The 4-hetarylidene-2-aryl(hetaryl)oxazol-5-ones were obtained by the method described in [1] and were purified by recrystallization from heptane.

The yields, melting points, and results of analysis of the synthesized compounds are presented in Table 1.

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SYNTHESIS OF SUBSTITUTED OXAZOLIDINONES FROM COMPOUNDS OF THE ETHYLENE SERIES

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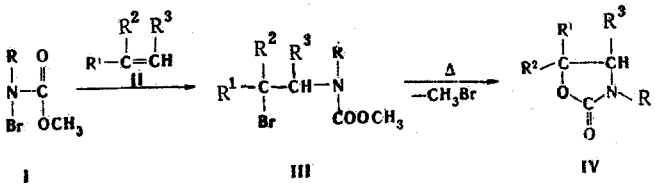
UDC 457.787.1.07

The reaction of N-bromocarbamates with ethylene compounds was investigated, and the high structural specificity of this reaction was demonstrated. The structures of the β-bromocarbamates obtained were confirmed by their IR and PMR spectra. When they are heated to 60-130°C, they are readily cyclized to the corresponding oxazolidinones.

2-Oxazolidinones are valuable starting compounds for the stereoselective synthesis of amino alcohols [1, 2]. In the present research we demonstrated the possibility of the synthesis of substituted oxazolidinones by the addition of N-bromocarbamates to ethylene compounds with subsequent pyrolysis of the resulting β-bromocarbamates. The reaction proceeds via the scheme



I III IV

III[a], IVa R=R²=R³=H, R¹=CN; IIIb, IVb R=R¹=H, R²=R³=—(CH₂)₄—; IIIc, IVc R=R²=R³=H, R¹=C₆H₅; IIId, IVd R=CH₃, R²=R³=H, R¹=C₆H₅; IIIe, IVe R=R²=CH₃, R¹=C₆H₅, R³=H

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TABLE 1. Characteristics of the Compounds Obtained

Compound	bp [mm (mercury column)] or mp, °C	n_D^{20}	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	Br	N		C	H	Br	N	
IIIa	110—112 (0,2)	1,5390	29,0	3,5	38,6	13,6	$C_5H_7BrN_2O_2$	29,0	3,4	38,6	13,5	69,9
IIIb	125—126	—	40,8	6,0	33,8	6,0	$C_8H_{14}BrNO_2$	40,7	6,0	38,8	5,9	72,0
IIIc	78—79	—	46,1	4,8	30,5	5,4	$C_{10}H_{12}BrNO_2$	46,4	4,7	30,9	5,4	71,0
IIId	35—37 (0,5)	1,3435	48,5	5,1	29,4	5,1	$C_{11}H_{14}BrNO_2$	48,4	5,2	29,3	5,1	70,3
IIIe	40—43 (0,1)	1,4845	50,3	5,5	27,5	4,7	$C_{12}H_{16}BrNO_2$	50,4	5,6	27,9	4,9	60,2
IVa	95—95,5	—	—	—	—	—	$C_4H_4N_2O_2$	—	—	—	—	69,0[3]
IVb	55—56	—	59,7	8,0	—	10,0	$C_7H_{11}NO_2$	59,6	7,8	—	9,9	80,0
IVc	89—90	—	—	—	—	—	$C_9H_9NO_2$	—	—	—	—	73,6[4]
IVd	56—57	—	67,5	6,3	—	8,0	$C_{10}H_{11}NO_2$	67,7	6,3	—	7,4	68,5 (A) 86,4 (B)
IVe	49—50	—	69,1	6,8	—	7,4	$C_{11}H_{13}NO_2$	69,1	6,8	—	7,3	84,8

We obtained the starting N-bromocarbamates (Ia, b) by reaction of methyl carbamate and methyl N-methylcarbamate with bromine in an alkaline medium; methyl N-bromocarbamate was isolated in pure form, while methyl N-methyl-N-bromocarbamate was used without prior purification. Like hydrobromic acid, the N-bromocarbamates add readily to a number of ethylene compounds to give β-bromocarbamates in good yields. One should note the high structural specificity of this reaction, which always leads to the formation of one of the two possible structural isomers in which the carbamate group is attached to the least substituted carbon atom; this was demonstrated conclusively by PMR spectroscopy.

