factor of 1000), while 9.5 ml, after dilution with water and acidification with nitric acid, was titrated by the method in [13]. The percentages of the starting and final aldehydes in the spectrophotometric solution were determined from Firordt's formulas [14].

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SYNTHESIS OF THIIRANE OXIMES FROM 3,4-DIBROMO-3-METHYL-2-BUTANONE OXIME

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2-(α-Oximinoethyl)-2-methylthiirane was obtained by the reaction of 3,4-dibromo-3-methyl-2-butanone oxime with sodium sulfide. At the same time, the O-carbamoyl derivative of the α,β-dibromo oxime was converted to the corresponding substituted α,β-unsaturated oxime under the same conditions. Thiirane oxime, like its O-carbamoyl derivative, underwent the desulfuration that is characteristic for thirranes under the influence of tributylphosphine.

It is known [1] that the reaction of vicinal dihaloalkanes with sodium or potassium sulfide does not lead to the expected thiiranes.

By the reaction of 3,4-dibromo-3-methyl-2-butanone oxime (I) with excess sodium sulfide in acetone at 20°C we obtained II, which, according to the results of elementary analysis, corresponds to the product of replacement of the bromine atoms in oxime I by a sulfur atom. The presence in the PMR spectrum of II of singlets at 1.68 and 1.76 ppm (CH_3C and $CH_3C=N$ groups, respectively), two doublets with $J=1.9$ Hz at 2.51 and 2.88 ppm (CH_2 group) [the chemical shifts and the spin–spin coupling constants (SSCC) of the methylene group are characteristic for the thiirane ring [1]], and a broad singlet of an =N–OH group at 9.9 ppm and the IR spectroscopic data made it possible to assign the 2-(α-oximinoethyl)-2-methylthiirane structure to it.

To confirm the structure of thiirane oxime II we carried out the desulfuration of the thiirane under the influence of trialkyl(aryl)phosphines [1]. In fact, treatment of oxime II with tributylphosphine in chloroform led to α,β-unsaturated oxime III.

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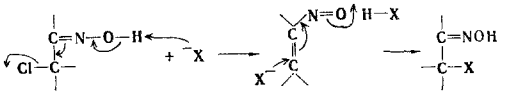
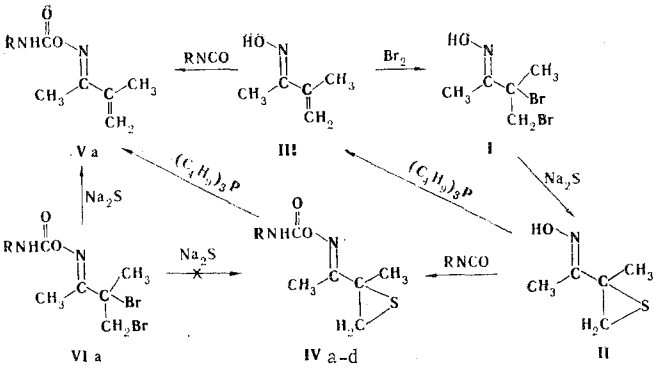
Such facile formation of thiirane oxime II can evidently be associated with the fact that the reaction of dibromo oxime I with sodium sulfide proceeds via the cleavage–addition mechanism that is characteristic for the reactions of α-halo oximes with nucleophilic reagents [2].



In contrast to dibromo oxime I, its O-carbamoyl derivative VI was not converted to the expected thiirane IV by the action of sodium sulfide, since the realization of a cleavage–addition mechanism is impossible. The formation in this case of carbamoylated α,β-unsaturated oxime V is the result of the dehalogenating action of sodium sulfide, which probably has the same nature as the debromination of vicinal dibromoalkanes by potassium iodide [3].

The reaction of thiirane oxime II with acylating agents of the aryl (alkyl) isocyanate type gave the corresponding O-carbamoyl derivatives IV, in the IR spectra of which the absorption bands at 1710-1730, 1520-1550, and 1200-1230 cm^{-1} are characteristic for a carbamic acid ester fragment. As in the case of thiirane oxime II, IVa undergoes desulfuration to O-carbamoylated α,β-unsaturated oxime Va under the influence of tributylphosphine.



