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FUNCTIONAL DERIVATIVES OF THIOPHENE.

18.* SYNTHESIS OF 4-OXOTHIENO[2,3-d]OXAZINE DERIVATIVES AND THIOPHENE-3-CARBOXYLIC ACID HYDRAZIDES

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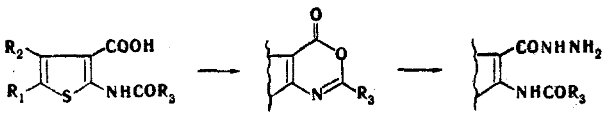
2-Aryl-4-oxothieno[2,3-d]oxazine derivatives were synthesized. Opening of the oxazine ring to give 2-benzamidothiophene-3-carboxylic acid hydrazide derivatives is observed when these compounds are treated with hydrazine hydrate.

We have found that 4-oxothieno[2,3-d]oxazines (IIa-h) can be obtained by the action of thionyl chloride on 2-aroylaminothiophene-3-carboxylic acids (Ia-h) in the presence of dimethylformamide (DMF), i.e., under the conditions of the synthesis of arenecarboxylic acid chlorides. The reaction evidently proceeds through a step involving the formation of thiophenecarboxylic acid chlorides. We obtained thiophenecarboxylic acids Ia, c, h for the first time by the method described in [2].

In the reaction of 2-aryl-4-oxothieno[2,3-d]oxazines (IIb-e, g) with hydrazine hydrate we observed opening of the oxazine ring to give 2-benzamidothiophene-3-carboxylic acid hydrazides (IIIb-e, g).

One absorption band of a carbonyl group is observed in the IR spectra of IIa-h at 1750-1760 cm^{-1}; in addition, the absorption bands of a hydroxy group at 2550-2600 cm^{-1} and of an amide group at 3140-3300 (NH) and 1640-1650 cm^{-1} (CO) that are characteristic for starting thiophene-3-carboxylic acids Ia-h vanish. Several absorption bands of stretching vibrations of an NH bond that characterize a primary amino group and a secondary amide are observed in the spectra of hydrazides IIIb-e, g at 3180-3300 cm^{-1}. The absorption of the carbonyl groups (CO) shows up in the form of one absorption band at 1640-1650 cm^{-1}. The shift of the absorption bands of the carbonyl groups in the low-frequency region is evidently explained by the development of hydrogen bonds. A similar pattern in the IR spectra is observed for 2-acylaminothiophene-3-carboxylic acids.



I a-h II a-h III b-e, g

I—III a $R_1=H$, $R_2=C_4H_3S$, $R_3=C_6H_5$, b $R_1=CH_3$, $R_2=H$, $R_3=C_6H_5$. c $R_1=C_2H_5$, $R_2=H$, $R_3=C_6H_5$, d $R_1=R_2=CH_3$, $R_3=C_6H_5$, e $R_1=R_2=(CH_2)_4$, $R_3=C_6H_5$, f $R_1R_2=(CH_2)_4$, $R_3=p\text{-}C_6H_4CH_3Cl$, g $R_1=H$, $R_2=R_3=C_6H_5$, h $R_1=H$, $R_2=C_6H_5$, $R_3=p\text{-}C_6H_4Cl$

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*See [1] for Communication 17.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
Ia	222—223*	58,9	3,4	4,1	20,0	$C_{16}H_{11}NO_3S_2$	58,4	3,4	4,2	19,5	74,5
Ic	201—202*	61,3	4,8	5,4	11,6	$C_{14}H_{13}NO_3S$	61,1	4,8	5,1	11,6	56
Ih	128—129*	60,8	3,7	3,8	8,6	$C_{18}H_{12}NO_3SCl$	60,4	3,4	3,9	8,9	66
IIa	162,5—164	61,6	3,0	4,5	22,6	$C_{16}H_9NO_2S_2$	61,6	2,9	4,5	22,9	67,5
IIb	168—169	64,3	3,7	5,8	13,2	$C_{13}H_9NO_2S$	64,2	3,7	5,8	13,4	44,3
IIc	102—103	65,1	4,3	5,4	13,0	$C_{14}H_{11}NO_2S$	65,3	4,3	5,4	12,5	55,4
IId	147—148	65,3	4,3	5,5	12,4	$C_{14}H_{11}NO_2S$	65,3	4,3	5,4	12,5	78,4
IIe	144—145	68,0	4,6	4,9	11,3	$C_{16}H_{13}NO_2S$	67,8	4,6	4,9	11,3	77,5
IIf	182—183	69,2	5,5	4,8	10,9	$C_{17}H_{15}NO_2S$	68,7	5,1	4,7	10,8	71,5
IIg	195,5—196	70,8	3,5	4,7	10,6	$C_{18}H_{11}NO_2S$	70,8	3,6	4,6	11,5	78,7
IIh	231—232	63,8	2,9	3,9	9,6	$C_{18}H_{10}NO_3SCl$	63,6	2,9	4,1	9,4	66,7
IIIb	226—226,5	56,5	4,9	15,3	11,6	$C_{13}H_{13}N_3O_2S$	56,7	4,8	15,3	11,6	67,6
IIIc	200,5—201,5	57,9	5,2	14,5	10,9	$C_{14}H_{15}N_3O_2S$	58,1	5,2	14,5	11,1	62,5
IIId	184—185	57,9	5,2	14,6	10,7	$C_{14}H_{15}N_3O_2S$	58,1	5,2	14,5	11,1	85,0
IIIe	137—139	61,0	5,4	12,9	9,9	$C_{16}H_{17}N_3O_2S$	60,9	5,4	13,3	10,1	81,8
IIIg	157—158	64,2	4,4	12,4	9,6	$C_{18}H_{15}N_3O_2S$	64,1	4,5	12,4	9,5	89,9

*Recrystallized from dioxane.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

2-Aryl-4-oxothieno[2,3-d]oxazines (IIa-h). Thionyl chloride (10 ml) and 0.8 ml of absolute DMF were added to a solution of 0.02 mole of the 2-aroylaminothiophene-3-carboxylic acid in 40 ml of absolute benzene, and the mixture was refluxed for 20 min. It was then poured into ice water, and the precipitate was extracted with benzene. The benzene solution was washed with water, the benzene was removed by distillation, and the residue was recrystallized from a mixture of methanol and dioxane (4:1).

Data for IIa-h are presented in Table 1.

2-Benzamidothiophene-3-carboxylic Acid Hydrazide Derivatives (IIIb-e, g). A 5-ml sample of hydrazine hydrate was added to 50°C to a solution of 0.05 mole of 4-oxothieno[2,3-d]-oxazine (IIb-e, g) in 40 ml of dioxane, and the mixture was allowed to stand at 20°C for 1 h. It was then diluted with water, and the precipitate was removed by filtration and recrystallized from a mixture of methanol and dioxane (2:1). Data for IIIb-e, g are presented in Table 1.

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