REACTION OF 5-ALKYLIDENERHODANINES WITH DIAZONIUM SALTS

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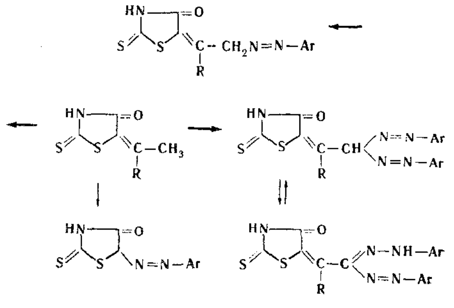
In the action of diazonium salts on 5-alkylidenerhodanines, azo compounds are formed by the replacement of one or two hydrogen atoms in the methyl group. In the case of 5-ethylidenerhodanines, the formation of an azorhodanine through the replacement of the alkylidene residue by an arylazo group takes place simultaneously. In the formazyl derivatives the long-wave absorption maximum is displaced hypsochromically by 15–20 nm as compared with the dyes having a single azo group.

The enhanced reactivity of the methylene group in the azolid-4-ones enables very diverse derivatives of these compounds at position 5 to be obtained. According to the principle of vinylogy, it could be assumed that the methyl group in 5-alkylidene derivatives of the azolid-4-ones should also possess an enhanced reactivity.

As shown previously [1, 2], the hydrogen atoms of the methylene group of rhodanine possess the greatest mobility. The investigations carried out have established that only the methyl group of 5-ethylidenerhodanine and its α-methyl and α-phenyl derivatives react with diazonium salts. The arylazo group replaces one or two hydrogen atoms in the methyl group. Other 5-alkylidene derivatives of azolid-4-ones, namely 5-ethylidene-2-thiohydantoin, 5-(α-methylpropylidene)rhodanine, and 5-(α-methylbutylidene)-rhodanine do not react with diazonium salts under these conditions.

However, in addition to the azo coupling reaction at the methyl group, the replacement of the alkylidene residue sometimes takes place with the formation of the corresponding azorhodanine. The formation of these products may be represented by the following scheme:



The replacement of the alkylidene residue by the arylazo group is observed in the case of 5-ethylidenerhodanine: acetaldehyde and an arylazorhodanine are found in the reaction product. The replacement of an acetophenone or acetone residue did not take place under these conditions, in contrast to information in the literature for derivatives of isoxazol-5-one [3].

The structure of the compounds obtained is confirmed not only by the analytical data but also by their solubility in alkalis and their capacity for undergoing hydrolysis with the formation of thiocyanic acid, which shows that position 3 of the thiazolidine ring is free.

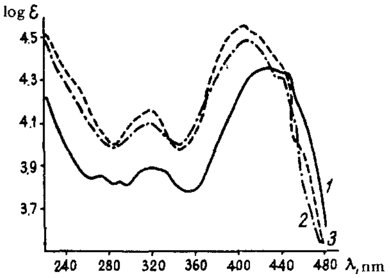


Fig. UV absorption spectra: 1) 5-(o-carboxyphenylhydrazonoethylidene) rhodanine (I); 2) 5-[bis(o-carboxyphenylazo) ethylidene]rhodanine (II) 5-[β-(o-carboxyphenylazo)-α-methylethylidene] rhodanine (III).

The similarity of the UV spectra of the formazyl derivative of 5-ethylidenerhodanine and the derivative of 5-isopropylidenerhodanine containing two arylazo groups shows that the latter has the formazyl, and not the bishydrazone, structure.

EXPERIMENTAL

5-Ethylidene-, 5-phenylethylidene-, and 5-isopropylidenerhodanines were obtained by published methods [4].

5-(β-Phenylazoethylidene)rhodanine (I). A solution of 1.1 g (0.007 mole) of 5-ethylidenerhodanine in 75 ml of 5% aqueous ammonia was coupled at 0° C with 0.014 mole of benzenediazonium hydrochloride, obtained from 0.014 mole of aniline. Considerable resinification took place. The yellow precipitate was filtered off from the red-orange solution. Acidification of the filtrate with hydrochloric acid (1 : 1) led to the separation of an additional amount of precipitate. Yield was 0.55 g. From glacial acetic acid it formed yellow microcrystalline powder.

