with helium as the carrier gas at a flow rate of 20 ml/min. The analyses were carried out on 10% solutions in ether with the addition of ∿50% (based on the amount of acyloxadiazoline) of a mixture of four n-alkanes C_nH_{2n+2} (n = 11, 13, 15, and 17) as reference components for calculation of the retention indexes. Acylhydrazones $R^1R^2CNNHCOR^4$ necessary for the comparative chromatographic-mass-spectrometric characterization [R^1, R^2, R^4: CH_3, CH_3, H; CH_3, C_2H_5, H; CH_3, CH_3, CH_3; CH_3, C_2H_5, CH_3; C_2H_5, C_2H_5, H; C_2H_5, C_2H_5, CH_3; C_2H_5, C_2H_5, C_2H_5; $(CH_2)_5$, H; $(CH_2)_5$, CH_3; CH_3, CH_3, C_6H_5; $(CH_2)_5$, C_6H_5] were synthesized by the methods used in [1]. Statistical treatment of the mass spectra of the individual compounds, calculation of the spectra of the ionic series, and averaging of these spectra were carried out by means of an NR 2114 V computer.

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DIAZO CARBONYL DERIVATIVES OF HETEROCYCLES.

4.* DIAZOACETYL DERIVATIVES OF MERCAPTOBENZAZOLES AND MERCAPTOQUINOLINES

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In a number of cases the classical method of acylation of diazomethane by the halides of the corresponding acids is not suitable for the synthesis of functionally substituted diazo ketones, since the reaction is accompanied by side processes. Different methods for the introduction of a diazo carbonyl function into molecules are used in these cases [2]. It seems expedient to use haloalkyl diazomethyl ketones with an active halogen atom in the α position for this purpose. The literature does not contain information on nucleophilic substitution reactions of the halogen atom in such diazo ketones.

We have previously demonstrated the possibility of the synthesis of 1-diazo-3-(2-benzimidazolylmercapto)propanone on the basis of bromomethyl diazomethyl ketone [3].

In the present research we extended the possibility of this method in order to prepare difficult-to-obtain diazo carbonyl derivatives of mercaptobenzazoles and mercaptoquinolines. We used 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptoquinoline, and 8-mercaptoquinoline as mercaptoheterocyclic models. We selected 1-diazo-3-bromopropanones IIa-c as the alkylating diazo ketones to study steric effects on the course of the reaction. The reaction was carried out at room temperature in methanol in presence of an equivalent amount of sodium methoxide:

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*See [1] for communication 3.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calc., %			R_f	Yield, %
		C	H	N		C	H	N		
IIIa	125	51,5	3,7	24,2	$C_{10}H_8N_4OS$	51,7	3,5	24,1	0,58[a]	60
IIIb	113	53,9	4,3	22,7	$C_{11}H_{10}N_4OS$	53,7	4,1	22,8	0,59[a]	52
IIIc	193	55,6	5,0	21,5	$C_{12}H_{12}N_4OS$	55,4	4,6	21,5	0,5[a]	45
IIId	52	51,6	3,2	18,2	$C_{10}H_7N_3O_2S$	51,5	3,0	18,0	0,45[b]	60
IIIe	Oil	53,2	3,6	16,7	$C_{11}H_9N_3O_2S$	53,4	3,6	17,0	0,5[b]	46
IIIf	53	48,1	2,8	16,9	$C_{10}H_7N_3O_2S$	48,2	2,8	16,9	0,6[c]	75
IIIg	Oil	50,5	3,5	15,8	$C_{11}H_9N_3O_2S$	50,2	3,4	16,0	0,65[c]	56
Va	83	59,4	3,6	17,3	$C_{12}H_9N_3OS_2$	59,3	3,7	17,3	0,52[a]	82
Vb	Oil	60,8	4,4	16,5	$C_{13}H_{11}N_3OS_2$	60,7	4,3	16,3	0,56[c]	76
Vc	92	62,0	4,7	15,6	$C_{14}H_{13}N_3OS$	62,0	4,8	15,5	0,6[c]	70
VIa	106	59,4	3,8	17,5	$C_{12}H_9N_3OS$	59,3	3,7	17,3	0,4[d]	75
VIb	56	60,8	4,4	16,1	$C_{13}H_{11}N_3OS$	60,7	4,3	16,7	0,52[b]	72
VIc	93	62,1	4,7	15,5	$C_{14}H_{13}N_3OS$	62,0	4,8	15,5	0,58[b]	60

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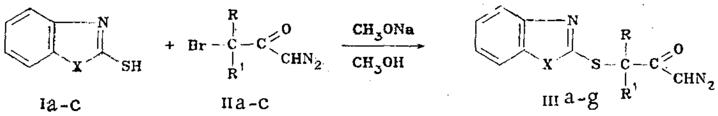
[a] Benzene—ethyl acetate (1:1).
[b] Benzene—ethyl acetate (3:1).
[c] Benzene—methanol (1:10).
[d] Benzene—ethyl acetate (2:1).

