4-THIAZOLIDINES, DERIVATIVES AND ANALOGS

V. Arylidene Derivatives of Isorhodanine*

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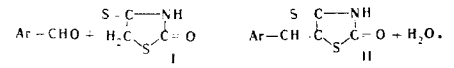
In order to prepare isomers of 5-arylidene derivatives of rhodanine, 4-thione-1, 3-thiazolid-2-one (isorhodanine) is condensed with aromatic aldehydes and furfural. The reaction takes place when the reactants are heated together in acetic acid containing sodium acetate. Twelve arylidenerhodanines are described.

The most readily accessible and numerous group of derivatives of azolid-4-ones are the products of condensation with various carbonyl compounds, in particular 5-arylidene(alkylidene)azolid-4-one. Of considerable interest is the possibility of using these compounds for practical purposes, e.g. in analytical chemistry (Feigl's reagent) and in medicine, because of the broad spectrum of antimicrobial and pharmacological activities [1] they exhibit.

The synthesis of these compounds primarily depends on the activity of the methylene group of the azolidone, and in isolated cases is difficult [2].

However, as was previously shown [3], the methylene group can be considerably activated by replacing the oxygen atom at position 4 by sulfur.

One of the compounds of enhanced reactivity which we have synthesized is a rhodanine isomer, 4-thione-1, 2-thiazolid-2-one (I) called isorhodanine [4]. The present paper describes condensations of I with aldehydes according to the reaction:

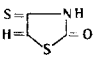


Syntheses of II, run in methanol and in methanol plus potassium chloride or sodium acetate (anhydrous), gave, except in the case of reaction with p-dimethylaminobenzaldehyde [4], poor results, the yield being quite low even in the best case. The best results were obtained in acetic acid-sodium acetate, by heating for 10–20 min, followed by boiling on gauze for 2–3 minutes, then precipitating the product with water. Longer boiling of the reactants in the same solvent, as well as synthesis in ammonia and ammonium chloride [5], leads to splitting off of H_2S, i.e., to decomposition of I.

The compounds synthesized are shown in the table. They are colored and crystalline, readily soluble in cold acetone, and in the lower alcohols and acetic acid on heating. They are insoluble in water and also, generally, in toluene and carbon tetrachloride. They exhibit acid properties, dissolving readily in cold alkalies, with the exceptions of the less soluble compounds nos. 3, 6, and 11.

Undoubtedly special interest attaches to investigation of their analytical sensitivities and biological

*For Part IV see [6].

5-Arylideneisorhodanines 

Run no.	Ar	Color	Mp, °C	Formula	Found, %		Calculated, %		Yield, %
					N	S	N	S	
1	C_6H_5	yellowish orange	172	$C_{10}H_7NOS_2$	6.39	28.62	6.33	28.97	59
2	o-$NO_2C_6H_4$	orange	169	$C_{10}H_6N_2O_3S_2$	10.56	23.95	10.52	24.08	70
3	m-$NO_2C_6H_4$	yellowish orange	139–140	$C_{10}H_6N_2O_3S_2$	10.53	23.58	10.52	24.08	76
4	p-$NO_2C_6H_4$	pale brown	203–204	$C_{10}H_6N_2O_3S_2$	10.76	24.01	10.52	24.08	98
5	m-ClC_6H_4	bright orange	151	$C_{10}H_6ClNOS_2$	5.62	25.38	5.47	25.07	72
6	p-ClC_6H_4	bright orange	194–195	$C_{10}H_6ClNOS_2$	5.39	25.23	5.47	25.07	63
7	p-Dimethylamino	red	261	$C_{12}H_{12}N_2OS_2$	10.75	23.98	10.60	24.24	70
8	o-HOC_6H_4	red	221	$C_{10}H_7NO_2S_2$	5.89	26.86	5.92	27.02	70
9	4-HO-(3-CH_3O)C_6H_3	cherry colored	225–226	$C_{11}H_9NO_3S_2$	5.38	23.92	5.25	23.99	41
10	Veratryl 3,4-(CH_3O)$_2C_6H_3$	pale red	188–189	$C_{12}H_{11}NO_2S_2$	5.33	22.82	4.98	22.79	60
11	α-$C_{10}H_7$	cherry colored	215–216	$C_{14}H_9NOS_2$	5.13	23.38	5.16	23.63	75
12	α-C_4H_4O	bright orange	220–221	$C_8H_5NO_2S_2$	6.80	30.27	6.66	30.35	71

For analysis compounds 1 and 7 were recrystallized from EtOH, 2 and 3 from MeOH, 4–6 and 8–11 from AcOH, and 12 from dichloroethane.

actions, and comparison with the same properties for isomeric 5-arylidenerhodanines.

EXPERIMENTAL

4-Thione-1, 3-thiazolid-2-one (isorhodanine) (I) [4] was prepared in 63% yield by refluxing thiazolidin-2, 4-dione with P_2S_5 in dry dioxane for 3 hr, followed by recrystallization from dichloroethane, mp 160° C.

5-(o-Nitrobenzylidene)-4-thione-1, 3-thiazolid-2-one. A mixture 1.55 g (0.01 mole) o-nitrobenzaldehyde, 1.34 g (0.01 mole) I, 10 ml glacial AcOH, and 1 g fused NaOAc was heated under reflux for 20 min on a steam bath, then boiled for 5 min over gauze. After cooling 10 ml water was added, the precipitate filtered off, washed with water, and dried at 60° C, yield 1.8 g. Recrystallized from MeOH it formed orange needles, mp 168°-170° C. Readily soluble in acetone, ethyl benzoate, in alcohols and amyl acetate in heat, slightly soluble in ether, hydrocarbons, and halogen derivatives.

The other II compounds were prepared similarly. Reacting with only 15 min heating, m- and p-chlorobenzaldehyde are the most reactive. For salicylaldehyde and veratryl aldehyde, the heating times were respectively 25 ± 2 and 30 ± 10 minutes.

REFERENCES

1. E. C. Brown, Chem. Rev., **61**, 508, 1961.

2. S. N. Baranov and I. D. Komaritsa, KhGS [Chemistry of Heterocyclic Compounds], 69, 1965.

3. A. P. Grishchuk, T. E. Gorizdra, I. D. Komartisa, and S. N. Baranov, Author's Certificate 172808, Byull. izobr,, no. 14, 1965.

4. A. P. Grishchuk, I. D. Komaritsa, and S. N. Baranov, KhGS [Chemistry of Heterocyclic Compounds], 706, 1966.

5. M. Girard, Ann. Chim., **16**, 326, 1941.

6. A. P. Grishchuk, G. I. Roslaya, and S. N. Baranov, KhGS [Chemistry of Heterocyclic Compounds], 661, 1967.

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