SYNTHESIS AND PROPERTIES OF 2-AMINO-5-(3,5,6-TRICHLORO-1,4-BENZOQUINON-2-YL)THIAZOLES

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The reaction of thiourea of N-substituted thioureas with 2-(2-N,N-diethylaminoethenyl)-3,5,6-trichloro-1,4-benzoquinone leads, through the formation of 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran, to 2-amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazoles (which exist in the form of betaines), the oxidation of which leads to 2-amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles.

The aim of this research was to synthesize new electron-acceptor compounds in series of chloro-substituted 1,4-benzoquinones containing a thiazole ring in their molecules. It is known that acceptors of the quinone type on reaction with strong electron donors can form charge-transfer complexes [1] or ion-radical salts, while the presence of simultaneously donor (aminothiazole) and acceptor (trichlorobenzoquinone) fragments in the molecule of these compounds creates the possibility for investigation of intramolecular charge transfer.

We used the readily accessible 2-(2-N,N-dialkylaminoethenyl)-3,5,6-trichloro-1,4-benzoquinones Ia, b [2] as the starting compounds. 2,5-Dihydroxy-3,4,6,7-tetrachlorocoumaran (II) is formed when Ia, b are heated with concentrated hydrochloric acid in dioxane solution [3].

For the first time we have established that the corresponding 2-amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazoles IIIa-f (Table 1) [4] are formed in the reaction of II with thiourea or N-substituted thioureas. This reaction is possibly realized owing to the existence in solution of the ring–chain tautomeric equilibrium IIB $\rightleftarrows$ IIA [3]: the open form – an α-chloro aldehyde derivative – undergoes condensation with thiourea or its derivatives. However, it is more likely that the mechanism of the reaction is as follows: instead of a $C_{(3)}$–Cl bond, which stabilizes the cyclic isomer, a $C_{(3)}$–S bond is formed as a result of substitution, after which the ring opens with subsequent condensation of the amino group with the carbonyl group.

TABLE 1. 2-Amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)-thiazoles

Compound	IR spectrum, cm^{-1}	Found, %			Empirical formula	Calculated, %			Yield, %
		Cl	N	S		Cl	N	S	
IIIa	3381, 3116, 2937; 2839, 2773, 1631, 1581	34,1	8,7	10,4	$C_9H_5Cl_3N_2O_2S$	34,1	9,0	10,3	96 (57)
IIIb	3257, 3185, 3095, 2938, 2899, 2820, 1617, 1602, 1557, 1505	32,4	8,1	9,9	$C_{10}H_7Cl_3N_2O_2S$	32,7	8,6	9,9	87 (52)
IIIc	3123, 2937, 2773, 1618, 1576, 1511	30,7	6,7	8,5	$C_{15}H_9Cl_3N_2O_2S$	27,4	7,2	8,3	99 (80)
IIId	3146, 3082, 2960, 2896, 2777, 2727, 1639, 1610, 1580, 1546	31,0	8,0	10,0	$C_{12}H_9Cl_3N_2O_2S$	30,3	8,0	9,1	95 (75)
IIIe	3330, 1682, 1570, 1545, 1524	29,4	8,0	8,7	$C_{11}H_7Cl_3N_2O_3S$	30,1	7,9	9,0	96(62)
IIIf	3143, 2727, 1625	31,7	7,4	9,6	$C_{11}H_9Cl_3N_2O_2S$	31,3	8,2	9,4	76

*These are the yields with respect to the scheme II → III; the yields with respect to the scheme I → III are given in parentheses.

