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REACTION OF 2-PYRIDINE ALDEHYDE WITH RHODANINES

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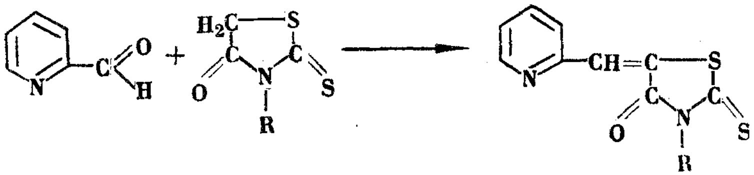
Reaction of 2-pyridine aldehyde or its methiodide in methanol solution in the presence of piperidine with rhodanine or 3-alkylrhodanines leads to crotenoid condensation and formation of 2-pyridinylidene-5-rhodanine and 2-pyridinylidene-5-(3-alkyl) rhodanines and their monomethiodides.

Heteryllidene compounds with pyridine and quinoline groups are known to find application in pharmacology [1], motion-picture chemistry [2], and synthetic organic chemistry [3, 4].

As an extension of the synthesis of 6-quinolidene-5-(3-alkyl)- rhodanines [5], a study has been made of the condensation of 2-pyridine aldehyde [6] and its methiodide with rhodanines [7].

Unlike the previously offered method of synthesizing 2-pyridinylidenerhodanine [8] and 3-alkyl-substituted rhodanines [9], where the yields of the latter were 75-78%, here the aldehyde has been reacted with rhodanines in the presence of piperidine and in methanol solution. The reactions gave quantitative yields of 2-pyridinylidene-5(3-alkyl) rhodanines.

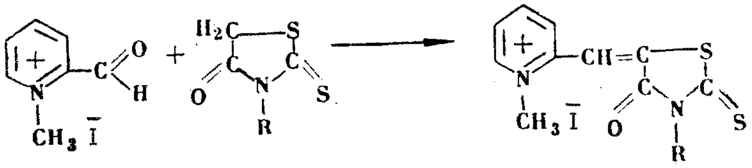


I—IV R=H, CH_3, C_2H_5, C_3H_5

The 2-pyridinylidene-5-rhodanine (I), 2-pyridinylidene-5-(3-methyl) rhodanine (II), 2-pyridinylidene-5-(3-ethyl) rhodanine (III), and 2-pyridinylidene-5-(3-alkyl) rhodanine (IV) synthesized are colored crystalline compounds which are stable on keeping (Table 1).

2-Pyridine aldehyde methiodide condenses just as readily with the same rhodanines when they are heated together for a short time in glacial acetic acid, and the products are 2-pyridinylidene-5-(3-alkyl)rhodanines methiodides (V-VIII).

These quaternary compounds are colored crystalline substances which are soluble in water (Table 2).



V—VIII R=H, CH_3, C_2H_5, C_3H_5

Unlike 6-quinolidene-5-(3-alkyl) rhodanines [5], free 2-pyridinylidenerhodanines I-IV do not add methyl iodide when the two are mixed and left to stand for a long time (35-45 days), and the same obtains after 5 hr heating in glacial acetic acid or acetic anhydride. Evidently the basicity of the pyridine ring nitrogen atom is greatly depressed, because of the mesomerism of the lone pair of electrons of the pyridine. They do not form picrates.

Consideration of the UV spectra of I-IV reveals an absorption band with a maximum at 385-387 mμ, which, in the cases of methiodides VI-VIII is shifted 20 mμ towards the shortwave region.

Experimental

2-Pyridinylidene-5-rhodanine (I). 1.2 g (9.0 mmole) 2-pyridine aldehyde (bp 178-181°) was poured into 0.96 g (9.0 mmole) rhodanine in 3 ml methanol (slight heating, onset of reaction), followed by 0.4 ml freshly-distilled piperidine (heat evolved). A precipitate rapidly formed. It was filtered off, washed with methanol, and then with ether.

Yield 1.0 g yellow green crystals, mp 256-257° (decomp).* The substance was recrystallized from glacial acetic acid. It was sparingly soluble in hot methanol, ethanol, and hot glacial acetic acid, very sparingly soluble in chloroform and benzene, but its solubility in ether was negligible, and it was insoluble in water.

