ethereal solution of diazomethane ($\sim$0.03 mole); it was allowed to stand at room temperature for a day. The reaction mass was evaporated, the remainder was separated on a column with a chloroform–petroleum ether (1:1) mixture. The isolated N- and O-methylation products IIa and IIIa, with yields of 48% [0.26 g (0.001 mole)] and 26% [0.14 g (0.005 mole)] and with mp of 229-231 and 163-165°C, were crystallized from chloroform. Compounds IIa and IIIa did not give melting-point depressions with the products obtained by methylating compound I with methyl iodide. Found %: C 62.3; H 3.8; N 16.0. $C_{14}H_{11}N_3OS$. Calculated %: C 62.4; H 4.0; N 15.6 (IIa). Found %: C 62.6; H 4.0; N 15.4. $C_{14}H_{11}N_3OS$. Calculated %: C 62.4; H 4.0; N 15.6 (IIIa).

Rearrangement of Oxobenzene IIa to Azoanisole IIIa. Compound IIa, 0.1 g (0.004 mole), was boiled for 4 h in 15 ml of absolute alcohol in the presence of 0.09 g (0.004 mole) of sodium. The ethanol was evaporated off and compounds IIa and IIIa were separated chromatographically with chloroform. Yield of IIa 75 mg (75%), IIIa 20 mg (20%).

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SYNTHESIS AND SOME PROPERTIES OF SUBSTITUTED 3,5-BIS(METHYLIDENE)-4-ARYL-1,2,4-DITHIAZOLIDINE

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UDC 547.892'794.1.07

It has been established that aryl amides of substituted thioneacetic acid form substituted benzothiazoles [1, 2] or aryl amides of substituted acetic acid [2, 3] by reacting with an equimolar amount of bromine depending on the conditions. According to the data of [3], the aryl amides of monoacetylthioneacetic acid (I) already dissociate at room temperature during the reaction with bromine.

We found that high-melting substances, for which the structure of 3-acetylmethylidene-4-aryl-5-methyl-1,2,4-dithiazepin-7-ones [4] was assumed, are formed in this reaction upon cooling. However, a study of the PMR spectra of these substances indicates that they in fact have the structure of 3,5-diacetylmethylidene-4-aryl-1,2,4-dithiazolidines (III). The oxidative bromination of compounds I can be depicted by Scheme 1.

The reaction of aryl amide I with bromine evidently begins with the addition of bromine at the thione group followed by dehydrobromination, which leads to the substituted sulfenyl bromide (Ib). There are indications in the literature of the formation of analogous compounds during the reaction of thioamides and thiourea with halogens [6]. The intermediate sulfenyl bromide Ib reacts with a second molecule of I in the thiol form, forming a disulfide which is converted to compound III.

The first representative of the series of compounds III (IIIa, R = H) was synthesized earlier [7] by the action of sulfuryl or thionyl chlorides on compound I (R = H) and is the identical substance obtained by our method.

The presence of several strong absorption bands in the 1400-1500 cm^{-1} region, one of which is usually the most intense, is a characteristic feature of the IR spectra of all of the compounds III synthesized. An analogous pattern was observed in the IR spectra of 3,5-