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TABLE 2. 2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)-thiazoles

Compound	Found, %					Empirical formula	Calculated, %					Yield, %
	C	H	Cl	N	S		C	H	Cl	N	S	
IVa	34,6	1,2	30,1	8,8	11,9	$C_9H_3Cl_3N_2O_2S$	34,9	1,0	34,4	9,0	10,4	94
IVb	36,2	1,4	28,3	8,5	10,4	$C_{10}H_5Cl_3N_2O_2S$	37,1	1,6	32,9	8,7	9,9	95
IVc	43,7	1,8	27,5	7,3	9,4	$C_{15}H_7Cl_3N_2O_2S$	46,7	1,8	27,6	7,3	8,3	89
IVd	42,2	2,0	30,2	8,1	9,5	$C_{12}H_7Cl_3N_2O_2S$	41,2	2,0	30,4	8,0	9,2	86
IVe	36,8	1,6	30,1	8,5	9,8	$C_{11}H_5Cl_3N_2O_3S$	37,2	1,4	29,9	7,9	9,0	75
IVf	39,1	1,8	30,6	8,5	10,0	$C_{11}H_7Cl_3N_2O_2S$	39,1	2,1	31,5	8,3	9,5	89

TABLE 3. Physicochemical Characteristics of 2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles

Compound	IR spectrum, ν, cm^{-1}			UV spectrum, λ_{max}, nm (ε)	Reduction potentials, V*	
	quinone C=O	quinone C=C	thiazole ring		E^1	E^2
IVa	1654, 1631	1605	1534	262 (7540), 318 (13 800), 597 (4700)	−0,14	−0,83
IVb	1662, 1645	1604	1512	264 (7600), 324 (12 800), 620 (5400)	−0,15	−0,85*1
IVc	1659, 1643	1596	1524	270*2, 333, 626	−0,10	−0,78*3
IVd	1669, 1652	1599	1512	248*2, 323, 615	−0,15	−0,85
IVe	1677*4, 1637	1598	1527	252 (8600), 392 (17 000), 513 (3400)	−0,07	−0,70
IVf	1675, 1644	1600	1563	255*2, 330, 637	−0,17	−0,83

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*The values of −0.08 and −0.39 in 96% ethanol and −0.08 in 50% ethanol.

*2Because of the poor solubility the spectra were obtained from saturated solutions.

*3The values are −0.07 and −0.40 in 96% ethanol.

*4Overlapped with the amide-I absorption; the amide-II band is located at 1548 cm^{-1}.

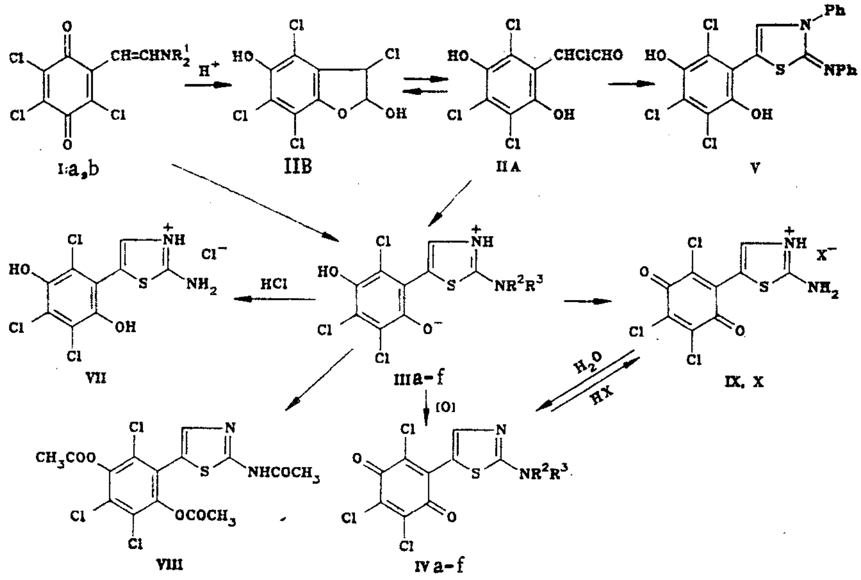
We were able to simplify the synthesis of thiazoles IIIa-e by combining two steps (I → II → III) into (I → III) by condensation of benzoquinone Ib with thiourea or N-substituted thioureas in the presence of concentrated hydrochloric acid in dioxane; thiazoles IIIa-e, which were identical to those previously synthesized, were obtained in good yields. This method is original [5] and is distinguished by the simplicity of the synthetic realization and the accessibility of the starting compounds.