When the β-bromocarbamates (IIIa-e) are heated without a solvent or in an inert solvent to 60-130°C, they readily split out methyl bromide to give oxazolidinones (IV a-e).

It should be noted that the cyclization of β-chlorocarbamates to the corresponding oxazolidinones takes place under considerably more severe conditions and gives the products in lower yields [3]. We have established that the cyclization of N-methyl-substituted β-bromocarbamates, which split out methyl bromide even when they are refluxed in solution in chloroform, takes place particularly readily. The structure of the oxazolidinones obtained was confirmed by an analysis of the PMR spectra of these compounds.

EXPERIMENTAL

The IR spectra of mineral oil suspensions and solutions of the compounds in CCl_4 were recorded with a UR-10 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Brucker spectrometer (60 MHz) with tetramethylsilane as the internal standard; the chemical shifts are presented on the δ scale.

Methyl N-Bromocarbamate (Ia). A 4.1-ml sample of bromine was added with vigorous stirring at −2 to 3°C in the course of 15-20 min to a solution of 7.5 g (0.1 mole) of methyl carbamate in 80 ml of dry chloroform, after which 1 ml of bromine and a cooled 4% solution of sodium hydroxide were added simultaneously at the same temperature, and the mixture was stirred at room temperature for 1 h. The chloroform layer was separated and dried with magnesium sulfate, the chloroform was removed by distillation, and the residue was distilled in vacuo to give 12.7 g (82.5%) of Ia as a red oil with bp 80-83°C (10-12 mm) and n_D^{20} 1.4970.

Methyl N-Bromo-N-methylcarbamate (Ib). This compound was obtained in 83.4% yield from methyl N-methylcarbamate by the method described above.

Methyl N-(2-Bromo-2-cyanoethyl)carbamate (IIIa). A solution of 10.77 g (0.07 mole) of methyl N-bromocarbamate in 25 ml of dry chloroform was added dropwise at 60°C in the course of 1 h to a solution of 3.7 g (0.07 mole) of acrylonitrile in 50 ml of dry chloroform, and the mixture was refluxed for 2 h. The chloroform was removed by distillation, and the residue was distilled in vacuo to give 10 g (69.9%) of carbamate IIIa with bp 110-120°C (0.2 mm). IR spectrum: 3380 (NH), 1710 (C=O), 1245 (C-O-C), 710 (C-Br), and 2280 cm^{-1} (CN). PMR spectrum: 5.82 (1H, t, NH), 4.45 (1H, t, CHBr), 3.65 (2H, t, CH_2N), and 3.5 ppm (3H, s, OCH_3).

trans-2-Bromo-1-methoxycarbonylaminohexane (IIIb). A solution of 12.6 g (0.082 mole) of methyl N-bromocarbamate in 50 ml of dry chloroform was added with stirring at 45°C to a solution of 6.7 g (0.082 mole) of cyclohexane in 100 ml of dry chloroform, and the mixture was stirred at this temperature for another 2 h. The chloroform was removed by distillation, and the residue was recrystallized from hexane–CCl_4 (3:1) to give 13.9 g (72%) of IIIb with mp 125-126°C. IR spectrum: 3280 (NH), 1710 (C=O), 1248 (C–O–C), and 710 cm^{-1} (C–Br). PMR spectrum: 3.75 (1H, m, CH–Br), 2.25 (1H, m, CH–N), and 1.60 ppm (8H, m, CH_2).

