3-Methyl-5-[(5-nitro-2-furfuryl)thio]-1,2,4-triazole Hydrochloride (VII). A 0.5 ml sample of concentrated HCl was added to a solution of 3.0 g (8.7 mmoles) of IIa in 40 ml of ethanol, and the mixture was refluxed for 5 min. It was then evaporated to a volume of 5 ml, and the concentrate was cooled and diluted with 15 ml of ether. The precipitate was washed with ether and air dried. Hydrochloride VII was similarly obtained from IIb-e.

3-Methyl-5-[(5-nitro-2-furfuryl)thio]-1,2,4-triazole (VIII). A 0.7 g (2.5 mmoles) sample of hydrochloride VII was added to a solution of 0.1 g (2.5 mmoles) of NaOH in 30 ml of a mixture of water and alcohol (1:1), and the mixture was stirred for 15 min. The precipitate was washed with water, dried, and recrystallized from ethyl acetate. Mass spectrum (m/z, relative intensity, %): 240 (100) M, 223 (73) (M − OH), 194 (46) $(M - NO_2)$, 126 (32) $(Fur - CH_2^+)$.

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SYNTHESIS OF SUBSTITUTED 1,3-THIAZINIUM PERCHLORATES

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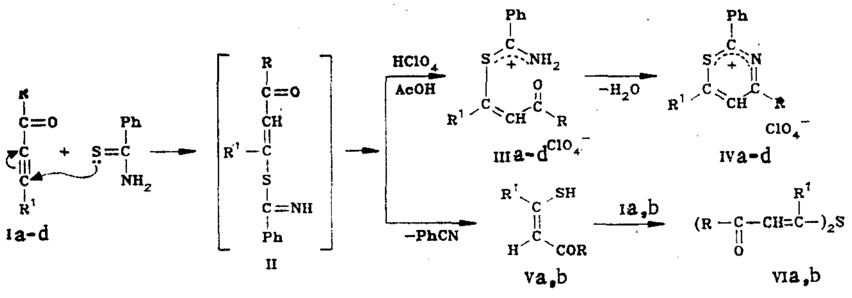
Substituted 1,3-thiazinium perchlorates were synthesized by the reaction of α-acetylenic ketones with thiobenzamide in acetic acid in the presence of perchloric acid.

It is known that the reaction of vinyl ketones with thioamides in acetic acid in the presence of perchloric acid leads to 3,6-dihydro-1,3-thiazinium perchlorates, which are dehydrogenated by trityl perchlorate to give substituted 1,3-thiazinium perchlorates [1]. Salts of this type were also obtained by the reaction of β-acylaminovinylthiocarbonyl compounds with perchloric acid in absolute ether at 20°C [2].

In the present research we studied the reaction of acylacetylenes Ia-d with thiobenzamide in the presence of perchloric acid.



I—VI a, b R=Ph; c,d R=α-C_4H_3S; a,c R^1=H; b, d R^1=Ph

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TABLE 1. Dependence of the Yields of IIIb, IVb, and Vb on the Reaction Conditions in the Presence of $HClO_4$

T_{re}, °C	Reaction time, h	Yield, %			T_{re}, °C	Reaction time, h	Yield, %		
		IIIb	IVb	Vb			IIIb	IVb	Vb
In commercial AcOH					In glacial AcOH				
5	1	74	5	—	5	1	—	36	10
5	3	48	20	—	5	3	—	45	12
5	6	45	22	—	5	6	—	48	12
20	3	—	52	—	20	6	—	20	45

TABLE 2. Acylvinylthiaimmonium Perchlorates IIIa-d and 2,4,6-Trisubstituted 1,3-Thiazinium Perchlorates IVa-d

Compound	mp, °C	Found, %					Empirical formula	Calculated, %					Yield,* %
		C	H	Cl	N	S		C	H	Cl	N	S	
IIIa	126—129	52,1	3,8	9,6	3,8	8,8	$C_{16}H_{14}ClNO_5S$	52,2	3,8	9,7	3,8	8,7	54
IIIb	179—181	59,2	4,2	8,0	3,3	7,4	$C_{22}H_{18}ClNO_5S$	59,5	4,1	8,1	3,2	7,2	48
IIIc	111—113	45,1	3,2	9,8	3,7	17,4	$C_{14}H_{12}ClNO_5S_2$	44,9	3,2	9,6	3,7	17,1	64
IIId	158—161	53,1	3,7	7,8	3,0	14,1	$C_{20}H_{16}ClNO_5S_2$	53,3	3,6	8,0	3,1	14,2	71
IVa	220—221	55,1	3,3	10,2	4,0	9,3	$C_{16}H_{12}ClNO_4S$	54,9	3,4	10,3	4,0	9,1	18
IVb	290—291	61,8	3,8	8,6	3,2	7,7	$C_{22}H_{16}ClNO_4S$	62,0	3,8	8,5	3,3	7,5	20
IVc	197—198	47,0	2,9	10,3	4,1	17,8	$C_{14}H_{10}ClNO_4S_2$	47,2	2,8	10,1	3,9	18,0	22
IVd	266—268	55,7	3,2	8,4	3,1	14,6	$C_{20}H_{14}ClNO_4S_2$	55,6	3,2	8,3	3,2	14,8	16

