^2=CHC_6H_4Br$-*p*; f $R^1—R^2=CHC_6H_4F$-*p*; II a $R^1=H$, $R^2=C_2H_5$, $R^3=C_6H_5$; b $R^1=H$, $R^2=C_2H_5$, $R^3=\beta$-naphthyl; c $R^1—R^2=CHC_6H_4Cl$-*p*, $R^3=C_6H_5$; d $R^1—R^2=CHC_6H_4Br$-*p*, $R^3=C_6H_5$; e $R^1—R^2=CHC_6H_4F$-*p*, $R^3=C_6H_5$; f $R^1=CH_2OH$, $R^2=CH_3$, $R^3=C_6H_5$; g $R^1=R^2=CH_2OH$, $R^3=t$-Bu; h $R^1=R^2=CH_2OH$, $R^3=C_6H_5CH_2$

Two-ring structures are not formed when o-substituted anilines are used as the amino component. We were unable to isolate a product of the reaction with o-chloroaniline, although, according to the data from thin-layer chromatography (TLC), it is present in the reaction mixture. Aminomethylation with o-iodoaniline leads to the formation of bis(aminomethyl) derivative III, for which cyclization to form a triazine ring is probably impossible because of considerable steric hindrance.



III

Two groups of signals, the multiplicities of each of which are characteristic for an A_2B system, are present in the PMR spectrum of III (Fig. 1). The signals of the protons of of the CH_2NH fragments may be of the A_2B form under the condition that the NH protons undergo slow exchange [2]. In our case the satisfaction of this condition is extremely likely, inasmuch as association with participation of the NH groups should be slight as a consequence of steric hindrance. The form of the spectrum does not change when D_2O is added to an ampul containing a sample of III, but the signals of the NH protons vanish when trifluoroacetic acid is added, and the character of the splitting of the signals of the CH_2 protons changes. The two narrow bands in the IR spectrum of III at 3370 and 3425 cm^{-1} are due to the stretching vibrations of unassociated NH groups [2].

TABLE 1. 6-Oxo-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazines

Compound	mp, °C	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}		PMR spectrum ppm		Found, %		Empirical formula	Calc., %		Yield, %
			C=O	C=N	2-H	4-H	N	S		N	S	
IIa	107	236 (4,21)	1715	1630	5,17	4,87	16,0	12,4	$C_{13}H_{15}N_3OS$	16,1	12,3	74
IIb	102	215 (4,89), 241 (4,98)	1700	1635, 1620, 1545	5,28	4,97	13,6	11,2	$C_{17}H_{17}N_3OS$	13,5	10,3	68
IIc	184	235 (4,36), 335 (4,51)	1710, 1680	1640	5,34	4,99	11,8	10,0	$C_{18}H_{14}ClN_3OS$[a]	11,8	9,0	76
IId	185	237 (4,26), 335 (4,53)	1710	1630	5,35	5,00	10,4	9,0	$C_{18}H_{14}BrN_3OS$[b]	10,5	8,0	90
IIe	178	235 (4,24), 330 (4,43)	1700	1630	5,31	4,99	12,3	9,9	$C_{18}H_{14}FN_3OS$[b]	12,4	9,5	83
IIf	154	235 (4,14)	1700	1615	5,10	4,85	15,5	11,4	$C_{13}H_{15}N_3O_2S$	15,2	11,5	91
IIg	159	219 (4,12)	1710	1630, 1625	4,92	4,66	15,4	11,4	$C_{11}H_{19}N_3O_3S$	15,4	11,7	22
IIh	136—138	210 (4,21)	1720	1635	4,49	4,35	14,1	10,1	$C_{14}H_{17}N_3O_3S$	13,7	10,4	28
IIi	126—127	217 (4,05)	1710	1635	4,79	4,52	16,6	9,9	$C_{16}H_{28}N_4O_2S$	16,4	9,4	12

[a]Found: Cl 10.0%. Calculated: Cl 10.0%. [b]Found: Br 20.8%. Calculated: Br 20.0%. [c]Found: F 5.2%. Calculated: F 5.6%.