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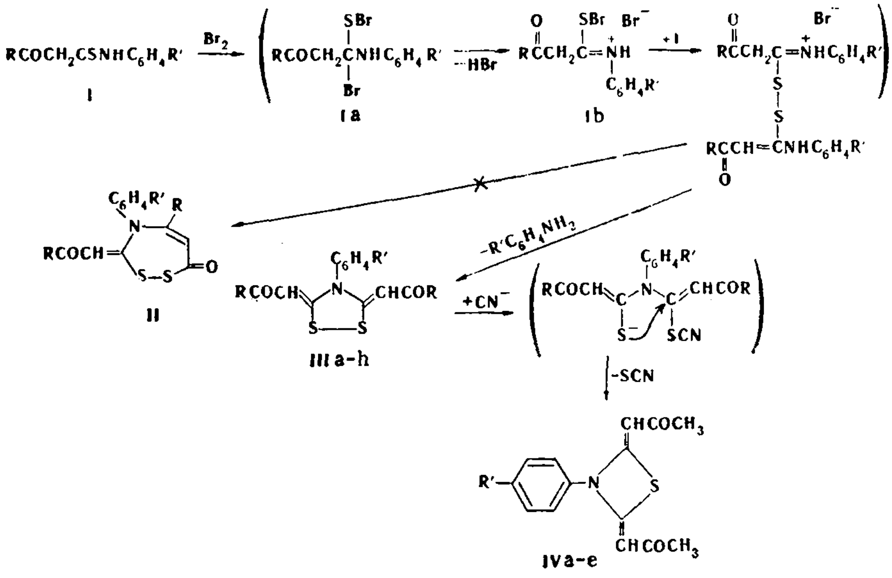
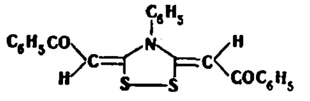
Scheme 1



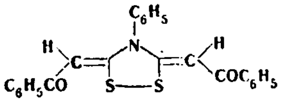
III a $R{=}CH_3$, $R'{=}H$; b $R{=}CH_3$, $R'{=}4\text{-}CH_3$; c $R{=}CH_3$, $R'{=}4\text{-}OCH_3$; d $R{=}CH_3$, $R'{=}2\text{-}OCH_3$; e $R{=}CH_3$, $R'{=}OC_2H_5$; f $R{=}CH_3$, $R'{=}4\text{-}Cl$; g $R{=}CH_3$, $R'{=}4\text{-}Br$; h $R{=}C_6H_5$, $R'{=}H$; IVa $R'{=}H$; b $R'{=}OCH_3$; c $R'{=}OC_2H_5$; d $R'{=}Cl$; e $R'{=}Br$

diacetylmethylidene-1,3,5-trithiols [9] and desaurins. Jensen [10] assigned these bands to the vibrations of the $\mathrm{C{=}C}\left\langle\begin{smallmatrix}\mathrm{S-}\\ \mathrm{S-}\end{smallmatrix}\right.$ group. By analogy one can assign them to the vibrations of the $\mathrm{C{=}C}\left\langle\begin{smallmatrix}\mathrm{N}\langle\\ \mathrm{S-}\end{smallmatrix}\right.$ group for compounds III, although one cannot exclude that they are the stretching vibrations of the dithiazolidine ring.

Two isomeric products were formed from the reaction of bromine with the anilide of benzoylthioneacetic acid. From the data on the measurements of the dipole moments the lower melting product, which is more soluble in chloroform, evidently has the trans structure and its isomer the cis structure:



trans-IIIh, μ calc. 3.8D; found 4.1D



cis-IIIh, μ calc. 6.5D; found 7.8D

The discrepancy between the calculated and found values of the dipole moments is explained by the strong intramolecular interaction. The shift in the infrared spectrum of the carbonyl band in compounds IIIh towards a lower frequency is confirmation of this. The structure of the cis isomer is further confirmed by the fact that the singlet at 6 ppm corresponds to the protons of the methine groups in the PMR spectrum of this compound. The signals of the protons in the methine groups for the trans isomer are overlapped by the multiplet of the protons in the phenyl rings in the 7-8 ppm region. Our conclusions concerning the configuration of compounds IIIh agree with the data [9, 11] for the isomers of 3,5-bis(acetylmethylidene)-1,2,4-trithiol. Their ability to react with the cyanide ion, forming 2,4-bis(acetylmethylidene)-3-arylthiazetidines (Scheme 1), which have not been described in the literature, is a characteristic property of compounds III.