Thiazoles IIIa-f are colorless crystalline substances that gradually decompose when they are heated at ~250°C. They are only slightly soluble in ordinary organic solvents but quite soluble in aprotic dipolar solvents (DMF, DMSO, HMPT), which indirectly confirms their dipolar structure III. 2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles IVa-f (Tables 2 and 3) were obtained by oxidation of thiazoles IIIa-f with ferric chloride in aqueous DMF [4, 5].

2-Phenylimino-3-phenyl-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazoline (V), the oxidation of which leads to 2-phenylimino-3-phenyl-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoline (VI), is formed in the reaction of tetrachlorocoumaran II with N,N'-diphenylthiourea.

Compounds IV and VI are intensely colored (IVa-d, f are blue, and IVe is violet) and only slightly soluble in organic solvents (except for DMF, DMSO, and HMPT); they gradually decompose when they are heated above 250°C.

Absorption bands of OH and NH groups (with the exception of IIIf) and a protonated thiazole ring (1617-1639 cm^{-1}) are observed in the IR spectra of IIIa-f (Table 1). According to the data in [6, p. 187; 7-9], two C=O absorption bands and a C=C band of a quinone, a band of a thiazole ring, and vibrations of an NH group (with the exception of IVf) at 3000-3500 cm^{-1} are observed in the spectra of quinones IVa-f (Table 3). The effect of substituents attached to the amino group on the shifts of the absorption band of the thiazole ring (1512-1563 cm^{-1}) corresponds to the data in [7].



I a $R^1=CH_3$; b $R^1=C_2H_5$; III, IV a-e $R^2=CH_3$; f $R^2=CH_3$; a $R^3=H$; b,f $R^3=CH_3$; c $R^3=Ph$; d $R^3=CH_2=CHCH_2$; e $R^3=COCH_3$; IX X=Br; X X=Cl

An intense absorption band at 318-392 nm, which can be ascribed to the $\pi \rightarrow \pi^*$ transition of the quinone system, a less intense band at 248-272 nm, which can be ascribed to the thiazole system, and a low-intensity band at 513-637 nm, which is associated with the existence of charge transfer in the molecule, are observed in the UV spectra of solutions of IVa-f (Table 3) in ethanol. The constancy of the ε coefficient in the spectra recorded at different concentrations confirms that the charge transfer is intramolecular.

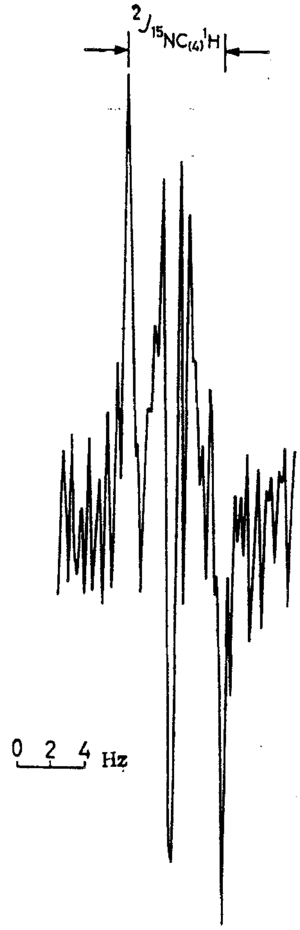
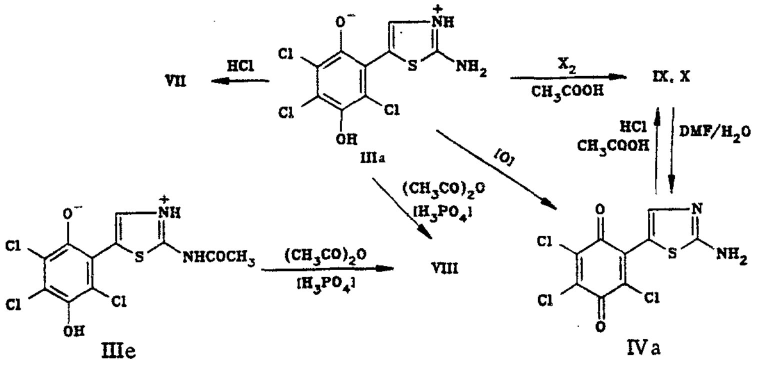