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*The yields were obtained when the reaction was carried out in 95% AcOH at 5°C for 3 h.

The first step in the reaction is evidently nucleophilic attack by the sulfur atom of the thiocarbonyl group on the electron-deficient carbon atom of the acetylenic bond with the formation of intermediate S-monoadducts II, which are protonated at the nitrogen atom of the imino group in the presence of $HClO_4$ with the formation of stable immonium salts IIIa-d. The stability of the latter can be explained by delocalization of the positive charge in the possible mesomeric structures.

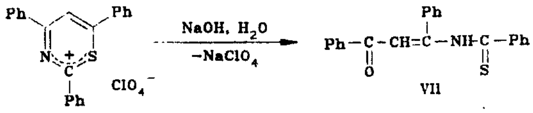
Under the reaction conditions salts IIIa-d then undergo dehydration to the corresponding 1,3-thiazinium perchlorates IVa-d. These perchlorates were also obtained by recrystallization of salts IIIa-d from AcOH or by storing them for 3-4 months at 20°C.

The direction of the reaction and the yields of IIIa-d and IVa-d depend substantially on the experimental conditions. This dependence was demonstrated in the case of the reaction of 1-benzoyl-2-phenylacetylene (Ib) with thiobenzamide in commercial (95%) and glacial acetic acid (100%) in the presence of an equimolar amount of $HClO_4$ (Table 1). Compound IIIb was isolated only when the reaction was carried out in 95% AcOH at 5°C. An increase in the reaction time and raising the temperature to 20°C lead to an increase in the yield of 2,4,6-triphenyl-1,3-thiazinium perchlorate (IVb). Compound IVb and a small amount of 1-benzoyl-2-mercapto-2-phenylethylene (Vb) are formed in glacial AcOH at 5°C. An increase in the temperature to 20°C leads to a decrease in the yield of IVb and a significant increase (up to 45%) in the yield of Vb.

Absorption bands of a conjugated C=O group at 1630-1650 cm^{-1}, of a C—S bond at 690-705 cm^{-1}, of a C=O bond at 1570-1580 cm^{-1}, and of an $=NH_2^+$ group at 3000-3300 cm^{-1} and intense absorption bands of a ClO_4^- anion at 1090-1110 cm^{-1} are present in the IR spectra of immonium salts IIIa-d. The IR spectra of perchlorates IVa-d do not contain absorption bands of NH_2 and C=O but do contain absorption bands of a C—S bond at 690-710 cm^{-1} and of ring C=N and C=C bonds at 1490-1510 and 1550-1565 cm^{-1}, respectively, and intense absorption bands of a ClO_4^- anion at 1080-1100 cm^{-1}.

Cleavage of the intermediate S-monoadducts II to benzonitrile and vinyl thiols Va, b which react with yet another molecule of acylacetylene Ia, b to give the corresponding bis(acylvinyl) sulfides VIa, b, occurs when the reaction of thiobenzamide is carried out with excess ketone Ia, b in glacial AcOH in the absence of $HClO_4$. We have previously obtained similar compounds in the reaction of thiobenzamide with acylacetylenes in MeOH or benzene in the presence of Et_3N and MeONa [3].

Cleavage of the 1,3-thiazine ring to give α-thiobenzoylamino-β-benzoylstyrene (VII) is observed in the alkaline hydrolysis of 2,4,6-triphenyl-1,3-thiazinium perchlorate (IVb) in ethanol at 20°C.



IVb

VII

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 mass spectrometer with an ionizing voltage of 70 eV; the temperature of the ionization chamber was 100°C.

The characteristics of the synthesized III and IV are presented in Table 2.