TABLE 2. IR and UV Spectra of Diazo Ketones IIIa-g, Va-c, and VIa-c

Compound	IR spectrum, cm^{-1}		UV spectrum, λ_{max}, nm (log ε)
	νC=O	νN=N	
IIIa	1610	2090	250 (4,10), 275 (4,22)
IIIb	1605	2070	212 (4,11), 255 (3,95), 274 (4,00)
IIIc	1610	2090	255 (4,10), 275 (4,22)
IIId	1620	2100	255 (3,97), 275 (4,25)
IIIe	1630	2105	252 (4,05), 272 (4,11)
IIIf	1610	2070	225 (4,07), 247 (3,91), 278 (3,99)
IIIg	1630	2100	230 (4,32), 249 (4,16), 280 (4,22)
Va	1610	2050	213 (3,9), 252 (3,80), 274 (4,07)
Vb	1630	2100	237 (3,60), 255 (3,50), 280 (4,11)
Vc	1620	2080	235 (3,70), 250 (4,01), 270 (4,16)
VIa	1600	2080	207 (4,10), 250 (3,90), 280 (4,20)
VIb	1615	2115	210 (4,45), 255 (4,88), 275 (4,30)
VIc	1610	2080	208 (3,95), 252 (4,15), 278 (4,28)

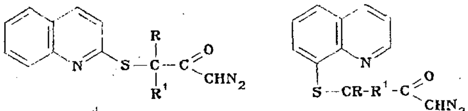


Ia-c IIa-c IIIa-g

Ia X=O, Ib X=NH, Ic X=S; IIa R=R¹=H, IIb R=H, R¹=CH_3, IIc R=R¹=CH_3; IIIa X=O, R=R¹=H, IIIb X=O, R=H, R¹=CH_3, IIIc X=NH, R=R¹=H, IIId X=NH, R=H, R¹=CH_3, IIIe X=NH, R=R¹=CH_3, IIIf X=S, R=R¹=H; IIIg X=S, R=H, R¹=CH_3

In the reaction of benzazoles Ia-c with diazo ketones IIa-c the fastest reaction was observed with 2-mercaptobenzoxazole (the starting diazo ketone was completely absent in the reaction mixture after 2 h); in the case of Ib, c the reaction was complete after 8 h. The reaction is slowed down substantially when substituents are introduced into diazo ketone II (the reaction time increases to 2 days when R = H and R¹ = CH_3), whereas we were able to realize the reaction only with 2-mercaptobenzimidazole (Ib) in the case of strongly sterically hindered diazo ketone IIc, and alkylation of Ia,c does not occur even with heating.

The reaction of 2- and 8-mercaptoquinolines (IV) with diazo ketones IIa-c under similar conditions leads to the corresponding hetarylmercaptoalkyl diazo ketones Va-c and VIa-c:



Va-c VIa-c

V, VI a R=R¹=H; b R=H, R¹=CH_3; в R=R¹=CH_3

TABLE 3. PMR Spectra of Diazo Ketones IIIa-g, Va-c, and VIa-c in $(CD_3)_2CO$

Compound	δ, ppm (J, Hz)		
	Het	R^1—C—R	CHN_2 (c)
IIIa	7,0—7,25 (4H, m); 5,25 (1H, br.s NH)	4,05 (2H, s)	6,00
IIIb	7,0—7,3 (4H, m); 5,3 (1H, br.s NH)	1,09 (3H, d., J=7); 4,52 (1H, q, J=7)	5,80
IIIc[a]	6,46—6,82 (4H, m); 7,3 (1H, s, NH)	1,91 (6H, s)	5,92
IIId[b]	7,15—7,6 (4H, m)	4,1 (2H, s)	5,82
IIIe	7,29—7,68 (4H, m)	1,68 (3H, d, J=7); 4,71 (1H, q, J=7)	6,25
IIIf	7,25—7,75 (4H, m)	4,17 (2H, s)	6,0
IIIg[b]	7,30—7,90 (4H, m)	1,62 (3H, d, J=7); 4,54 (1H, q, J=7)	5,83
Va	7,40—8,85 (6H, m)	4,13 (2H, s)	6,13
Vb	7,42—8,80 (6H, m)	1,95 (3H, d, J=7); 4,52 (1H, q, J=7)	5,75
Vc	7,2—8,2 (6H, m)	1,68 (6H, s)	6,37
VIa	7,3—8,8 (6H, m)	3,85 (2H, s)	6,0
VIb	7,3—8,8 (6H, m)	1,49 (3H, d., J=7); 4,09 (1H, q, J=7)	5,95
VIc	7,42—9,0 (6H, m)	1,57 (6H, s.)	6,58

[a] The spectrum was recorded in $(CD_3)_2CO$ with added d_6-DMF.
[b] The spectrum was recorded in $CDCl_3$.

Alkylation of the mercapto group by even sterically hindered diazo ketone IIc occurred readily at room temperature. The properties of IIIa-g, Va-c, and VIa-c are presented in Tables 1-3.