Table 1

Properties of the Rhodanines and Synthesis Conditions

Compound number	R	Quantities of reactants, g (mmole)		Mp, °C	UV spectra		Formula	Found, %				Calculated, %				Yield, %
		2-Pyridine aldehyde	Rhodanine and 3-alkyl-rhodanine		λmax, mμ	ε · 10⁻⁴		C	H	N	S	C	H	N	S	
I	H	0.96 (9.0)	1.20 (9.0)	258–260	387	2.94	$C_9H_6N_2OS_2$	48.41	2.60	12.84	28.48	48.60	2.72	12.60	28.86	50.0
II	CH_3	0.60 (5.6)	0.82 (5.5)	222	385	3.00	$C_{10}H_8N_2OS_2$	58.97	3.25	11.72	27.52	50.80	3.41	11.86	27.15	91.0
III	C_2H_5	0.34 (3.1)	0.52 (3.2)	197	385	3.00	$C_{11}H_{10}N_2OS_2$	52.83	4.36	11.38	25.73	52.75	4.02	11.19	25.63	95.0
IV	C_3H_5	0.30 (2.8)	0.48 (2.8)	189	385	3.30	$C_{12}H_{10}N_2OS_2$	54.60	4.18	10.88	24.89	54.91	3.84	10.68	24.45	96.0

Table 2

Properties of Rhodanine Methiodides and Synthesis Conditions

Compound number	R	Quantities of reactants, g (mmole)		Mp, °C	UV spectra		Formula	Found, %			Calculated, %			Yield, %
		2-Pyridine aldehyde	Rhodanine and 3-alkyl-rhodanine		λmax, mμ	ε . 10⁻⁴		I	N	S	I	N	S	
V	H	2.24 (9.0)	1.2 (9.0)	244–245	385	2.50	$C_{10}H_9IN_2OS_2$	34.74	8.31	18.13	34.85	7.69	17.61	88.4
VI	CH_3	1.0 (4.0)	0.59 (4.0)	219–220	365	1.86	$C_{11}H_{11}IN_2OS_2$	33.84	7.27	17.30	33.56	7.40	16.96	92.0
VII	C_2H_5	0.78 (3.1)	0.50 (3.1)	202–203	365	1.94	$C_{12}H_{13}IN_2OS_2$	32.49	7.33	16.63	32.36	7.14	16.35	83.0
VIII	C_3H_5	0.50 (2.0)	0.35 (2.0)	183–184	365	1.84	$C_{13}H_{13}IN_2OS_2$	31.13	6.81	16.16	31.40	6.93	15.86	83.0

2-Pyridinylidene-5-(3-alkyl) rhodanines II-IV were synthesized in a similar way: 0.2 ml piperidine was added. II and III were recrystallized from glacial acetic acid, IV from benzene. Compound II was lemon yellow in color, III and IV formed glistening yellow crystals.

2-Pyridinylidene-5-rhodanine methiodide (V). 2.24 g (9.0 mmole) aldehyde methiodide (mp 156-157°) and 1.2 g (9.0 mmole) rhodanine in 5 ml glacial acetic acid were refluxed for 5 min. A precipitate was rapidly formed, the mixture was diluted with dry ether, and the precipitate filtered off and washed with dry ethanol. Yield 2.9 g reddish-brown crystals, which after washing with hot ethanol had mp 243-244° (decomp). Recrystallization from dilute (1:1) acetic acid gave claret-colored crystals. The compound was very sparingly soluble in hot methanol, hot ethanol and hot glacial acetic acid, but is soluble in water.

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*In determining the melting points of the rhodanines they were rapidly heated to 200° in the capillary. If a capillary was heated from room temperature or from 150° it was difficult to determine the melting point. In all the experiments the melting points of the methiodides were determined starting at 150°.

2-Pyridinylidene-5-(3-alkyl) rhodanines VI-VIII were prepared similarly. They were sparingly soluble in alcohols and glacial acetic acid, but soluble in hot water. VI and VII were recrystallized from dilute (2:1) acetic acid, and then repeatedly from dry ethanol; VIII was recrystallized from glacial acetic acid. They formed dark red crystals with a brownish reflex, or reddish orange crystals depending on the solvent used.

The UV spectra of I-VIII were determined with a SF-4 spectrophotometer, layer thickness 1 cm, concentration 5.1-5.0 mole/1 in ethanol.*

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