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INTERACTIONS OF BENZOXAZOLIN(BENZOTHIAZOLIN)ONES AND -THIONES WITH α-BROMOPROPIONYL CHLORIDE

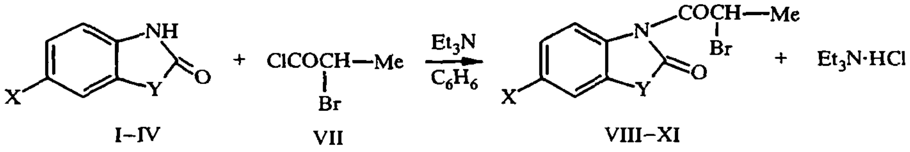
A. T. Ayupova and N. A. Aliev

At interaction of benzoxazolin(benzothiazolin)ones with α-bromopropionyl chloride N-acylation takes place, while in the case of benzoxazoline(benzothiazoline)thiones, the reaction is accompanied by S-alkylation.

Benzazolinones and benzazolinethiones can be acylated with acid anhydrides and chlorides [1], and also with isocyanates and isothiocyanates [2], carbamoyl chlorides [3], and by transacylation [4]. In the reactions of benzoxazolinones with α,β-dichloropropionyl chloride alkylation along with acylation takes place [5].

We have studied the reactions of benzoxazolinone (I) and of its 6-chloro- (II) and 6-bromo derivative (III), as well as the reactions of benzothiazolinone (IV), benzoxazolinethione (V), and benzothiazolinethione (VI) with α-bromopropionyl chloride (VII). The reactions were performed in dry benzene in the presence of triethylamine and using of equimolar amounts of the reagents.

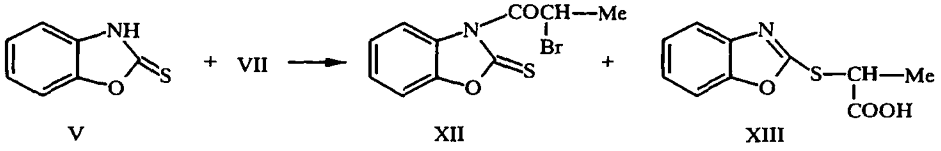
Compounds I-IV react with α-bromopropionyl chloride to give acylation products: N-(α-bromopropionyl)benzoxazolinones (VIII-X) and N-(α-bromopropionyl)benzothiazolinone (XI).



I, VIII X = H, Y = O; II, IX X = Cl, Y = O; III, X X = Br, Y = O; IV, XI X = H, Y = S

The mass spectra of products VIII-XI have peaks corresponding to the molecular ions (Table 1). The PMR spectra have methyl group proton signals as doublets at 1.6-1.8 ppm, while the methine group is represented by a quadruplet at 4.5-4.8 ppm, and the multiplet signal from the aromatic protons is in the region of 7.1-7.6 ppm.

In the case of benzoxazolinethione V, we mainly isolated N-acylation product (XII) together with a small amount of S-alkylation product (XIII).



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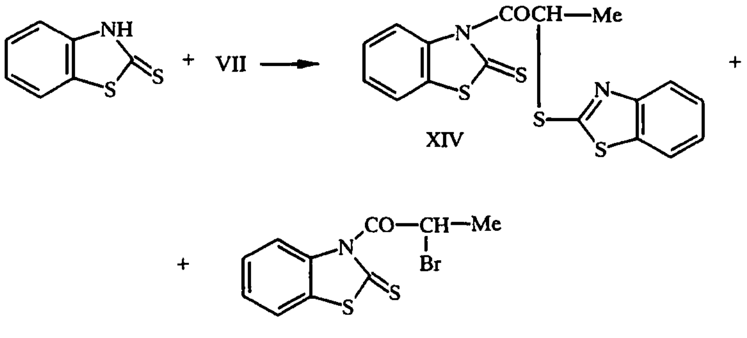
Maximum in the UV spectrum of compound XII at 300 nm indicates the N-substitution, while the maximum in the spectrum of compound XIII at 287-289 nm indicates the S-substitution [6].

The mass spectra of compounds XII and XIII have peaks of the molecular ions M^+ 286 and 223 respectively. The absorption bands in the regions of 1670 and 3300-3500 cm^{-1} for the acid XIII indicate that there are carbonyl and hydroxyl groups in the molecule. Absorption due to the carbonyl group of compound XII occurs at 1695 cm^{-1}.



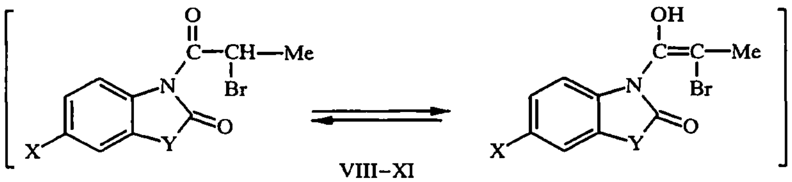
XIV

XV

The main product from the reaction of benzothiazolinethione VI with α-bromopropionyl chloride is N-[α-(2'-benzothiazolylthio)propionyl]benzothiazolinethione (XIV) (λ_{1max} = 268-289 nm, λ_{2max} = 300-312 nm), which is deposited as a pale yellow precipitate. The benzene solution retains N-(α-bromopropionyl)benzothiazolinethione (XV) (λ_{1max} = 310-312 nm).