Fig. 1. ^1H NMR spectrum of the 4-H signal of IIIa after the use of a sequence of pulses that excite the $^{15}N-^1H$ two-quantum coherence. The number of buildups was 1700.

A comparison of the data obtained from the ^1H and ^{13}C NMR spectra for thiazoles III and IV with the literature data demonstrates that the substituent is located in the 5 position of the thiazole ring. This is attested to by the position of the signal of the $C_{(4)}$ atom of the thiazole ring, which is found in a region close to that for 2-aminothiazole [10]; for thiazole IIIa the ^{13}C chemical shifts indicate preponderance of the $N_{(3)}$-protonated form [10], i.e., the compound has a betaine structure. The identical character of the chemical shifts of the carbon atoms of the thiazole ring in the spectra of solutions of IIIa in d_6-DMSO and CF_3COOH also confirms the dipolar structure of thiazole IIIa (Table 4). The $^2J_{^{15}N,C(4),H}$ spin-spin coupling constant (SSCC), the decrease in which in the spectrum of IIIa as compared with the spectrum of IVa is characteristic for the protonated ^{15}N nucleus [11], also constitutes evidence for this. In addition, the $^2J_{^{15}N,C(4),H}$ SSCC in the spectra of IIIa and IVa confirm that the substituent is located in the 5 position of the thiazole ring [11]. The data from the spectroscopic studies of thiazoles IIIa-f and IVa-f constitute evidence that the compounds do not display amino-imine tautomerism and exist exclusively in the amine form, which is also in agreement with the data in [7-9, 12].

The reduction potentials of IVa-f relative to a saturated calomel electrode, which characterize a one-electron two-step reduction process, were determined by cyclical voltamperometry (Table 3). Their values are close to those for trichloro-1,4-benzoquinone (−0.08 and −0.78 V) [13, p. 771] and depend little on the substituent attached to the nitrogen atom of the amino group. Reduction is facilitated in hydroxy-containing solvents (ethanol), but the one-electron processes become less reversible.

The chemical properties of thaizole IIIa are due to transformations in the aminothiazole and hydroquinone fragments of the molecule. Thiazole hydrochloride VII was obtained by protonation of IIIa with gaseous hydrogen chloride in solution in ethanol. In the reaction of IIIa with acetic anhydride in the presence of orthophosphoric acid we obtained 2-acetamido-5-(2,5-diacetoxy-3,4,6-trichlorophenyl)thiazole (VIII).



The structure of VIII was confirmed by its ^{13}C and ^1H NMR spectra (Table 4) and by its IR spectrum, in which absorption bands that are characteristic for OCOMe and NHCOMe groups

TABLE 4. ^1H and ^{13}C Chemical Shifts and Spin-Spin Coupling Constants (SSCC) of Thiazoles in Solution in d_6-DMSO

Compound	Chemical shifts, δ, ppm						SSCC, J, Hz	
	^1H		^{13}C					
	4-H	remaining protons	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	remaining C	$^{13}C_{(4)}$, H	$^{15}N_{(3)}$, $C_{(4)}$, H
IIIa	7,47	10,0 (OH); 9,6 (NH_2)	170,2	127,6	115,2	164,4; 143,8; 123,5; 122,4; 120,4; 116,6	195,9	5,6
IIIa*	7,37		172,0	127,2	117,0	146,3; 144,1; 123,8; 121,4; 120,5; 118,5		
IVa	8,34	8,2 (NH_2)	170,5	139,3	116,8	176,1; 175,9; 151,9 (2C); 134,9; 127,3	189,3	14,0
VIII	7,44	12,3 (NH); 2,44 (NHCOMe); 2,20 (OCOMe)	159,9	139,6	118,9	144,8; 142,9; 128,1; 127,8; 126,3; 126,2 (phenyl ring C); 168,9; 167,7; 167,2 (CO), 22,4 and 19,9 (2C) (Me)	188,0	