1-Bromo-2-methoxycarbonylamino-1-phenylethane (IIIc). A solution of 20.77 g (0.07 mole) of methyl N-bromocarbamate in 50 ml of dry chloroform was added with stirring at 50-55°C in the course of 50 min to a solution of 7.3 g (0.07 mole) of styrene in 50 ml of dry chloroform, after which the solution was stirred at 50°C for another 30 min. It was then cooled, the chloroform was removed by distillation, and the residue was recrystallized from hexane to give 12.8 g (71%) of IIIc with mp 78-79°C. IR spectrum: 3280 (NH), 1740 (C=O), 1230 and 1050 (C–O–C), 935 and 860 (aromatic CH), and 700 cm^{-1} (C–Br). PMR spectrum: 7.30 (5H, s, aromatic), 4.95 (1H, t, CHBr, 1H, NH), 3.75 (2H, d, CH_2N), and 3.5 ppm (3H, s, OCH_3).

N-Methyl-1-bromo-2-methoxycarbonylamino-1-phenylethane (IIId). A solution of 8.4 g (0.05 mole) of methyl N-bromo-N-methylcarbamate was added with stirring at 12-20°C in the course of 50 min to a solution of 5.2 g (0.05 mole) of styrene in 50 ml of dry chloroform, and the mixture was stirred at this temperature for another 30 min. The chloroform was removed by vacuum distillation, and the residue was distilled to give 9.5 g (70%) of IIId with bp 35-37°C (0.05 mm) and n_D^{20} 1.3435. IR spectrum: 3275(NH), 1740 (C=O), 1240 and 1050 (C–O–C), 935 and 860 (aromatic CH), and 700 cm^{-1} (C–Br).

N-Methyl-1-methyl-1-bromo-2-methoxycarbonylamino-1-phenylethane (IIIe). This compound was similarly obtained from 11.8 g (0.1 mole) of α-methylstyrene and 16.8 g (0.1 mole) of methyl N-bromo-N-methylcarbamate. The yield of product with bp 40-43°C (0.1 mm) and n_D^{20} 1.4845 was 16.9 g (60%). IR spectrum: 1740 (C=O), 1230 and 1050 (C–O–C), and 935 and 860 cm^{-1} (aromatic CH).

5-Cyano-2-oxazolidinone (IVa). A 2.1-g (0.01 mole) sample of IIIa was heated at 110-115°C for 20 min, after which the reaction mixture was worked up to give 0.79 g (69%) of IVa with mp 95.5°C (from hexane) [3].

8,9-cis-Perhydrobenzoxazol-2-one (IVb). A 2.35-g (0.01 mole) sample of IIIb was heated at 130°C for 1 h, after which the reaction mixture was cooled and recrystallized from hexane to give 1.12 g (80%) of a product with mp 55-56°C. IR spectrum: 3250 (NH), 1710 (C=O), and 1240 and 1050 cm^{-1} (C–O–C). PMR spectrum: 5.45 (1H, s, NH), 4.50 (1H, q, CH–O), 3.66 (1H, q, CH–NH), and 1.6 ppm (8H, m, CH_2).

5-Phenyl-2-oxazolidinone (IVc). A 2.58-g (0.01 mole) sample of IIc was heated at 130°C for 1 h. Workup gave 1.2 g (73.6%) of IVc with mp 89-90°C (from hexane) [4].

N-Methyl-5-phenyl-2-oxazolidinone (IVd). A) A solution of 8.4 g (0.05 mole) of methyl N-bromo-N-methylcarbamate in 50 ml of chloroform was added with stirring at 60°C to a solution of 5.2 g (0.05 mole) of styrene in 50 ml of dry chloroform, and the mixture was stirred at this temperature for 1 h. The chloroform was removed by distillation, and the residue was recrystallized from hexane–CCl (3:1) to give 5.9 g (68.5%) of IVd with mp 56-57°C. IR spectrum: 1740 (C=O); 1230 and 1050 cm^{-1} (C–O–C). PMR spectrum: 7.65 (5H, s, aromatic), 5.66 (CH, t, CH–O), 4.20 and 3.63 (2H, m, CH_2N), and 3.10 ppm (3H, s, N–CH_3).

