REACTIVITY AND TAUTOMERISM IN THE AZOLIDINE SERIES

V.* SYNTHESIS OF 5-BENZYLIDENETHIORHODANINES

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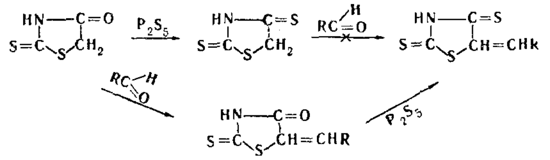
A series of 5-benzylidenethiorhodanines was obtained by the reaction of 5-benzylidenerhodanines with P_2S_5. An interpretation of the mechanism for the replacement of an oxygen atom by sulfur is given.

A number of physiologically active rhodanine derivatives are known [1]. It seemed of interest to us to study the replacement of the oxygen atom in rhodanine by a sulfur atom. Judging from the literature data, thiorhodanine has increased reactivity. Due to the sulfur atom in the 4-position, the thiorhodanine molecule readily condenses with amines to form the corresponding imino derivatives of rhodanine [2].

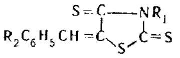
Reactions due to the active methylene group of thiorhodanine also take place, particularly condensation with several aromatic aldehydes (o-nitrobenzaldehyde and p-dimethylaminobenzaldehyde [3]). Our attempts to extend this reaction to other aromatic aldehydes to obtain 5-benzylidenethiorhodanines were unsuccessful. The condensation did not take place in either alcohol or glacial acetic acid in the presence of sodium acetate as the condensing agent.

We were able to obtain 5-benzylidenethiorhodanines as a result of sulfuration of 5-substituted rhodanines with P_2S_5 in anhydrous dioxane.



Compounds I-VII, the characteristics of which are presented in Table 1, were obtained by this method.

TABLE 1. 5-Benzylidenethiorhodanines



Compound	R_1	R_2	mp, °C	Crystallization solvent	Empirical formula	Found, %		Calc., %		Yield, %
						N	S	N	S	
I	H	H	198	Toluene	$C_{10}H_7NS_3$	5,68	39,88	5,88	40,35	60
II	H	p-CH_3	213	Ethanol	$C_{11}H_9NS_3$	5,32	38,50	5,55	38,11	58
III	H	p-CH_3O	208	Ethanol	$C_{11}H_9NOS_3$	5,36	36,09	5,21	35,84	74
IV	H	p-$(CH_3)_2N$	214	Ethanol–water	$C_{12}H_{12}N_2S_3$	9,80	34,30	9,95	34,18	67
V	H	p-NO_2	224	Propanol	$C_{10}H_6N_2O_2S_3$	9,58	33,50	9,89	33,95	59
VI	H	p-Br	205	Propanol	$C_{10}H_6BrNS_3$	4,53	31,02	4,41	30,32	70
VII	CH_3	H	198	Toluene	$C_{11}H_9NS_3$	5,42	38,39	5,57	38,26	85
VIII	H	m-NO_2	170	Ethanol	$C_{10}H_6N_2O_2S_3$	9,20	34,28	9,89	33,95	64

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[*] See [5] for communication IV.

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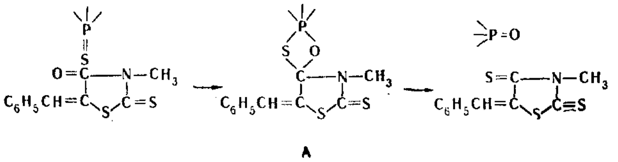
It has been assumed [3] that the replacement of a carbonyl group by a thiocarbonyl group is accompanied by enolization of the carbonyl group. In thiazolidinediones, which have two carbonyl groups, the carbonyl group with the greater enolizability is replaced.

In this study, 3-methyl-5-benzylidenerhodanine, which is not enolizable, was used to synthesize VIII. The formation of VIII in good yield indicates that enolization is not necessary for sulfuration. The following mechanism for replacement of oxygen by sulfur in rhodanines can be assumed:



The formation of an intermediate complex of the A type was found for the sulfuration of acid amides [4].

EXPERIMENTAL

5-Benzylidenethiorhodanine (I). 5-Benzylidenerhodanine [11 g (0.05 mole)] was dissolved with heating in 80 ml of dry dioxane in a three-necked flask equipped with a reflux condenser and stirrer, and 5 g (0.02 mole) of P_2S_5 was added with stirring, during which vigorous gas evolution was observed, and the solution became intensely red. The solution was refluxed for 0.5 h, filtered, and cooled. The resulting orange-red precipitate was filtered and recrystallized from toluene to give a product with mp 198 deg. Found %: N 5.68; S 39.88. $C_{10}H_7NS_3$. Calc. %: N 5.88; S 40.35.

Compounds II-VIII were similarly synthesized. Compounds II-IV did not crystallize on cooling and were precipitated from the reaction mixture with hexane.

LITERATURE CITED

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