This reaction proceeds with the cleavage of a sulfur atom as the thiocyanate ion and the formation of a monosulfide, as is characteristic for other disulfides [12]. The colorimetric measurements carried out by the method in [13] showed that the amount of the thiocyanate ion formed during the synthesis of compounds IV corresponds approximately to the yield of thiazetidine (IV). There are sharp carbonyl bands in the 1673-1665 cm^{-1} region and bands of the C=C bonds at 1615-1607 cm^{-1} in the IR spectra of compounds IV. There are very strong absorption bands in the 1550-1510 cm^{-1} region, which can probably be attributed to

TABLE 1. Substituted 3,5-Bis(methylidene)-4-aryl-1,2,4-dithiazolidines (III)

Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
a	197—198	57,2	4,4	4,7	21,8	$C_{14}H_{13}NO_2S_2$	57,7	4,5	4,8	22,0	80
b	222—224	58,7	4,1	4,5	21,0	$C_{15}H_{15}NO_2S_2$	59,0	4,9	4,5	21,0	67
c	213—215	55,6	4,5	—	19,8	$C_{15}H_{15}NO_3S_2$	56,0	4,6	—	20,0	75
d	203—204	55,7	4,5	—	20,0	$C_{15}H_{15}NO_3S_2$	56,0	4,6	—	20,0	30
e	210—212	56,9	4,9	—	18,8	$C_{16}H_{17}NO_3S_2$	57,3	5,0	—	19,1	65
f	220—222	51,3	3,7	--	19,4	$C_{14}H_{12}ClNO_2S_2$	51,6	3,7	--	19,7	50
g	224—225	45,0	3,1	--	17,0	$C_{14}H_{12}BrNO_2S_2$	45,4	3,2	—	17,3	51
trans-h	157—158	69,4	4,1	3,5	15,3	$C_{24}H_{17}NO_2S_2$	69,6	4,1	3,4	15,4	26
cis-h	243—244	69,3	4,1	3,4	15,2	$C_{24}H_{17}NO_2S_2$	69,6	4,1	3,4	15,4	30

TABLE 2. 2,4-Bis(acetylmethylidene)-3-aryl-1,3-thiazetidines IV

Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
a	181—182	64,8	5,0	5,8	12,1	$C_{14}H_{13}NO_2S$	64,8	5,0	5,5	12,4	74
b	166—167	62,0	5,1	4,7	11,0	$C_{15}H_{15}NO_3S$	62,2	5,2	4,8	11,1	60
c	167—168	63,1	5,6	—	10,4	$C_{16}H_{17}NO_3S$	63,3	5,6	—	10,5	70
d	192—193	56,8	4,7	—	11,2	$C_{14}H_{12}ClNO_2S$	57,2	4,8	—	10,9	65
e	211—212	49,6	3,6	—	9,5	$C_{14}H_{12}BrNO_2S$	49,7	3,6	—	9,5	55

the stretching vibrations of the thiazetidine ring, for all compounds IV. The symmetry of the structure of compounds IV is confirmed by the presence of singlets of the protons which characterize the methyl and methine groups in their PMR spectra.

The long-wave absorption maxima in the UV spectrum of compounds IV are shifted bathochromically by 15-16 nm in relation to the analogous absorption maxima of the original compounds III, which evidently is connected with the possibility of the transfer of the electronic effect through the sulfur atom of the thiazetidine ring.

EXPERIMENTAL

The IR spectra were run on a UR-20 instrument as KBr tablets, the UV spectra on an SF-4A instrument, the PMR spectra on a Tesla BS 487B instrument in trifluoroacetic acid; the external standard was HMDS. The mass spectrometric determination of the molecular weight was done on the MX-1303 instrument. The energy of the ionizing radiation was 70 eV; the temperature of the compartment was 200°C; the emission current was 1 mA. The dipole moments were measured on a E-5 instrument in methylene chloride. The dielectric constants and densities of the monomers were determined from the concentration measurements. The dipole moment was calculated from Onsager's formula.