B) A 2.72-g (0.01 mole) sample of IIId was dissolved in 40 ml of dry chloroform, and the solution was refluxed for 20 min. The solvent was removed by distillation, and the residue was recrystallized from hexane–CCl_4 (3:1) to give 1.53 g (86.4%) of IVd with mp 56-57°C.

N-Methyl-5-methyl-5-phenyl-2-oxazolidinone (IVe). A 2.86-g (0.01 mole) sample of IIIe was dissolved in 60 ml of dry chloroform, and the solution was refluxed for 1 h. The solvent was removed by distillation, and the residue was recrystallized from hexane–CCl_4 (3:1) to give 1.62 g (84.8%) of IVe with mp 49-50°C. IR spectrum: 1730 (C=O), 1230 and 1080 cm^{-1} (C–O–C). PMR spectrum: 7.65 (5H, s, aromatic), 3.75 (2H, s, NCH_2), 2.95 (3H, s, CH_3N), and 1.75 ppm (3H, s, CH_3–C).

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SYNTHESIS AND STEREOCHEMISTRY OF 3-HYDROXY-4-ALKYLTHIOSULFOLANES

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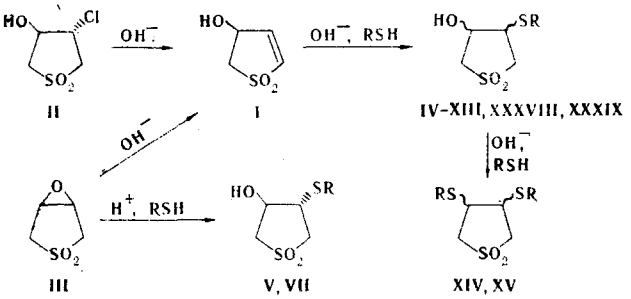
4-Hydroxy-2-sulfolene, 3-hydroxy-4-chlorosulfolane, and 3,4-epoxysulfolane react with thiols in alkaline media to give mixtures of cis,trans-3-hydroxy-4-alkylthisulfolanes in a ratio of 2:3.

In order to synthesize new 3,4-disubstituted sulfolanes, which are of interest both as biologically active compounds [1, 2] and as extractants for aromatic hydrocarbons [3], we carried out the reactions of 4-hydroxy-2-sulfolene (I), 3-hydroxy-4-chlorosulfolane (II), and 3,4-epoxysulfolane (III) with a number of thiols and studied the stereochemistry of these reactions.

The addition of thiols to sulfolene I proceeds readily and quantitatively in alkaline media [4]. Compounds II and III also react readily and quantitatively with thiols under the same conditions.



IV, V R = C_2H_5; VI, VII R = C_5H_{11}; VIII, IX, XIV, XV R = C_6H_{13}; X, XI R = $C_{10}H_{21}$; XII, XIII R = $C_{12}H_{25}$; XXXVIII, XXXIX R = CH_2CH_2OH

3-Hydroxy-4-alkylthiosulfolanes (Table 1) are formed as a result of the reaction. The ratio of the cis and trans isomers remains constant (2:3), regardless of the reaction time, the temperature, and the starting compound (I-III). This confirms the previously obtained data [5-7] that II and III are converted to sulfolene I in alkaline media. The explanation [8] of the formation of cis-3-hydroxy-4-RX-sulfolanes (X = O, S) from trans-2-hydroxy-4-chlorosulfolane by replacement of the chlorine atom is incorrect, since the inertness of the chlorine atom in the sulfolane ring has been confirmed by kinetic studies [9]. The inertness of chlorosulfolanes to nucleophilic substitution reactions [9, 10] is in contrast to the ease of elimination of HCl. Thus, for example, chlorohydrin II is readily titrated at room temperature [7].

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