1,5-Diphenyl-5-oxo-2-thia-3-pentene-1-immonium Perchlorate (IIIa) and 2,4-Diphenyl-1,3-thiazinium Perchlorate (IVa). A solution of 0.89 g (5 mmoles) of 57% $HClO_4$ (d_4^{20} 1.49) in 20 ml of 95% AcOH was added with vigorous stirring to a cooled (to 5°C) mixture of 0.65 g (5 mmoles) of benzoylacetylene (Ia) and 0.69 g (5 moles) of thiobenzamide, and the mixture was stirred for 3 h at 5°C. The resulting yellow precipitate of immonium salt IIIa was removed by filtration, washed with cold AcOH and ether, and dried in vacuo. The yield was 1.0 g. The solution after separation of IIIa was allowed to stand for 2 days at 20°C. The resulting precipitate was removed by filtration, washed with cold ether, and dried in vacuo to give 0.32 g of perchlorate IVa in the form of gold needles.

Compounds IIIb-d and IVb-d were similarly obtained.

1-Benzoyl-2-mercapto-2-phenylethylene (Vb) and 2,4,6-Triphenyl-1,3-thiazinium Perchlorate (IVb). A solution of 0.89 g (5 mmoles) of 57% $HClO_4$ in 20 ml of glacial AcOH was added with vigorous stirring at 20°C to a mixture of 1.03 g (5 mmoles) of 1-benzoyl-2-phenylacetylene (Ib) and 0.69 g (5 mmoles) of thiobenzamide, and the mixture was stirred for 6 h at 20°C. The resulting precipitate was removed by filtration, washed with ether, and dried in vacuo to give 0.35 g (20%) of perchlorate IVb.

The solution after separation of salt IVb was allowed to stand for 2 days at 5°C. The resulting precipitate was removed by filtration, washed with ether, and dried in vacuo to give 0.54 g (45%) of Vb in the form of red crystals with mp 82-83°C (mp 84-85°C [4]). IR spectrum: 1635 (C=O), 1590 (C=C), 705 (C–S), 2480 cm^{-1} (SH). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 240 (12), $[M - PhCO]^+$ 135 (10), $[Ph{-}C{=}S]^+$ 121 (15), $[PhCO]^+$ 105 (100), $[Ph]^+$ 77 (75). Found: C 75.2; H 5.2; S 13.1%. $C_{15}H_{12}OS$. Calculated: C 75.0; H 5.0; S 13.3%.

Di(benzoylvinyl) Sulfide (VIa). A solution of 0.69 g (5 mmoles) of thiobenzamide in 10 ml of glacial AcOH was added to a solution of 1.3 g (10 mmoles) of benzoylacetylene (Ia) in 10 ml of glacial AcOH, and the mixture was stirred for 1 h at 20°C. It was then cooled to 5°C, and the resulting precipitate was removed by filtration, washed with cold AcOH and ether, and dried in vacuo. The yield was 1.06 g (72%) based on ketone Ia; the product had mp 144-168°C (for a mixture of isomers) mp 146-170°C (for a mixture of isomers) [3]. IR spectrum: 1642 (C=O), 1570 (C=C), 695 (CH=CH, cis), 942 (CH=CH, trans), 715 cm^{-1} (C–S).

Bis(1,3-diphenyl-3-oxo-1-propenyl) Sulfide (VIb). This compound was obtained from 2.06 g (10 mmoles) of ketone Ib and 0.69 g (5 mmoles) of thiobenzamide by a procedure similar to that used to prepare sulfide VIa. The yield was 1.36 g (61%). The yellow crystals had mp 185-186°C (mp 184-186°C [3]). IR spectrum: 1648 (C=O), 1570 (C=C), 695 cm^{-1} (C–S).

Alkaline Hydrolysis of 2,4,6-Triphenyl-1,3-thiazinium Perchlorate (IVb). A 1.06 g (2.5 mmoles) sample of IVb was added slowly to a solution of 0.1 g (2.5 mmoles) of NaOH in 30 ml of ethanol, and the mixture was stirred for 40 min at 20°C. The resulting precipitate was removed by filtration, washed with water–ethanol (1:1), and dried to give 0.7 g (82%) of α-thiobenzoylamino-β-benzoylstyrene (VII). The gray crystals had mp 149-150°C (mp 149-151°C [2]). IR spectrum: 1642 (C=O), 1585 (C=C), 1125 (C=S), 3440 cm^{-1} (NH). Mass spectrum, m/z (I_{rel}, %): $[M]^{+\cdot}$ 343 (12), $[M - PhCO]^+$ 238 (100), $[M - (PhC{=}S)]^+$ 222 (15), $[Ph{-}C{=}S]^+$ 121 (20), $[PhCO]^+$ 105 (85), $[Ph]^+$ 77 (90), $[HN{=}C{=}S]^{+\cdot}$ 59 (30). Found: C 76.8; H 5.0; N 4.2; S 9.2%. $C_{22}H_{17}NOS$. Calculated: C 77.0; H 5.0; N 4.1; S 9.3%.

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