SYNTHESIS AND SOME TRANSFORMATIONS OF SULFIDES OF THE THIOPHENE SERIES

XXV.* PREPARATION OF 2-SUBSTITUTED 4-KETO-2,3-DIHYDROTHIENO-[3,2-e]-1,3-THIAZINES

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Some 2-substituted 4-keto-2,3-dihydrothieno[3,2-e]-1,3-thiazines were obtained by condensation of 2-mercapto-5-ethylthiophene-3-carboxamide with aldehydes and ketones in the presence of gaseous HCl.

Substituted 4-keto-2,3-dihydrothieno[3,2-e]-1,3-thiazines are representatives of new condensed heterocyclic systems that include a thiophene ring. Like the analogous benzene derivatives [2-4], they may be of interest for testing as physiologically active substances. We have found that I-VI (see Table 1) are formed in good yields by the reaction of 2-mercapto-5-ethylthiophene-3-carboxamide with aldehydes and ketones in the presence of gaseous hydrogen chloride. (See scheme on following page.)

According to the IR spectra of the solids and solutions (in chloroform), they exist in the amide form: absorption bands of the C=O (1660-1665 cm^{-1}) and NH (3390 cm^{-1}) groups are observed in the spectra of I, IV, and V.

*See [1] for communication XXIV.

TABLE 1. 2-Substituted 4-Keto-2,3-dihydrothieno[3,2-e]-1,3-thiazines (I-VI)

Comp.	R	R′	mp, °C	Empirical formula
I	H	C_6H_5	160 —161[a]	$C_{14}H_{13}NOS_2$
II	H	$C_6H_4NO_2$-*p*	216 —217[a]	$C_{14}H_{12}N_2O_3S_2$
III	H	C_2H_5	96,5—97[b]	$C_{10}H_{13}NOS_2$
IV	CH_3	CH_3	98,5—100[b]	$C_{10}H_{13}NOS_2$
V		$-(CH_2)_5-$	170,5—171,5[c]	$C_{13}H_{17}NOS_2$
VI	CH_3	C_6H_5	184 —186[a]	$C_{15}H_{15}NOS_2$

Comp.	Found, %			Calc., %			Yield, %
	C	H	S	C	H	S	
I	61,1; 61,3	4,5; 4,6	23,4; 23,3	61,3	4,4	23,4	95
II	52,6; 52,4	3,7; 3,7	19,7; 19,8	52,6	3,5	20,1	75
III	52,9; 52,7	5,6; 5,6	27,7; 27,7	53,1	5,7	28,3	~100
IV	52,8; 52,5	6,1; 5,9	28,4; 28,4	53,1	5,7	28,3	83
V	58,5; 58,5	6,5; 6,5	23,6; 23,6	58,4	6,4	24,0	87
VI	62,1; 62,1	5,5; 5,3	21,9; 22,0	62,2	5,2	22,3	89

[a]From alcohol and ethyl acetate. [b]From heptane. [c]From alcohol.

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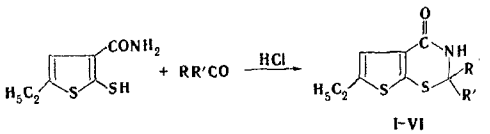

I-VI

EXPERIMENTAL

4-Keto-2,3-dihydrothieno[3,2-e]-1,3-thiazines (I-VI, see Table 1). A 0.05-mole sample of crude 2-mercapto-5-ethylthiophene-3-carboxamide [5] and 0.05 mole of freshly distilled or recrystallized aldehyde or ketone in a threefold volume of absolute ethanol was heated to 50°C under nitrogen, and dry HCl was bubbled through the solution formed after 10-15 min at 50°. The alcohol was removed by vacuum distillation, and the residue (crystals or a viscous oil) was crystallized from a suitable solvent.

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