In the aminomethylation of some derivatives of Ia in hydroxy-containing solvents products of hydroxymethylation at the $C_{(5)}$ position of the thiazoline ring were isolated from the reaction mixture instead of the expected Mannich bases [3]. In a number of cases, in addition to aminomethylation, which involves the amidine part of the Ia, b molecules, one observes hydroxymethylation in the $C_{(5)}$ position, as a result of which "mixed" aminomethyl-hydroxymethyl derivatives IIf-h are formed.

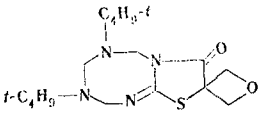
Compound IIf was isolated from the reaction mixture by aminomethylation of 2-imino-5-methylthiazolidin-4-one (Ib) with aniline in the presence of a fivefold excess of formaldehyde. Compounds IIg, h were obtained in the aminomethylation of Ia with tert-butylamine and benzylamine. The formation of a triazine ring is confirmed by the presence of signals of protons of 2- and 4-CH_2 groups in the PMR spectra of IIf-h (see Table 1). The triplet of hydroxy protons is due to vicinal spin-spin coupling with the methylene protons owing to retarded exchange because of the participation of the hydroxy group in a weak intramolecular hydrogen bond (IMHB) or (and) a hydrogen bond (HB) with the solvent. The nonequivalence of the methylene protons of the hydroxymethyl group in IIf can be explained by the presence of a chiral center.

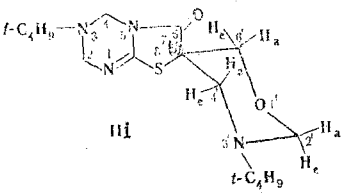
We assigned the narrow intense band at 3490 cm^{-1} in the IR spectrum of a crystalline sample of IIg to the stretching vibrations of a hydroxy group participating in the formation of a weak intramolecular hydrogen bond [2]. The two intense broad bands at 3310 and 3110 cm^{-1} belong to the vibrations of associated hydroxy groups. The IR spectrum in the region of the vibrations of C=O and C=N bonds and the UV spectrum of IIg are similar to the spectra of methylated derivatives of Ia with a fixed imino structure in which the nitrogen—carbon bond is located outside of the ring [4]. A derivatographic study showed that a weight loss, which is accompanied by an endothermic heat effect, begins to occur in a sample of IIg at temperatures above 140°C; however, the visually determined melting point of 159-160°C corresponds to the projection of the final point of the enthalpy peak onto the temperature curve.

Compound IIh has an IR spectrum that is similar to that for IIg, except for the fact that the high-frequency band at 3490 cm^{-1} is absent. The multiplet at 3.75-3.80 ppm in the PMR spectrum of IIh belongs to the protons of the methylene group of the benzyl group (3.75 ppm) and the methylene protons of two hydroxymethyl groupings, the signals of which are split by the vicinal hydroxy protons. The triplet of hydroxy protons (5.60 ppm, J = 5 Hz) and splitting of the methylene protons of the hydroxymethyl groups vanish when D_2O is added.

The masses of the molecular ions in the mass spectra of IIg, h correspond to their compositions. "Low-melting" IIi was also isolated from the reaction mixture in the aminomethylation of Ia with tert-butylamine. The mass of its molecular ion, which was found from the high-resolution mass spectrum with 3-methyl-6-oxo-7-(p-bromobenzylidene)-2,3,4,5,6,7-

hexahydrothiazolo[3,2-a]triazine [1] (M 338.23) as the internal standard, is 340 amu. Bands that might have been assigned to the vibrations of NH and OH bonds are absent in the IR spectrum of IIi (Fig. 2), but, in other respects, it is similar to the IR spectrum of "high-melting" product IIg. The UV spectrum of IIi changes with time, which constitutes evidence for decomposition of the compound under spectrophotometric conditions. Of the two possible isomeric structures, viz., thiazolotetraazocine-spiro-oxetane and thiazolotriazine-spiro-oxazine, the latter is in greater agreement with the observed character of the PMR spectrum.