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*In solution in CF_3COOH.

at 1779 and 1702 cm^{-1}, respectively, as well as bands of NH stretching vibrations at 3164 cm^{-1} and an amide II band at 1557 cm^{-1}, are observed. We also obtained VIII from 2-acetamidothiazole IIIe by acylation of its hydroxy groups.

Heating a solution of IIIa in glacial acetic acid with bromine or bubbling chlorine through a hot solution of IIIa in acetic acid leads to the formation of the corresponding 2-aminothiazole hydrohalides IX and X. Protonation of the nitrogen atom of the thiazole ring is realized simultaneously with oxidation of the hydroquinone fragment. Confirmation of this is provided by protonation in a solution of the previously synthesized quinone IVa in glacial acetic acid with hydrogen chloride and hydrolysis of IX and X reversibly to IVa by the action of aqueous DMF solution. Compounds IX and X are intensely red crystalline substances, heating of which leads to splitting out of the hydrogen halide and the formation of IVa. Compounds IX and X are readily hydrolyzed with the formation of IVa in solvents such as DMF, ethanol, and aqueous acetone but are relatively stable in anhydrous acetone and glacial acetic acid.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were obtained with a WH-360 spectrometer (360 and 90.5 MHz); the chemical shifts were measured relative to tetramethylsilane (TMS), the $^{13}C-^{1}H$ SSCC were measured with respect to the ^{13}C satellites in the ^{1}H spectra, the $^{15}N-^{1}H$ SSCC were measured at the natural percentage of the ^{15}N isotope using the method of transfer of the heteronuclear two-quantum coherence [14] in the ^{1}H NMR spectra, and the error in the measurements was ±0.1 Hz. The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with Specord IR-75 and ISK-14A spectrometers. The electronic spectra of solutions of the quinones in ethanol ($c = 5 \cdot 10^{-5}$ M) were recorded with a Specord UV-vis spectrophotometer. The cyclical voltamperograms were obtained with a PAR-170 electrochemical system with respect to a three-electron system relative to an aqueous saturated calomel electrode. A glass-graphite electrode (with an area of 0.28 cm^2) was used as the working electrode. The investigations were made at room temperature in solution in anhydrous acetonitrile (and in 96% and 50% ethanol) with tetrabutylammonium perchlorate as the polarographic background. The concentration of the inert electrolyte was 0.1 M, and the depolarizer concentration was 10^{-4} M. The potential-sweep rate was 200 mV/sec. Thin-layer chromatography on Silufol UV-254 plates was used to monitor the course of the reactions and the purity of the compounds obtained.

The characteristics of the synthesized compounds are presented in Tables 1-4.

2-(2-N,N-Dialkylaminoethenyl)-3,5,6-trichloro-1,4-benzoquinones Ia, b were obtained by the method in [2], and 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran (II) was obtained by the method in [3].

2-Amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazoles IIIa-f. A. A solution of 2 mmoles of coumaran II and 2 mmoles of the corresponding thiourea in 5 ml of ethanol was refluxed for 2 h, after which the mixture was cooled, and the precipitate was separated, washed with water, and dried at 100°C. In the synthesis of IIId a small amount of hot hexane was added to the hot ethanol solution after completion of the reaction, and the mixture was allowed to stand for crystallization.

B. A solution of 2 mmoles of quinone Ib, 2 mmoles of the corresponding thiourea, and 1 ml of concentrated hydrochloric acid in 20 ml of dioxane was refluxed for 2 h, after which the mixture was cooled, and the precipitate was separated, washed with water, and dried at 100°C. If the substance did not precipitate after cooling of the reaction mixture, the same amount of hexane was added to the hot solution.

