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SYNTHESIS OF 5-ARYLIDENE DERIVATIVES OF THIAZANE-2, 4-DITHIONE

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Thiazane-2, 4-diones and their 3-aryl derivatives readily condense with aromatic aldehydes to give 5-arylidene derivatives. The compounds obtained are characterized by absorption maxima in the 290-310 mμ band, as well as by ill-defined bands at 260-270 and 420-440 mμ. The IR spectrum of 5-benzylidenethiazane-2, 4-dithione has bands at 7.02 (N—C—S), 7.52 (CH_2), 14.62 and 15.01 (C—S—C)μ.

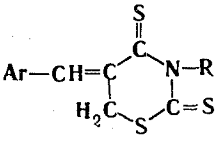
2-Thiothiazolide-4-one (rhodanine) readily condenses with carbonyl compounds, because of the presence of mobile hydrogen atoms at position 5 [1, 2]. Unlike this, the 6-membered analog of rhodanine 2-thiothiazol-4-one is incapable of reacting even with aromatic aldehydes [3], and does not form 5-arylidene derivatives.

Taking into account the fact that on passing from thiazolidin-2, 4-dione to rhodanine [4], or from barbituric acid to thiobarbituric acid [5], the lability of position 5 hydrogen atoms increases considerably, we attempted to replace the oxygen atom at position 4 in the 2-thiothiazane-4-one molecule with a sulfur atom to increase the mobility of the H atoms in the thiazane ring. Actually, thiazane-2, 4-dithione previously synthesized by us [6] readily undergoes condensation with aromatic aldehydes, the equation being:

We ran the condensation in glacial acetic acid in the presence of fused sodium acetate as the condensing agent. The table gives the compounds synthesized.

5-Arylidenethiazane-2, 4-dithiones are brown crystalline compounds, very sparingly soluble in ordinary organic solvents. They are insoluble in NaOH solutions, and suspensions in those solutions do not give a nitroprusside reaction.

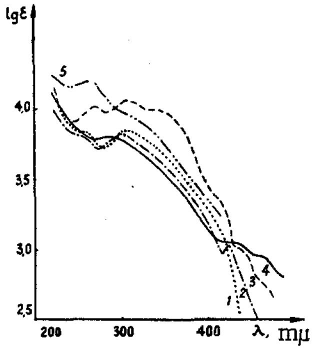
5-Arylidenethiazane-2, 4-dithiones



Ar	R	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
C_6H_5	H	172	$C_{11}H_9NS_3$	52.33	3.85	5.63	52.56	3.60	5.57	10.0
p-ClC_6H_4	H	165	$C_{11}H_8NS_3Cl$	46.09	3.03	4.90	46.22	2.82	4.90	87.4
p-$NO_2C_6H_4$	H	207	$C_{11}H_8N_2O_2S_3$	44.53	2.93	9.25	44.58	2.72	9.45	85.0
3,4-$(CH_3O)_2C_6H_3$	H	133	$C_{13}H_{11}NO_2S_3$	50.08	4.29	4.23	50.13	4.20	4.49	43.0
p-$(CH_3)_2NC_6H_4$	p-$C_2H_5OC_6H_4$	164	$C_{21}H_{22}N_2OS_3$	60.96	5.25	6.48	60.84	5.35	6.75	88.1

It is seen from the UV absorption spectra plots of the accompanying figure, that 5-arylidenethiazane-2, 4-dithiones are characterized by three bands at 260-270, 290-310, and 420-440 mμ. In all the plots the maxima are at the second band only. Due to the superposition of two high-intensity bands, i. e., the K bands and the third thione bands, characteristic obliteration of the absorption spectra above 310 mμ is observed.

In the IR spectra of 5-benzylidenethiazane-2, 4-dithione, the most marked bands are those due to valence vibrations of N—C—S (7.01μ), CH_2 (7.52μ), and C—S—C (14.62 and 15.01 mμ). Like bands at 6.84, 7.43, and correspondingly, 14.93, were observed by us for unsubstituted thiazane-2, 4-dithione [7].



UV spectra: 1) p-chlorobenzylidenethiazanethione; 2) 5-benzylidenethiazanedithione; 3) 5-p-nitrobenzylidenethiazanedithione; 4) 5-veratrylidenethiazanedithione; 5) 5-p-dimethylaminobenzylidene-3-p-ethoxyphenylthiazanedithione.

Experimental

Condensing thiazane-2, 4-dithiones with aldehydes. A mixture of 10-20 mmole thiazane-2, 4-dithione, 15-20 mmole aromatic aldehyde, 10-20 mmole fused NaOAc, and 10-15 ml glacial acetic acid was refluxed for 2.5-4 hr in a flask. Precipitation from the initially clear solution was observed only in the condensation with p-nitrobenzaldehyde. Next the reaction mixture was diluted with water, or else that was done after distilling off part of the solvent, the precipitate filtered off, and purified by recrystallization from EtOH and AcOH, as well as by washing with ether and dioxane.

To prepare 5-p-dimethylaminobenzylidene-3-p-ethoxyphenylthiazane-2, 4-dithione, a mixture of 3.28 mmole 3-p-ethoxyphenylthiazane-2, 4-dione, 3.49 mmole p-dimethylaminobenzaldehyde, and 10 ml glacial acetic acid was refluxed for 1 hr, and then evaporated in air almost to dryness. The residue was washed with ether, water, and boiling EtOH.

The UV spectra of the compounds investigated were determined in EtOH solution, using an SF-4 spectrophotometer. The IR spectra were determined with the compounds tabletted with KBr, using a UR-10 spectrophotometer.

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DIRECT N-ARYLATION OF 5-MEMBERED HETEROCYCLIC NITROGEN RINGS

III. Synthesis of N-Arylimidazoles*

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Ring-substituted bromoaryl derivatives are used to arylate imidazole at the NH group.

Continuing our researches on the direct N-arylation of nitrogen ring compounds [1, 2], we have synthesized 1-arylimidazoles with various substituents (halogen atom, formyl, acetyl, methoxy, and dimenthylamino group) in the aryl group. The reaction was carried out by reacting the bromoaryls with imidazole under the previously described conditions [2].

The presence of an acetyl or formyl group para to the bromine enables the reaction time to be sharply cut. Thus only 13 hours heating gives a 65% yield of p-(N-imidazolyl) acetophenone. Because of possible side reactions [see 3] during formylation, cutting reaction time favorably affects the arylation product yield. Cutting the times from 30 to 18 hr raises the yield of p-(N-imidazolyl) benzaldehyde from 8 to 30%.

The N-arylimidazoles obtained contain reactive groups, and they can be changed further at the aryl group. Thus heating the methoxy derivatives with hydrobromic acid is a route to N-hydroxyphenylimidazoles.

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* For Part II see [2].