IIi

Four signals that lie in the region of the resonance of the methylene protons have a multiplet structure (Fig. 2), and the intensity ratio is 3H:2H:3H:2H. Two signals of methyl protons with intensities of 9H each belong to two nonequivalent tert-butyl groups. The form of the PMR spectrum does not change when D_2O is added to a solution of IIi in $CDCl_3$. As in the case of IIg, we assigned the signals at 4.79 and 4.52 ppm to the resonances of the protons of the methylene groups of the triazine ring. The quartet [3.02, 3.13, 3.20, and 3.31 ppm (2H)] at weak field belongs to the axial and equatorial protons of the $C_{(7)}$—CH_2—N group of the oxazine ring. The splitting may be due both to the effect of the diamagnetic anisotropy of the bonds of the oxazine ring, which exists in a rigid hindered chair conformation [2, 5], and to the different degree of shielding of the carbonyl group in the β position with respect to the methylene group under consideration. The resonance at 3.96 ppm should be assigned to the O—CH_2—N group of the oxazine ring, for which a significant difference in the chemical shifts of the axial and equatorial protons is impossible for the conformation depicted in Fig. 2.* The split signal, which is superimposed on the resonances at 4.79 and 3.96 ppm, is then related to the resonance of the H_e and H_a protons of the $C_{(7)}$—CH_2—O group. The marked difference in the chemical shifts of these protons is due to the manifestation of the diamagnetic anisotropy of the carbonyl group owing to the peculiar geometry of the molecule. This assignment, however, is not indisputable, inasmuch as a boat conformation may prove to be energetically favorable for the oxazine ring [5, 6]. The signal at 3.96 ppm is then due to the resonance of the $C_{(7)}$—CH_2—O protons, which is extremely likely in analogy with IIg, whereas the separate signals, which are superimposed on the resonances at 4.79 and 3.96 ppm, belong to the H_e and H_a protons of the O—CH_2—N group, which should be located close to the carbonyl oxygen atom in the case of a boat (or distorted boat [5]) conformation.

According to TLC data, "high-melting" product IIg is not formed in the hydrolysis of the "low-melting" IIi by refluxing in water for 1 h; a spot of starting thiazolidone Ia is also is not observed in the hydrolysis of both IIg and IIi. Both IIg and IIi are stable when they are refluxed in ethanol for several minutes.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with Tesla BS-467 (60 MHz), Tesla BS-487C (80 MHz), and Tesla BS-497C (100 MHz) spectrometers with hexamethyldisiloxane as the internal standard. The PMR spectra of solutions of IIb-h (in d_6-DMSO), IIa, i (in $CDCl_3$), and IIf and III (in $CDCl_3$ and d_6-DMSO) were recorded at operating frequencies of 60 MHz [IIa, b, f (d_6-DMSO) and IIh and III (d_6-DMSO) [sic]], 80 MHz [IIc-e, f ($CDCl_3$)], and 100 MHz [IIg, i and III ($CDCl_3$)]. The IR spectra of suspensions of the compounds in mineral oil and perfluorinated mineral oil were recorded with an IKS-29 spectrometer. The UV spectra of solutions in ethanol were recorded with an SF-16 spectrophotometer. The molecular masses were determined with MKh-1303 and MKh-1320 spectrometers with a system for direct introduction of the samples; the ionizing voltages were 15 and 70 eV, and the temperature of the input system was 30-40°C below the melting points of the samples. The derivatogram was recorded with the derivatograph of the Paulik—Paulik—Erdey system; the sample weight was 25 mg, the time required for one revolution of the drum was 100 min, the DTA, DTG, and TG sensitivities were 1/3, 1/30, and 50 mg, respectively, the heating rate was 8 deg/min, and the standard was Al_2O_3. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates

*The tert-butyl group is equatorially oriented [5].

by elution with ethanol–chloroform (1:4 for IIa-g, i and 1:10 for III) and acetone–hexane (1:2 for IIh). The following solvents were used to recrystallize the compounds obtained: benzene–hexane (2:1 for IIa-f), benzene–hexane (1:5 for IIi), and benzene (for IIg, h and III).

3-β-Naphthyl-6-oxo-7-ethyl-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine (IIb) and 3-Phenyl-6-oxo-7-arylidene-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazines (IIc-e). These compounds were obtained as a result of aminomethylation of 2-iminothiazolidin-4-one (Ia) by the method in [1], except that the reaction mixture was refluxed for 1 h in the preparation of IIc-e.