2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles (IVa-f). A 3 mmole sample of thiazole IIIa-f was dissolved in 6 ml of DMF, a solution of 5 g of ferric chloride hexahydrate in 20 ml of water was added, and the mixture was shaken with a mechanical rocker at room temperature for 2 h. It was then filtered, and the precipitate was washed with water and dried at 100°C. This procedure gave dark-blue crystals of IVa-f.

2-Phenylimino-3-phenyl-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazoline (V). A solution of 0.58 g (2 mmoles) of coumaran and 0.46 g (2 mmoles) of N,N'-diphenylthiourea in 5 ml of ethanol was refluxed for 4 h, after which the reaction mixture was diluted with 50 ml of water. The precipitate was separated to give 0.58 g (89%) of colorless crystals with mp 192-194°C (from ethanol). IR spectrum: 3250-3400 (broad), 1603, 1562 cm^{-1}. Found: C

53.4; H 2.9; Cl 23.2; N 6.2; S 6.8%. $C_{21}H_{13}Cl_3N_2O_2S$. Calculated: C 54.4; H 2.8; Cl 22.9; N 6.0; S 6.9%.

2-Phenylimino-3-phenyl-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoline (VI). A 0.46 g (1 mmole) sample of the thiazoline was dissolved in 5 ml of DMF, a solution of 2.5 g of ferric chloride hexahydrate in 10 ml of water was added, and the mixture was shaken with a mechanical rocker at room temperature for 2 h. The precipitate was separated, washed with water, and air dried to give 0.45 g (99%) of dark-blue crystals with mp 132-135°C. IR spectrum: 1667, 1616, 1581, 1531 cm^{-1}. UV spectrum, λ_{max} (ε): 290 (13600), 660 nm (3070). Found: C 54.9; H 1.9; Cl 22.5; N 6.5; S 7.2%. $C_{21}H_{11}Cl_3N_2O_2S$. Calculated: C 54.6; H 2.4; Cl 23.0; N 6.1; S 6.9%.

2-Amino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazole Hydrochloride (VII). Dry hydrogen chloride was passed through a solution of 0.31 g (1 mmole) of thiazole IIIa in 40 ml of anhydrous ethanol. The solution turned orange, and 0.25 g (78%) of a colorless crystalline substance that decomposed above 200°C precipitated. IR spectrum: 3272, 3090, 2924, 2835, 2776, 1630, 1582, 1560 (shoulder) cm^{-1}. Found: Cl 40.6; N 8.0; S 9.8%. $C_9H_5Cl_3N_2O_2S \cdot HCl$. Calculated: Cl 40.7; N 8.0; S 9.2%.

2-Acetamido-5-(2,5-diacetoxy-3,4,6-trichlorophenyl)thiazole (VIII). A solution of 0.62 g (2 mmoles) of thiazole IIIa, 5 ml of acetic anhydride, and 0.1 ml of orthophosphoric acid was refluxed for 1 h in a flask equipped with a reflux condenser, after which the solution was cooled and poured into 60 ml of water. After 24 h, the precipitate was separated, washed with water, and dried at 100°C to give 0.86 g (99%) of colorless crystals that decomposed above 250°C. IR spectrum: 3164, 3088, 2933, 1776, 1701, 1558, 1531 cm^{-1}. Found: Cl 24.2; N 6.4; S 8.1%. $C_{15}H_{11}Cl_3N_2O_5S$. Calculated: Cl 24.3; N 6.4; S 7.3%.

Compound VIII was also obtained by the method described above from 2-acetamido-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazole (IIIe). The yield was 98%.

