5-PYRANYLIDENE SUBSTITUTED 4-AZOLIDONES

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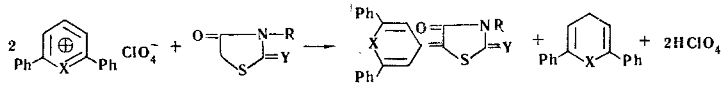
The reaction of 2,6-diphenylthiapyrylium perchlorate with rhodanine in glacial acetic acid in the presence of sodium acetate or the condensation of 2,6-dimethyl-4-thiapyrone with N-ethylrhodanine results in 5-pyranylidine-substituted rhodanine, which is related to the class of zero-methine merocyanines [1, 2]. We have studied the reaction of various 4-azolidones with γ-unsubstituted pyrylium salts which occurs on refluxing in a polar organic solvent (dimethylformamide or acetonitrile). In this case, no catalyst is needed; the process is universal and proceeds readily, regardless of the substituents in the pyran ring. The use of dimethylformamide as the solvent results in the highest yields. It is assumed that the reaction proceeds via the scheme



I X=O, Y=O, R=H; II X=O, Y=S, R=Ph; III X=O, Y=O, R=Ph; IV X=O, Y=S, R=H;
V X=S, Y=S, R=H

The structures of the reaction products were confirmed by IR spectra, qualitative reactions for the double bond, and the alternative synthesis of 5-(2,6-diphenylthiapyranylidene)rhodanine. The compounds obtained are presented in Table 1.

TABLE 1. 5-Pyranylidene-Substituted 4-Azolidones

Comp.	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
I	316 (dec.)	$C_{20}H_{13}NO_3S$	68,9	4,1	8,9	69,2	3,8	9,2	78
II	320—322	$C_{26}H_{17}NO_2S_2$	71,0	4,2	14,6	71,1	3,9	14,6	56
III	301—302	$C_{26}H_{17}NO_3S$	73,0	5,0	7,7	73,4	4,7	7,5	92
IV	319 (dec.)	$C_{20}H_{13}NO_2S$	66,1	4,1	17,0	66,1	3,6	17,6	98
V	284 (dec.)	$C_{20}H_{13}NOS_3$	63,7	4,0	25,2	63,3	3,7	25,3	82

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