IV–VI a R = 4-ClC_6H_4; IV b R = 3-ClC_6H_4; c R = 3,4-$Cl_2C_6H_3$; d R = cyclohexyl

EXPERIMENTAL

The IR spectra of KBr pellets and solutions of the compounds in CCl_4 were recorded with a Perkin-Elmer 457 spectrometer. The PMR spectra of solutions in $(CD_3)_2CO$ and CCl_4 were obtained with a Varian FT-80A spectrometer with tetramethylsilane as the internal standard.

3,4-Dibromo-3-methyl-2-butanone Oxime (I). A solution of 4.04 g (25.2 mmole) of bromine in 10 ml of CCl_4 was added dropwise with stirring to a solution of 2.5 g (25.2 mmole) of 3-methyl-3-buten-2-one [4] in 30 ml of dry CCl_4 while gradually raising the temperature from −10 to 20°C. The mixture was then allowed to stand for 30 min. The solvent was evaporated, and the residue was crystallized in hexane cooled to −10°C. The precipitate was removed by filtration to give 5 g (76.4%) of I with mp 57-58°C (mp 58°C [5]). IR spectrum (KBr): 1630 (C=N), 965 (N–O), 600 (C–Br); (CCl_4): 3590 cm^{-1} (OH). PMR spectrum (CCl_4): 2.05 (s, 6H, $2CH_3$); 3.78, 4.05 (AB system, J_{AB} = 10 Hz, 2H, CH_2); 9.18 (broad s, 1H, OH).

2-(α-Oximinoethyl)-2-methylthiirane (II). A 13-g (54 mmole) sample of $Na_2S \cdot 9H_2O$ was added in one portion with vigorous stirring to a solution of 13 g (50 mmole) of I in 250 ml of acetone. After 40 min, the inorganic precipitate was removed by filtration, and the filtrate was dried for ~1 h over $MgSO_4$. The solvent was evaporated, 150 ml of hexane was added to the residue, and the suspension was filtered. The filtrate was evaporated, and the oily residue was treated with 50 ml of pentane cooled to −50°C. The white precipitate that formed upon trituration was removed by filtration and air dried to give 2.63 g (40%) of II with mp 44-46°C. Found: C 45.6; H 7.0; N 10.8; S 24.0%. C_5H_9NOS. Calculated: C 45.8; H 6.9; N 10.7; S 24.4%. IR spectrum (CCl_4): 3600; (KBr): 1430, 1370, 1140, 1060, 1050, 1020, 985, 950, 940, 780, 610, 550, 510 cm^{-1}.

Carbamoylation of Thiirane Oxime II. A) Two to three drops of triethylamine and (in one portion) an equimolar amount of the corresponding isocyanate were added to a solution of 2.2 mmole of thiirane II in 10 ml of acetone. At the end of the reaction [as monitored by thin-layer chromatography (TLC) on Silufol by elution with THF–hexane (1:4)], the solvent was evaporated, and the residue was crystallized in cold ether. In the case of IVd the oily residue was purified by means of preparative column chromatography (on silica gel

TABLE 1. Compounds IVa-d

Compound	mp, °C	Found, %					Empirical formula	Calculated, %					Yield, %
		C	H	Cl	N	S		C	H	Cl	N	S	
IVa	142—143	50,3	4,4	12,8	9,8	11,3	$C_{12}H_{13}ClN_2O_2S$	50,6	4,6	12,5	9,8	11,3	76
IVb	121—123	50,4	4,5	12,6	9,7	11,0	$C_{12}H_{13}ClN_2O_2S$	50,6	4,6	12,5	9,8	11,3	72
IVc	156—158	44,8	3,7	22,0	8,7	9,8	$C_{12}H_{12}Cl_2N_2O_2S$	45,2	3,8	22,0	8,8	10,0	75
IVd	66—67	56,4	7,9	—	11,1	12,2	$C_{12}H_{20}N_2O_2S$	56,2	7,7	—	10,9	12,5	69

