REACTION OF ARYLPYROTARTARIC ACIDS WITH RHODANINE

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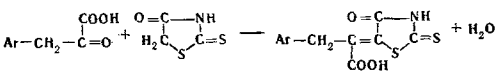
The reaction of arylpyrotartaric acids with rhodanine in ethanol in the presence of aqueous ammonia and ammonium chloride has yielded 5-(β-aryl-α-carboxyethylidene)rhodanines.

There are descriptions in the literature of the product of the condensation of rhodanine with several α-dicarbonyl compounds such as ethyl oxalate [1], glyoxalic acid [2], pyrotartaric acid [3], biacetyl [4], and benzil [5, 6]. As our investigations have shown, aromatic α-ketoacids (derivatives of phenylpyrotartaric acid) condense with rhodanine in the presence of alkaline, but not acid, catalysts, according to the equation:



The 5-(β-aryl-α-carboxyethylidene)rhodanines form colored crystalline substances soluble in alcohols, acetone, dioxane, acetic acid, and some other organic solvents and readily soluble in sodium bicarbonate solution, with the evolution of carbon dioxide.

EXPERIMENTAL

The required arylpyrotartaric acids were obtained by the alkaline hydrolysis of 5-arylidene-2-thioxooxazolid-4-ones [7] or by the acid hydrolysis of the azalactones obtained from aceturic acid and the corresponding aromatic aldehydes. The properties of the compounds obtained corresponded to literature data.

5-(α-Carboxy-β-phenylethylidene)rhodanine. A mixture of 1.33 g (0.01 mole) of rhodanine, 1.64 g (0.01 mole) of phenylpyrotartaric acid, 1 g of ammonium chloride, 1 ml of concentrated aqueous ammonia, and 10 ml of ethanol was boiled for 1 hr. After cooling, 30 ml of water was added, the mixture was acidified with hydrochloric acid, and the precipitate was filtered off (2.6 g).

The other compounds given in the table were obtained similarly.

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5-(β-Arylethylidene-α-carboxy)rhodanines

Ar	External form	Mp (decomp.), °C*	Empirical formula	Found, %		Calculated, %		Yield, %
				N	S	N	S	
C_6H_5	Orange plates	226	$C_{12}H_9O_3NS_2$	5.32	22.75	5.02	22.96	93
p-$CH_3 \cdot C_6H_4$	Orange plates	221	$C_{13}H_{11}O_3NS_2$	4.78	22.05	4.77	21.86	73
p-$CH_3O \cdot C_6H_4$	Orange-red plates	219	$C_{13}H_{11}O_4NS_2$	4.31	20.50	4.53	20.75	86
4′-OH-3′-$CH_3O \cdot C_6H_3$	Orange-red plates	211	$C_{13}H_{11}O_5NS_2$	4.45	19.35	4.31	19.65	80
3′,4′-$(OCH_3)_2C_6H_3$	Dark red plates	215	$C_{14}H_{13}O_5NS_2$	4.45	18.88	4.13	18.89	80
o-$NO_2 \cdot C_6H_4$	Orange needles	201**	$C_{12}H_8O_5N_2S_2$	8.66	19.41	8.64	19.77	85
m-$NO_2 \cdot C_6H_4$	Yellow prisms	231	$C_{12}H_8O_5N_2S_2$	8.70	19.55	8.64	19.77	92
p-$NO_2 \cdot C_6H_4$	Light brown needles	227***	$C_{12}H_8O_5N_2S_2$	8.56	19.43	8.64	19.77	94
p-$Br \cdot C_6H_4$	Orange-yellow needles	241	$C_{12}H_8O_3NS_2$	4.27	18.59	3.91	18.87	82
p-$Cl \cdot C_6H_4$	Orange-yellow needles	222	$C_{12}H_8O_3NS_2$	4.72	20.18	4.46	20.41	89

*From acetic acid.
**From aqueous ethanol.
***From isopropanol.