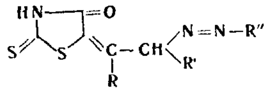
In a similar manner to I, 5-ethylidenerhodanine and p-sulfamoylbenzenediazonium hydrochloride gave **5-[β-(sulfamoylphenylazo)-ethylidene]rhodanine (II) (table).**

5-[β-(o-Carboxyphenylazo)ethylidene]rhodanine (III) and 5-[β, β-bis(o-carboxyphenylazo)ethylidene]rhodanine (IV). A solution of 2.4 g (0.015 mole) of 5-ethylidenerhodanine in 80 ml of 5% aqueous ammonia was coupled with 0.03 mole of o-carboxybenzenediazonium hydrochloride. After acidification, the precipitate was filtered off and treated with boiling methanol. Part of the substance passed into ethanolic solution, the dilution of which with water yielded a yellow substance (III). From acetic acid it formed yellow plates. The residue after the ethanol treatment was recrystallized from glacial acetic acid, which gave a yellow microcrystalline powder (IV).

Similarly, 5-isopropylidenerhodanine and o-carboxybenzenediazonium chloride gave V. After recrystallization from methanol it formed a brick-red microcrystalline powder.

5-[α-Phenyl-β, β-bis(o-carboxyphenylazo)ethylidene]rhodanine (VI). With gentle heating, 1.2 g (0.005 mole) of 5-(α-phenylethyli-

5-Arylazoalkylidenerhodanines



Compound	R	R′	R″	Mp, °C	Color	Empirical formula	Found, %		Calculated, %		Yield, %
							N	S	N	S	
I	H	H	C_6H_5	208—210	Yellow	$C_{11}H_9ON_3S_2$	16.53	24.56	16.58	25.32	31
II	H	H	p-H_2N—SO_2—C_6H_4	311—312*	Light yellow	$C_{11}H_{10}O_3N_4S_3$	16.63	27.95	16.36	28.09	47
III	H	H	o-HOOC—C_6H_4	234—235	Yellow	$C_{12}H_9O_3N_3S_2$	13.99	20.85	13.67	20.86	
IV	H	o-HOOC—C_6H_4—N=N	o-HOOC—C_6H_4	225—226	Light yellow	$C_{19}H_{13}O_5N_5S_2$	14.92	14.39	15.37	14.08	
V	CH_3	o-HOOC—C_6H_4—N=N	o-HOOC—C_6H_4	207—209	Yellow	$C_{20}H_{15}O_5N_5S_2$	14.83	13.25	14.91	13.61	72
VI	C_6H_5	H	o-HOOC—C_6H_4	201—202	Dark red	$C_{18}H_{13}O_3N_3S_2$	10.43	16.63	10.95	16.72	73
VII	C_6H_5	H	p-CH_3—C_6H_5	225—226**	Brown	$C_{18}H_{15}ON_3S_2$	12.14	17.82	11.88	18.12	62

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*From water.

**From methanol.

dene)rhodanine was dissolved in 35 ml of 5% ethanolic KOH. The solution was cooled to 0° C, and to it was slowly added a solution of o-carboxybenzenediazonium chloride prepared from 0.68 g (0.005 mole) of anthranilic acid. The solution immediately became dark red, and then it deposited a small amount of crystals. The mixture was left in ice for another 30 min and was then acidified with 10% hydrochloric acid. The ground precipitate was filtered off, washed with water, and dried. Yield 1.4 g; thin dark red needles from methanol.

5-[α-Phenyl-β-(p-tolylazo)ethylidene]rhodanine (VII) was obtained similarly using p-toluenediazonium chloride.

5-(p-Tolylazo)rhodanine. A solution of 0.8 g (0.005 mole) of 5-ethylidenerhodanine in 30 ml of 5% aqueous ammonia was coupled with the p-toluenediazonium chloride obtained from 0.5 g (0.005 mole) of p-toluidine. During the coupling reaction, the solution foamed, the smell of acetaldehyde was perceived and a yellow precipitate deposited. After 30 min, the solution was acidified, and the precipitate was separated off and recrystallized from methanol. Orange needles with mp 229–230° C, which corresponds to literature data for 5-(p-tolylazo)rhodanine [5]. Found, %: N 17.08; S 25.55. Calculated for $C_{10}H_9ON_3S_2$, %: N 16.71; S 25.51.

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