SYNTHESIS AND REACTIONS OF OXO AND THIO DERIVATIVES OF 1,3-THIAZANE

III. Reaction of 1,3-Thiazane-2,4-dithione with Amino and Diazo Compounds*

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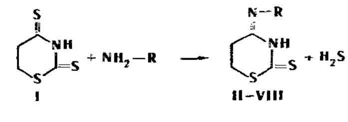
The reaction of 1,3-thiazane-2,4-dithione with amino compounds and diazonium salts has given the corresponding 4- and 5-substituted derivatives. The high reactivity of the thione group in position 4 has been noted. The optimum conditions for azo coupling have been found.

The method that we have developed for obtaining 1,3-thiazane-2,4-dithione (I), [1,2] from the readily available thiazane-2,4-dione has broadened the possibility of the study of I and, furthermore, has additionally confirmed the special role of dioxane as a medium for the conversion of oxo compounds into their thio analogs [3]. We were interested, on the one hand, in products of the condensation of I with amines as propiorhodanine derivatives and possible physiologically-active substances and, on the other hand, in products of the azo coupling of I with diazonium salts and the comparison of them with the structurally similar azo compounds. The reaction of I with amines takes place rapidly when the components are heated in the water bath with the formation of only the 4-substituted derivatives of I by the reaction:



Under these conditions, even with an excess of amine, only the C=S group in position 4 exhibits thioketone nature. The 4-imino derivatives of I synthesized and their properties are given in the table. The majority of them are light yellow, while III, IV, and VII are pale pink; II–V are sparingly soluble in organic solvents.

The azo coupling reactions of (I) were studied in various media. In a neutral medium, I does not couple with diazonium salts, unlike its five-membered analog, thiorhodanine [4], i.e., it possesses far less active methylene groups than thiorhodanine. In ammonia solution, in which rhodanine couples smoothly, the coupling of I again does not take place because of

Derivatives of 1,3-Thiazane-2,4-dithione

Compound	Name	Time of heating, min	Mp, °C*	Empirical formula	Found, %		Calculated %		Yield, %
					N	S	N	S	
II	1,3-Thiazane-2,4-dithione azine	10	carbonizes above 360° C	$C_8H_{10}N_4S_4$	18.89	43.70	19.28	44.17	42
III	1,3-Thiazane-2,4-dithione 4-oxime	300	185 (decomp.)	$C_4H_6N_2OS_2$	17.11	39.30	17.26	39.52	55
IV	1,3-Thiazane-2,4-dithione 4-semicarbazone	30	180	$C_5H_8N_4OS_2$	27.80	31.70	27.41	31.38	88
V	1,3-Thiazane-2,4-dithione 4-thiosemicarbazone	5	160 (decomp.)	$C_5H_8N_4S_3$	26.00	44.10	25.41	43.65	85
VI	1,3-Thiazane-2,4-dithione 4-p-nitrophenylhydrazone	5	165 (decomp.)	$C_{10}H_{10}N_4O_2S_2$	19.89	22.99	19.84	22.71	98
VII	4-(m-Carboxyphenylimino)thiazane-2-thione	15	188 (decomp.)	$C_{11}H_{10}N_2O_2S_2$	10.11	23.70	10.51	24.07	50
VIII	4-(m-Bromophenylimino)-thiazane-2-thione	300	149	$C_{10}H_9N_2S_2Br$	9.28	21.28	9.29	21.47	64
IX	5-(o-Tolylazo)-1,3-thiazane-2,4-dithione	—	181	$C_{11}H_{11}N_3S_3$	14.41	33.81	14.93	34.19	75
X	5-(p-Ethoxyphenylazo)-1,3-thiazane-2,4-dithione	—	171	$C_{12}H_{13}N_3OS_3$	13.50	30.99	13.49	30.89	56
XI	5-(p-Methoxyphenylazo)-1,3-thiazane-2,4-dithione	—	167 (decomp.)	$C_{11}H_{11}N_3OS_3$	13.95	32.70	14.12	32.35	84

*Solvents for crystallization: II–IV is dimethylformamide + water; VI is methanol; VII–IX is acetic acid; X–XI is dichloroethane.

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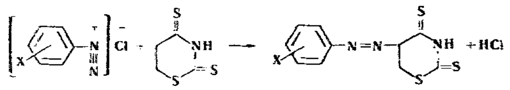
*For part II, see [1].

its reaction with the ammonia. The best results were shown by coupling in weak solutions of caustic soda, which led to the production of the individual azo compounds given in the table. The acid nature of the compounds obtained, determining the influence of the $C{=}S$ group on the activity of the neighboring methylene group, and also the possibility of the reaction of I in the enolic form point to coupling in position 5 by the following scheme:



I IX-XI

The azo compounds obtained are dark red substances readily soluble in organic solvents.

EXPERIMENTAL

1,3-Thiazane-2,4-dithione azine (II). By the action of 0.28 g (0.005 mole) of potassium hydroxide in 5 ml of methanol 0.26 g (0.0025 mole) of hydrazine hydrochloride was converted into the base the solution was filtered from potassium chloride, and to the filtrate was added a solution of 0.82 g (0.005 mole) of I in 10 ml of methanol. After heating for 10 minutes, a yellow precipitate deposited, 0.26 g (36%). It was purified by reprecipitation with water from dimethylformamide. It carbonized above 360° C. Sparingly soluble in organic solvents.

1,3-Thiazane-2,4-dithione 4-thiosemicarbazone (V). A mixture of 0.23 g (0.0025 mole) of thiosemicarbazide in 4 ml of methanol and 0.41 g (0.0025 mole) of I in 7 ml of methanol was heated for 5 minutes, and a yellow precipitate deposited from the hot solution; 0.47 g (85%), mp 159° C (decomp., from dioxane).

Other amino compounds were added similarly. Compounds IV–VII precipitated during the reaction, and compounds III and VIII after a day.

5-(o-Tolylazo)-1,3-thiazane-2,4-dithione (IX). The diazonium solution from 1.07 g (0.01 mole) of o-toluidine was added to a solution of 1.63 g (0.01 mole) of I and 1.5 g of NaOH in 100 ml of ice water at −3° C. After 10 min, the dark red solution was poured into 400 ml of ice water containing 6 ml of concentrated HCl, and the dye that precipitated was filtered off. Yield 2.2 g (78%). Readily soluble in dichloroethane, methanol, acetone, and other organic solvents. The alkaline solutions were bright red. From acetic acid it formed dark red crystals with mp 181° C.

The other azo-coupling products were obtained similarly.

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