3,5-Bis(acetylmethylidene)-4-phenyl-1,2,4-dithiazolidine (IIIa). Into a solution of 1.95 g (0.01 mole) of acetylthione acetanilide in 20 ml of chloroform at —10°C and with agitation for 5 min was added dropwise a solution of 0.8 g (5 mmole) of bromine in 5 ml of chloroform. The mixture was agitated another 30 min, 25 ml of alcohol was added, the mixture was agitated for 10 min, and the solution was chromatographed on an aluminum oxide column; the height of the packing was 50 cm. The first yellow zone was eluted with chloroform, the eluate was filtered and evaporated under vacuum from an aspirator, the residue was triturated in 15 ml of benzene, the precipitate was filtered, and dried. The yield of compound IIIa was 1.2 g (80%). IR spectrum (KBr): 3060, 3030, 3010 (C_6H_5), 2930 (CH_3), 1615 cm^{-1} (C═O). UV spectrum (in ethanol), λ_{max} (log ε): 343 nm (4.80). PMR spectrum: 8.15, 7.15 (m, C_6H_5), 5.65 (2H, s, ═CH), 2.15 ppm (6H, s, CH_3); mol. wt. 309 (cryoscopically in dioxane); mol. wt. 280 (ebullioscopically in dichloroethane); calculated 290.3.

Substances IIIb-g (Table 1) were obtained under similar conditions. In contrast to compounds IIIa compounds IIIb, d, f were washed with ethyl alcohol after isolation from the chromatographic column and then crystallized from ethanol. The mixture of the isomeric dithiazolidines IIIh was eluted together in the first zone and their separation was carried out after evaporating the solvent from the eluate. The residue was carefully mixed with 20 ml of benzene and the cis-dithiazolidine was filtered off. The yield was 1.2 g (25%), mp 243-244°C (twice from an alcohol—chloroform mixture, 3:1). IR spectrum (KBr): 3110 (C—H), 3065 (C_6H_5), 1600 (C=O), 1570 cm^{-1} (C=C). UV spectrum (in chloroform), λ_{max} (log ε): 267 (3.53), 286 (4.04), 366 (4.41), and 380 nm (4.34). PMR spectrum: 7-7.6 (m, 18H, phenyl groups), 6.0 ppm (s, 2H, =CH).

The benzene filtrate was evaporated in vacuo after separating out the cis-dithiazolidine IIIh, the residue was triturated with 10 ml of ethanol, the precipitate was filtered off, and washed off once more on the filter with alcohol. The yield of trans-IIIh was 1.4 g (30%), mp 157-158°C (from ethanol). IR spectrum (KBr): 3080, 3060, 3050 (C_6H_5), 1600 (C=O), 1587, 1570 cm^{-1} (C=C). UV spectrum (ethanol), λ_{max} (log ε): 270 (3.85), 310 (3.6), 395 (3.75), and 445 nm (4.02).

2,4-Bis(acetonylidene)-3-phenyl-1,3-thiazetidine (IVa). To a solution of 1.5 g (0.051 mole) of 3,5-bis(acetylmethylidene)-4-phenyl-1,2,4-dithiazolidine (IIIa) in 20 ml of DMF was added 0.28 g (0.05 mole) of sodium cyanide. The reaction liquid was agitated and heated to 50°C, and then agitated for 6 h without heating. The solution was poured into 200 ml of ice water. The precipitate was filtered off, washed on the filter with water, and dried. The yield of substance IVa was 0.95 g (74%), mp 181-182°C (twice from absolute alcohol). PMR spectrum (in $CDCl_3$): 7.5-8 (m, 5H, C_6H_5), 6.47 (s, 2H, =CH), 2.55 ppm (s, 6H, CH_3). IR spectrum (KBr): 3083, 3068, 3053 (C_6H_5), 2925 (CH_3), 1665 (C=O), 1610 (C=C), 1590 (C=C), 1520 cm^{-1} (>N—C—S—). UV spectrum (in ethanol), λ_{max} (log ε): 223 (4.26), 240 (4.04), 288 (3.93), 351 (4.65), and 356 nm (4.64). Mol. wt. 259 (mass spectrometrically); calculated 259. Compounds IVb-e (Table 2) were obtained under analogous conditions. Substances IVa-e are orange crystalline products soluble in chloroform, acetone, DMSO, and difficultly soluble in alcohol.

Quantitative Determination of the Thiocyanate Ion. The orange portion was extracted with chloroform from the filtrate after separating out substance IVa, the aqueous layer was isolated, and the thiocyanate ion content was determined in it colorimetrically by the method in [13] as the copper(II) thiocyanate complex with pyridine.

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