cm^{-1} (CH_2SCH_2). Found %: N 8.4; S 40.3; mol. wt. 302. $C_{10}H_{18}N_2O_2S_4$. Calculated %: N 8.6; S 39.6; mol. wt. 326.

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ALKYLATION OF THE 2-BENZOTHIAZOLYLAZOPHENOL ANION

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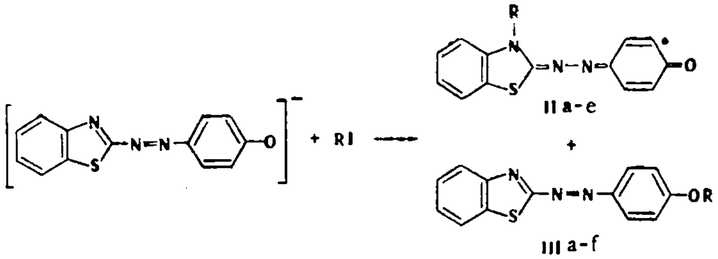
The alkylation of benzothiazolylazophenol (I) has not been sufficiently studied. There is a report on the methylation of I resulting in the formation of (3-methylbenzothiazolyl)-2-azino-4-(1,4-dihydro)-1-oxobenzene [1] (IIa).

We established that the anion of azophenol I is alkylated with a satisfactory yield by various alkyl halides in an ethanolic sodium ethylate solution at two reaction centers forming N- and O-substitution products (Table 1). The structure of methyl derivatives IIa and IIIa was demonstrated on the basis of the IR spectra and by comparison with stabilized quinoneazine and hydroxyazoid forms obtained according to [2-4]. A mixture of isomers IIa and IIIa was also isolated by methylating anion I with diazomethane.



a $R=CH_3$; b $R=C_2H_5$; c $R=i\text{-}C_3H_7$; d $R=n\text{-}C_4H_9$; e $R=n\text{-}C_8H_{17}$; f $R=CH_2C_6H_5$

A nonsynchronous accumulation of the methylation products was noted in separate experiments: in the first hours isomer IIa is formed, the portion of which decreases during the reaction through the accumulation of isomer IIIa (Table 2); in connection with this the reaction in which compounds IIa and IIIa are formed can be assigned to a thermodynamically controlled one.

An increase in the length of the carbon chain and degree to which the alkyl is branched, as the Stuart–Briegleb model shows, leads to an increase in the steric hindrances for the N-alkylated product, which leads to a decrease in the portion of the N-isomer. The possibility of a transition of isomer IIa to isomer IIIa during boiling in the ethanolic sodium ethylate solution, dimethylformamide, and mesitylene should be mentioned. At this time anion I is not detected. Evidently polar compound IIa [2] can exist as a charge-transfer type of associated dimer. During heating in a solvent the synchronous transfer of the methyl groups from the nitrogen to the oxygen atom takes place. Thus the accumulation of the thermodynamically more stable compound IIIa does not proceed through the dealkylation of isomer IIa forming anion I but through the intermolecular transfer of the methyl groups. The following fact points to the lesser stability of the N-alkyl bond in going from methyl derivative IIa to ethyl derivative

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TABLE 1. Characteristics of the N(O)-Alkyl Derivatives of Benzothiazolylazophenol I

Compound	mp, °C	λ_{max}, nm (log ε) (ethanol)	ν, cm^{-1} (C=O)	R_f*	Found, %			Empirical formula	Calculated, %			Yield, %
					C	H	N		C	H	N	
IIa	229—231	514 (3,59)	1645	0,91	62,4	3,8	15,5	$C_{14}H_{11}N_3OS$	62,4	4,0	15,6	43
IIIa	163—165	400 (3,26)	Absent	0,88	62,6	4,0	15,6					2
IIb	150—152	500 (3,54)	1650	0,80	63,5	4,7	15,0	$C_{15}H_{13}N_3OS$	63,6	4,6	14,8	37
IIIb	133—135	420 (3,39)	Absent	0,90	63,6	4,8	14,6					12
IIc	123—125	517 (3,26)	1655	0,91	64,7	5,1	14,0	$C_{16}H_{15}N_3OS$	64,6	5,1	14,1	7
IIIc	130—132	418 (3,13)	Absent	0,88	64,6	5,4	14,0					35
IId	85—86	510 (3,51)	1660	0,91	65,3	5,3	13,7	$C_{17}H_{17}N_3OS$	65,6	5,4	13,5	9
IIId	124—125	417 (3,42)	Absent	0,84	65,4	5,4	13,2					27
IIe	95—97	518 (3,83)	1655	0,94	68,8	7,0	11,4	$C_{21}H_{25}N_3OS$	68,7	6,8	11,4	3
IIIe	134—136	417 (3,27)	Absent	0,95	68,7	6,9	11,6					39
IIIf	170—172	410 (3,45)	Absent	0,55	69,6	4,1	12,2	$C_{20}H_{15}N_3OS$	69,6	4,3	12,2	45

*R_f from a chloroform—petroleum ether mixture (1:1).

TABLE 2. Alkylation of Compound I in Various Solvents

Alkylating agent	Alkylating time, h	Solvent	Composition of alkylation products, %	
			IIa:	IIIa:
Methyl iodide	4	Ethanol	45	0,2
	6		44,1	0,9
	8		43,6	1,6
	10		43,4	1,9
			IIc:	IIIc:
Isopropyl iodide	10	Ethanol	7	35
	10	DMSO	27	8
	10	HMPT	41	12
	10	Dioxane	10	26

IIb: an attempt to hydrolytically split the quaternary salt of 3-ethylbenzothiazolylazodimethylaniline results in the formation of the starting base, benzothiazolylazodimethylaniline.

The effect of the nature of the solvent on the course of the alkylation was studied using the reaction of anion I with isopropyl iodide (Table 2). During an analysis of the properties of the chosen solvents it was found that the portion of the O-isomer IIIc increases with an increase in the electrophilicity E and a decrease in the nucleophilicity B [5]. Evidently the more electrophilic ethanol greatly weakens the N-methyl bond in isomer IIc, assisting the rearrangement.

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EXPERIMENTAL

The IR spectra were run on a UR-20 spectrophotometer in mineral oil, the electronic absorption spectra on a Hitachi—Perkin—Elmer instrument in ethanol (c = 1•10^{-5} mole/liter). The purity of the individual compounds and the course of the reaction was followed by TLC on Silufol. The chromatography was carried out on a column packed with neutral Al_2O_3, II degree of activity.

Alkylation of Azophenol I with Alkyl Halides. A mixture of 0.5 g (0.002 mole) of azophenol I, 0.09 g (0.004 mole) of sodium in 20 ml of absolute ethanol, and 0.01 mole of the alkyl halide was boiled for 10 h, then the ethanol was evaporated. The mixture of isomers formed was separated from unreacted compound I and partitioned on a column with chloroform. The N(O)-alkylation products (IIa-d, IIIa, c) were crystallized from chloroform; IIe, IIIb, d-f from benzene (Table 1).

Alkylation of Azophenol I with Diazomethane. To a mixture of 0.5 g (0.002 mole) of azophenol I, 20 ml of absolute ethanol, and 0.1 g (0.003 mole) of KOH was added 30 ml of an ethereal solution of diazomethane (~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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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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