2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazole Hydrobromide (IX). A 0.19 g (1.2 mmole) sample of bromine was added to a solution of 0.31 g (1 mmole) of thiazole IIIa in 3 ml of glacial acetic acid, and the mixture was refluxed for 1 h. It was then cooled, and the precipitated crystals were separated and dried in a desiccator to give 0.3 g (78%) of intensely red crystals of IX, which decomposed above 150°C. IR spectrum: 3297, 3190, 3117, 1702, 1680, 1637, 1602, 1538 cm^{-1}. Found: C 27.4; H 1.3; N 6.9; S 8.6%. $C_9H_4BrCl_3N_2O_2S$. Calculated: C 27.7; H 1.0; N 7.2; S 8.2%.

2-Amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazole Hydrochloride (X). A. Dry chlorine was passed for 30 min into a slightly heated solution of 0.31 g (1 mmole) of thiazole IIIa in 15 ml of glacial acetic acid. The precipitate was separated and dried in a desiccator to give 0.28 g (65%) of intensely red crystals, which decomposed above 150°C.

B. Dry hydrogen chloride was passed for 15 min through a solution of 0.31 g (1 mmole) of thiazole IVa in 15 ml of glacial acetic acid. The precipitate was separated and dried in a desiccator to give 0.34 g (98%) of red crystals. IR spectrum: 3300, 3260, 3182, 3110, 1697, 1678, 1637, 1602, 1545 cm^{-1}. Found: C 31.4; H 1.0; N 7.8; S 9.0%. $C_9N_4Cl_4N_2O_2S$. Calculated: C 31.2; H 1.2; N 8.1; S 9.3%.

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4-ACETYL-1-(R-BENZYLIDENE)-3-(5-NITRO-2-FURFURYL)THIOSEMICARBAZIDES — CARRIERS OF SYNTHONES FOR OBTAINING THIAZOLE AND TRIAZOLE RINGS

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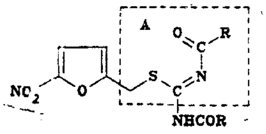
The corresponding thiosemicarbazonium salts, which form 4-acetyl- and 2,4-diacetyl-1-benzylidene-3-(5-nitro-2-furfuryl)thiosemicarbazides with acetic anhydride, were obtained by the reaction of 5-nitrofurfuryl bromide with 1-benzylidenethiosemicarbazides. Under the influence of bases the monoacetylated derivatives undergo cyclization to the corresponding 2-benzylidenehydrazino-5-(5-nitro-2-furyl)thiazoles. Intramolecular cyclization of the monoacetylated products to 3-methyl-5-[(5-nitro-2-furfuryl)thio]-1,2,4-triazole, which is accompanied by the elimination of the corresponding benzaldehyde, occurs in the presence of hydrochloric acid.

It has been previously established [1] that S-(5-nitro-2-furfuryl)thiuronium bromide reacts with carboxylic acid anhydrides to give substituted 5-(5-nitro-2-furyl)thiazoles. An analysis of the reaction intermediates showed that the key intermediates are 1,3-diacyl-2-(5-nitro-2-furfuryl)thioureas that contain structural fragment (synthone) A, the intramolecular cyclization of which leads to the formation of a thiazole ring.



The products of the reaction of thiosemicarbazonium salts with carboxylic acid anhydrides should also have the same structural fragments. We therefore investigated the possibility of the use of S-(5-nitro-2-furfuryl) derivatives of thiosemicarbazide for the synthesis of 2-hydrazino-5-(5-nitro-2-furyl)thiazoles.

Refluxing the nitrofurfuryl bromide with an equimolar amount of the benzylidenethiosemicarbazide in alcohol leads to thiosemicarbazonium salts Ia-e. A characteristic band of NH stretching vibrations at 3300 cm^{-1} and its intense overtone at 1650 cm^{-1} are present in the IR spectra of salts I (Table 1).

Whereas S-(5-nitro-2-furfuryl)thiuronium bromide reacts with carboxylic acid anhydrides in one step to give 5-(5-nitro-2-furyl)thiazole derivatives [1, 2], thiosemicarbazonium salts I give complex mixtures of products under the same conditions. Colorless substances, the results of elemental analysis and the spectral characteristics of which correspond to monoacetylation products II or III, are obtained when the reaction is carried out in the presence

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