When a similar reaction is performed with compounds I-IV in excess of the latter, it is not found that products of XIV type are formed, evidently because in the resulting bromoacyl derivatives VIII-XI the bromine atoms are deactivated by enolization [5].

Benzene as the solvent (dielectric constant 2.3) favors shifting the equilibrium towards the enol form.



VIII–XI

The structures of compounds XIV and XV were confirmed by the mass spectra, which had peaks from the molecular ions M^+ 388 and 302, respectively. The mass spectrum also contains the intense fragment having *m/z* 223, which confirms the structure chosen for compound XIV.

On acylation of compounds V and VI containing the thioamide group S=C—NH, which provides the dual reactivity, N-acylation and S-alkylation products have been isolated. The tendency to form the latter when reaction was carried out in a low-polarity solvent has been observed in the case of alkylation of azolidines [7, 8].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer using KBr disks, while the UV spectra were recorded on a Hitachi EPS-3-T spectrometer using solutions in ethanol.

The PMR spectra were recorded on a Jeol-060 HL instrument in deuterochloroform and deuteromethanol, internal standard HMDS.

The mass spectra were recorded on an MX-1303 spectrometer with ionizing energy of 30 eV at 150-210°C, with direct specimen input to the ion source. TLC was performed on Silufol UV-254 plates, eluent benzene-ethanol, 21:2, spots were visualised by 0.5 g $KMnO_4$ in 2 ml H_2SO_4 and 48 ml of water. The characteristics of the compounds synthesized are given in table 1.

TABLE 1. Characteristics of Compounds VIII-XV

Compound	Empirical formula	Found, % Calculated, %			mp, °C (recrystallization solvent)	R_f*	M^+	Yield, %
		C	H	N				
VIII	$C_{10}H_8BrNO_3$	43,9 44,4	2,71 2,96	4,95 5,18	90...92 (methanol)	0,68	270	45
IX	$C_{10}H_7ClBrNO_3$	39,0 39,3	2,12 2,29	4,00 4,59	123...125 (ethanol)	0,75	304...306	57
X	$C_{10}H_7Br_2NO_3$	35,0 34,38	1,92 2,01	3,98 4,01	128...130 (ethanol)	0,80	349	59
XI	$C_{10}H_8BrNO_2S$	40,9 41,9	2,35 2,79	4,12 4,89	75...80 (benzene)	0,53	286	37
XII	$C_{10}H_8BrNO_2S$	39,9 41,9	2,05 2,79	4,27 4,89	102...103 (methanol)	0,42	286	13
XIII	$C_{10}H_9NO_3S$	52,9 53,8	3,98 4,03	6,11 6,27	140...142 (ethanol)	0,28	223	12
XIV	$C_{17}H_{12}N_2OS_4$	56,25 57,73	2,98 3,09	7,01 7,21	318...320	—	388	25
XV	$C_{10}H_8BrNOS_2$	39,0 39,73	2,12 2,64	4,02 4,63	302...305	—	302	12

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* In the 10:1 benzene-methanol system.

Reactions of Benzoxazolinones I-III and Benzothiazolinone IV with α-Bromopropionyl Chloride. To suspension of 5 mmol of compound I-IV in 20 ml of dry benzene containing 5 mmol of triethylamine at room temperature we added by drops with vigorous stirring 5 mmol of α-bromopropionyl chloride VII in a small amount of dry benzene. The mixture was kept on boiling water bath for 2 h. The precipitate of triethylamine hydrochloride was filtered off, benzene was evaporated, and the residual products VIII-XI were recrystallized from the corresponding solvents (Table 1).

Reactions of Benzothiazoline VI and Benzoxazolinethione V with α-Bromopropionyl Chloride. To solution of 1.67 g (10 mmol) of compound VI in 40 ml of dry benzene containing 1.01 g (10 mmol) of triethylamine we added by drops with stirring 1.72 g (1 mmol) of α-bromopropionyl chloride in 10 ml of benzene. Towards the end of addition of the chloride, a pale yellow precipitate began to form. The reaction mixture was additionally kept on boiling water bath for 2 h. The crystals were filtered off, were washed with water and hot methanol, and dried to give 0.8 g of product XIV. The benzene filtrate was evaporated and the residue was washed with hot alcohol and dried to give 0.3 g of product XV.

The reaction between compound V and α-bromopropionyl chloride was carried out similarly. The product after evaporation of benzene was treated with saturated solution of sodium bicarbonate and the insoluble residue was filtered off. The filtrate was neutralized with 4 N hydrochloric acid, and the precipitated crystals were filtered off, dried, and recrystallized from ethanol to give 0.3 g of product XIII. The residue not dissolved in sodium bicarbonate solution was recrystallized from methanol to give 0.7 g of product XII.

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