Intense absorption bands of a diazo group at 2050-2115 cm^{-1} and of a diazo ketone C=O group at 1610-1630 cm^{-1} are observed in the IR spectra of IIIa-g, Va-c, and VIa-c. A singlet of a methylidyne proton of a diazo carbonyl fragment, which is shifted to weak field at 5.75-6.58 ppm, and characteristic signals of protons of the aliphatic and aromatic parts are observed in the PMR spectra (see Tables 2 and 3).

The primary process in the fragmentation of the molecular ions of diazo ketones IIIa-g, Va-c, and VIa-c is elimination of a molecule of nitrogen (the intensities of the $M^{+\cdot}$ ions do not exceed 1%). In contrast to the electron-impact method, peaks of MH^+ ions, which correspond to the calculated molecular masses, are also observed in the mass spectra of these compounds obtained by the chemical-ionization method.

The proposed method is evidently a unique method for the synthesis of diazo carbonyl derivatives of mercaptoheterocycles of the benzazole and quinoline series that are of interest as potential biologically active compounds and starting models for the synthesis of new condensed heterocyclic systems.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions in methanol were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in acetone were recorded with a Tesla BD-497 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with a Finigan 3200 mass spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 70 eV and an emission current of 0.4 μA. The purity of the substances was monitored by thin layer chromatography (TLC) in ethyl acetate—benzene and benzene—methanol systems on Silufol UV-254 plates.

Halo diazo ketones IIa-c were synthesized by the methods in [1, 4].

1-Diazo-3-(2-benzazolylmercapto)propanones (IIIa-g) and 1-Diazo-3-(2-quinolylmercapto)-propanones (Va-c) (General Method). A 0.015-mole sample of CH_3ONa was added to a solution of 0.015 mole of mercapto derivative Ia-c or IVa-c in 20 ml of dry methanol, and a solution of 0.015 mole of diazo ketone IIa-c in 20 ml of methanol was added dropwise with stirring. After 2-8 h, the methanol was removed by distillation, and the residue was separated with a column packed with silica gel (40/100 μ) by elution with benzene—methanol (9:1). The fraction with the appropriate R_f value (see Table 1) was collected, the solvent was removed by distillation, and the residue was recrystallized from heptane.

1-Diazo-3-(8-quinolylmercapto)propanones (VIa-c) (General Method). These compounds were similarly obtained from 0.02 mole of the potassium salt of 8-mercaptoquinoline and 0.02 mole of diazo ketone IIa-c (see Table 1).

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DIAZO CARBONYL DERIVATIVES OF HETEROCYCLES. 5.* INTRAMOLECULAR CYCLIZATION OF 2-HETARYLMERCAPTOALKYL-DIAZO KETONES. SYNTHESIS OF CONDENSED 1,3-THIAZIN-5-ONES

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787.3'836.7'831.1.07:542.97:543.
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The intramolecular heterocyclization of 2-benzazolylmercaptoalkyl diazomethyl ketones under the influence of acidic agents leads to 1,3-thiazino[2,3-b]benzimidazole, 1,3-thiazino[2,3-b]benzothiazolium, and 1,3-thiazino[2,3-b]benzoxazolium systems. Under similar conditions 2-quinolylmercaptoalkyl diazomethyl ketones form 1,3-thiazino[2,3-a]quinolinium systems.

We have previously reported a new method for obtaining a thiazine ring by intramolecular alkylation of the sulfur atom in the corresponding thioureidoalkyl α-diazo ketones under the influence of acidic agents [2]. However, the described method does not make it possible to obtain condensed heterocyclic systems that contain a 1,3-thiazine ring. In addition, the synthesis of the starting diazo ketones is extremely laborious. Nevertheless, precisely condensed 1,3-thiazines are included in the structures of valuable biologically active compounds such as antibiotics [3]. We have recently shown that acid-catalyzed heterocyclization at the nitrogen atom of the imidazole ring in 2-benzimidazolylmercaptomethyl diazomethyl ketone leads to 5-keto-3,4,5,6-tetrahydro-1,3-thiazino[2,3-b]benzimidazole [4].

In order to expand the possibilities of the use of intramolecular alkylation of diazo carbonyl derivatives of 2-mercaptoheterocycles for the synthesis of various condensed 1,3-thiazines, in the present research we studied the transformations of 2-hetarylmercaptoalkyl diazomethyl ketones Ia-c, VIIIa-d, and XIa-c, which we obtained in [1], under the influence of acidic agents.

We found that the introduction of a methyl group into the side chain (Ib) promotes heterocyclization and that the corresponding 1,3-thiazino[2,3-b]benzimidazole VIb is formed more easily. Thus the formation of VIb is observed at room temperature even without the participation of an acid. The mechanism of this transformation evidently includes self-catalysis by the acidic proton of the imidazole ring (via an intramolecular process, as shown in scheme A, or via intermolecular pathway B); the nucleophilicity of the nitrogen atom of the imidazole ring increases in intermediates IIb and IIIb, and this also promotes heterocyclization. Let us note that the thermal transformation of diazo ketone Ia also leads to cyclic compound VIa.

The acid-catalyzed heterocyclization of diazo ketone Ib, which leads to VIb (pathway B), also proceeds more rapidly as compared with homolog Ia. The acceleration of the reaction is

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*See [1] for communication 4.

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