TABLE 2. PMR Spectra of Thiiranes IVa-d in d_6-Acetone

Compound	Chemical shifts, ppm, SSCC, Hz				
	CH_3—C=N	CH_3—C	—CH_2—	Ar	NH
IVa	1,96 s	1,81 s	2,66 d; 3,07 d; ^2J=1,9	7,20—7,68	8,92 br s
IVb	1,95 s	1,80 d ^4J=0,4	2,66 d; ^2J=1,9; 3,08m; ^4J=0,4;	6,92—7,76	8,92 br s
IVc	1,98 s	1,80 s	2,66 d; 3,07 d; ^2J=1,9	7,38—7,87	9,03 br s
IVd	1,91 s	1,76 s	2,59 d; 3,0 d; ^2J=1,9	*	6,49 br s

*δ > CH=N=3.45 ppm; δ − $(CH_2)_3$− =1.12-2.1 ppm.

by elution with chloroform); the product crystallized when the eluate was allowed to stand. The results of elementary analysis, the melting points, and the spectral characteristics are presented in Tables 1 and 2.

B) A 16-mmole sample of $Na_2S \cdot 9H_2O$ was added in one portion with stirring to a solution of 15 mmole of oxime I in 50 ml of acetone. At the end of the reaction (after ~40 min), the inorganic precipitate was removed by filtration, and two to three drops of triethylamine and 20 mmole of p-chlorophenyl isocyanate were added to the filtrate with stirring. The reaction mixture was maintained at 20°C for 3 h. The solvent was evaporated, and the residue was crystallized from cold ether to give IVa, with mp 144-145°C (CH_3CN), in 70% yield. According to the IR spectral data, the isolated compound was identical to the compound obtained by method A.

O-(4-Chlorophenylcarbamoyl)-3-methyl-3-buten-2-one Oxime (Va). Compound Va was obtained from oxime III and p-chlorophenyl isocyanate by the procedure described for the preparation of II (method A). Compound Va, with mp 138-139°C, was obtained in 89% yield. Found: C 56.8; H 5.2; N 11.0%. $C_{12}H_{13}ClN_2O_2$. Calculated: C 57.0; H 5.2; N 11.1%. IR spectrum (CCl_4): 3380 (NH); (KBr): 1720 (C=O); 1500, 1600 (Ar); 1535 (NH− C=O); 1210 (−COO−); 950, 920 cm^{-1} (N−O, C=C). PMR spectrum (CCl_4): 2.04 (s, 3H, CH_3C=C); 2.22 (s, 3H, CH_3C=N); 5.64 (m), 5.39 (m, 2H, =CH_2); 7.22-7.56 (4H, Ar); 8.34 (broad s, 1H, NH).

Reaction of Thiirane Oximes II and IVa with Tributylphosphine. An equimolar mixture of II or IVa and tributylphosphine was refluxed in chloroform for 1 h, after which the solvent was evaporated, and the residue was separated by means of preparative column chromatography (on silica gel, elution with chloroform). The crystalline products, which had mp 41-43 and 137-138°C, were identical to III and Va, respectively, according to the IR and PMR spectroscopic data.

Reaction of α,β-Dibromo Derivative VIa with Sodium Sulfide. A 0.24-g sample of $Na_2S \cdot 9H_2O$ was added in one portion with stirring to a solution of 0.41 g of VIa, obtained from Va, in 30 ml of acetone. After 1 h, the inorganic precipitate was removed by filtration, the solvent was evaporated, and the residue was treated with cold ether. The precipitate was removed by filtration to give 0.15 g (60%) of a reaction product with mp 136-137°C, which, with respect to the IR spectroscopic data, was identical to Va. Compound VIa, with mp 86-88°C, was obtained in 75% yield. Found: C 34.5; H 3.1; N 7.0%. $C_{12}H_{13}Br_2ClN_2O_2$. Calculated: C 34.9; H 3.2; N 6.8%. IR spectrum (KBr): 1730 (C=O); 1500, 1605 (Ar); 1550 (NH− C=O); 1210 (−COO−); 960 (N−O); 600 cm^{-1} (C−Br). PMR spectrum (d_6-acetone): 2.14 (d, J^4=0.6 Hz, 3H, CH_3C); 2.21 (s, 3H, CH_3C=N); 4.12, 4.35 (AB system, J_{AB}=10.6, $^4J_{HACH_3}$=0.6 Hz, 2H, CH_2); 7.16-7.68 (4H, Ar); 8.92 (broad s, 1H, NH).

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