3-Phenyl-6-oxo-7-ethyl-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine (IIa). A mixture of 1.4 g (0.01 mole) of 1-imino-5-ethylthiazolidin-4-one, (Ic), 0.93 g (0.01 mole) of aniline, and 4 ml (∿0.05 mole) of formalin in 30 ml of ethanol was stirred for 30 min until starting thiazolidone Ic had dissolved completely. Compound IIa began to precipitate after the wall of the beaker was rubbed with a glass rod; the precipitate was removed by filtration after 4 h.

3-Phenyl-6-oxo-7-methyl-7-hydroxymethyl-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine (IIf). A 2.6-g (0.02 mole) sample of 2-imino-5-methylthiazolidin-4-one (Ib) and 1.9 g (0.02 mole) of aniline were refluxed in 8 ml (∿0.10 mole) of formalin in 30 ml of ethanol for 5 min until starting Ib dissolved, after which heating was discontinued, and the reaction mixture was allowed to evaporate freely overnight. After evaporation of the solvent, the oily residue was dissolved in 25 ml of benzene, and the wall of the beaker containing the solution was rubbed with a glass rod. After ∿5 min, IIf precipitated. PMR spectrum ($CDCl_3$, 80 MHz): 6.88-7.33 (5H, m, aromatic protons); 5.10 (2H, s, 2-CH_2); 4.85 (2H, s, 4-CH_2); 4.10 (1H, OH); 3.90, 3.75, 3.55, and 3.40 [2H, $C_{(7)}$–CH_2]; 1.46 ppm (3H, s, CH_3). PMR spectrum (d_6-DMSO, 60 MHz): 6.70-7.32 (5H, m, aromatic protons); 5.52, 5.43, and 5.33 (1H, OH); 5.07 (2H, s, 2-CH_2); 4.80 (2H, s, 4-CH_2); 3.55, 3.48, 3.45, and 3.40 [2H, $C_{(7)}$–CH_2]; 1.32 ppm (3H, s, CH_3).

3-tert-Butyl-6-oxo-7,7-bis(hydroxymethyl)-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine (IIg). A mixture of 4.6 g (0.04 mole) of Ia, 2.9 g (0.04 mole) of tert-butylamine, and 14.4 ml (∿0.18) of formalin was stirred at room temperature for 30 min, after which the mixture was treated with three 20-ml portions of benzene. The IIg that precipitated from the aqueous layer after several hours was removed by filtration and washed with hexane. PMR spectrum (with hexamethyldisiloxane as the external standard): 5.64 (2H, t, J = 5 Hz, OH); 4.92 (2H, s, 2-CH_2); 4.66 (2H, s, 4-CH_2); 3.94 and 3.88 [4H, $C_{(7)}$–CH_2]; 1.34 ppm (9H, s, tert-Bu).

3-Benzyl-6-oxo-7,7-bis(hydroxymethyl)-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine (IIh). A 23.-g (0.02 mole) sample of Ia, 3.2 g (0.03 mole) of benzylamine, and 8 ml (∿0.10 mole) of formalin were stirred in 30 ml of ethanol for ∿1 h (until Ia disappeared), after which the ethanol was removed by distillation, and the residue was treated with warm (30-40°C) benzene (three 20-ml portions). The benzene extract was dried with sodium sulfate, the benzene was removed by distillation, and a viscous white oil, which solidified upon trituration, was precipitated by means of hexane. If the oil did not solidify, the hexane was decanted, and reprecipitation was repeated. PMR spectrum: 7.50 (5H, m, C_6H_5), 5.60 (2H, t, J = 5 Hz, OH), 4.49 (2H, s, 2-CH_2), 4.35 (2H, s, 4-CH_2), 3.80 [4H, d, J = 5 Hz, $C_{(7)}$–CH_2], and 3.75 ppm [2H, s, $C_{(3)}$–CH_2].

2-(o-Iodoanilinomethylimino)-3-(o-iodoanilinomethyl)thiazolidin-4-one (III). A mixture of 4.6 g (0.04 mole) of Ia, 8.8 g (0.04 mole) of o-iodoaniline, and 16 ml (∿0.20 mole) of formalin in 60 ml of ethanol was stirred for 30 min, after which the reaction mixture was allowed to stand for 24 h. The precipitated III was removed by filtration and crystallized from benzene to give 7.4 g (32% with respect to Ia) of a product with mp 140°C. IR spectrum: 3425, 3370 (NH); 1730 (C=O); 1635 cm^{-1} (C=N + Het). UV spectrum (in ethanol), λ_{max} (log ε): 215 (4.78) and 243 nm (4.44). PMR spectrum (d_6-DMSO): 6.25-7.65 (8H, m, aromatic protons), 5.50 [1H, q, $N_{(2')}CH_2NH$], 5.13 [2H, t, J = –8.2 Hz, $N_{(2')}CH_2NH$], 4.93 [1H, q, $N_{(3)}CH_2NH$], and 4.76 ppm [2H, t, J = –6.7 Hz, $N_{(3)}CH_2NH$]. Found: I 44.4; N 10.0; S 6.3%; M 500 (by reverse ebullioscopy, dichloroethane). $C_{17}H_{16}I_2N_4OS$. Calculated: I 43.9; N 9.7; S 5.6%; M 578.21.

3-tert-Butyl-6-oxo-2,3,4,5,6,7-hexahydrothiazolo[3,2-a]-1,3,5-triazine-7-spiro-5'-(3'-tert-butyltetrahydro-1',3'-oxazine) (IIi). A 4.6-g (0.04 mole) sample of Ia, 2.9 g (0.04

mole) of tert-butylamine, and 14.4 ml (∿0.18 mole) of formalin was stirred at room temperature for 30 min, after which the mixture was extracted with benzene (three 20-ml portions). The benzene extract was dried with sodium sulfate, the benzene was removed by distillation, and IIi was precipitated from the residue by means of hexane. PMR spectrum: ∿4.79 (1H, m, 6'-CH_2); 4.79 (2H, s, 2-CH_3); 4.52 (2H, s, 4-CH_2); ∿3.96 (1H, m, 6'-CH_2); 3.96 (2H, s, 2'-CH_2); 3.02, 3.13, 3.20, 3.31 (2H, 4'-CH_2); 1.18 (9H, s, tert-Bu); 1.08 ppm (9H, s, tert-Bu).

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PRODUCTS OF TRANSFORMATION OF ALDEHYDE BENZAZOLYLHYDRAZONES IN ACETIC ACID IN THE PRESENCE OF n-AMYL NITRITE

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The reaction of aldehyde benzazolylhydrazones with amyl nitrite in acetic acid leads to an oxidative transformation to give N,N'-diacyl derivatives of 2-hydrazinobenzazoles rather than to nitrosation of the hydrazones, whereas in the case of benzaldehyde benzothiazolylhydrazone it leads to 1,4-dibenzothiazolyl-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine.

The nitrosation of aldehyde benzothiazolyl- and benzimidazolylhydrazones with n-amyl nitrite in alkaline and neutral media leads to the formation of the corresponding azo ketoximes [1]. However, some hydrazones, such as benzaldehyde benzothiazolylhydrazone, cannot be subjected to reaction under these conditions. At the same time, it is known that under the influence of a nitrosating agent in acetic acid arylhydrazones give nitroso products, which undergo isomerization to arylazo ketoximes [2].

In this connection, we investigated the reaction of benzazolylhydrazones I-III (see the scheme) with amyl nitrite in acetic acid. Instead of the expected oximes, we obtained compounds, the formation of which can be explained by transformations with the participation of n-amyl nitrite as an oxidizing agent rather than as a nitrosating agent. It is known [3, 4] that the oxidation of monosubstituted hydrazones proceeds in extremely diverse ways. Depending on the electronic properties of the substituent in the hydrazone molecule and the nature of the oxidizing agent and the solvent, the following products may be obtained: azo hydroxyperoxides, azo acetates, azo olefins, and dimeric compounds and products of their subsequent transformation, viz., substituted 1,2,4-triazoles, tetrazines, etc.

Compounds I-III were subjected to reaction with amyl nitrite at room temperature or with brief heating (3-5 min) using a twofold excess of freshly prepared n-amyl nitrite. Chromatographic analysis [by thin-layer chromatography (TLC)] of the reaction mixture showed

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