SYNTHESIS AND STRUCTURE OF AZIRIDINE-2-CARBOXYLIC ACID DERIVATIVES WITH ASYMMETRIC SUBSTITUENTS ATTACHED TO THE NITROGEN ATOM

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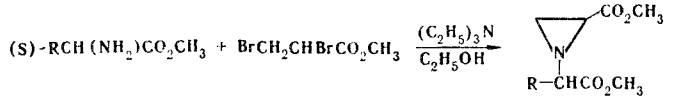
The synthesis, investigation of the structure, separation, and x-ray diffraction analysis of diastereomeric aziridine-2-carboxylic acid derivatives obtained from 2,3-dibromopropionic acid methyl ester or amide and methyl esters of amino acids are described.

Aziridine-2-carboxylic acid derivatives are of interest as intermediates in the asymmetric synthesis of serine and other amino acids and peptides [1-4], as well as for the modification of peptides [5-12] in order to obtain biologically active compounds [13, 14].

The goal of the present research was to isolate, characterize, and determine the structure and absolute configurations of diastereomeric derivatives of aziridine-2-carboxylic acids obtained on the basis of esters of (S)-α-amino acids. The corresponding esters I-VI (Table 1) were obtained via the scheme:



I R = CH_3; II R = $C_6H_5CH_2$; III R = i-C_3H_7; IV R = $CH_3O_2CCH_2$; V R = $CH_3O_2C(CH_2)_2$; VI R = $CH_3S(CH_2)_2$

I-VI

Esters I-VI are produced in the form of mixtures of diastereomers with only a small preponderance of one of them (Table 2). They are viscous uncrystallizable liquids that are only poorly separated in the case of chromatography on silica gel in various solvent systems. We

TABLE 1. Esters and Amides of Aziridinecarboxylic Acids (I-VIII)

Compound	bp (10^{-3} mm), °C	$[\alpha]_D^{20}$, (c 1.0, EtOH)	IR spectrum, ν, cm^{-1}			Ma	Found, %			Empirical formula	Calc., %			Yield, %
			CO	aziridine	ring CH		C	H	N		C	H	N	
I	82—87	−27,0	1733	1238	3075	187	52,1	6,7	7,7	$C_8H_{13}NO_4$	51,3	7,0	7,5	82
II	93—98	−39,4	1738	1243	3066	263	63,1	6,7	5,5	$C_{14}H_{17}NO_4$	63,9	6,5	5,3	80
III	88—92	−24,3	1740	1245	3073	215	55,1	7,1	6,7	$C_{10}H_{17}NO_4$	55,8	7,9	6,5	78
IV	108—114	−36,6	1735	1242	3056	245	49,2	6,2	5,6	$C_{10}H_{15}NO_6$	49,0	6,1	5,7	77
V	117—123	−20,8	1740	1245	3040	259	49,8	6,8	5,1	$C_{11}H_{17}NO_6$	50,9	6,6	5,4	75
VI	130—135	−16,9	1738	1248	3066	247	48,0	6,7	5,3	$C_{10}H_{17}NO_4$	48,6	6,9	5,7	68
VIIa+ VIIb (1 : 1)	mp 93—95	−9,2	1637 1728	1232	3050	172	49,3	7,3	16,3	$C_7H_{12}N_2O_3$	48,8	7,0	16,3	84
VIIa	mp 120—122	+63,9	—	—	—	—	—	—	—	—	—	—	—	7[b]
VIIb	mp 130—131	−111,7	—	—	—	—	—	—	—	—	—	—	—	0,4[c]
VIII	mp 172—174	−78,8[d]	1646 1739	1230	3047	248	63,6	6,8	11,6	$C_{13}H_{16}N_2O_3$	62,9	6,4	11,3	91[e]

[a]By mass spectrometry. [b]After three crystallizations of VIIa + VIIb from ethanol. [c]After three crystallizations from ethyl acetate of the VIIa + VIIb mixture enriched (70%) in VIIb. [d]c 1.0 in DMSO. [e]The yield prior to crystallization (mp 164-166°C).

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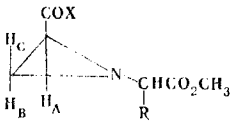
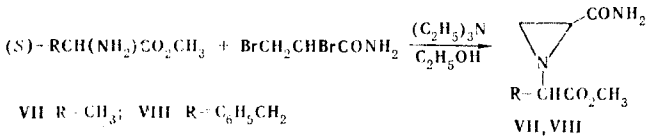
TABLE 2. Paramters of the PMR Spectra of Derivatives I, II, VII, and VIII



Compound	X	R	Solvent	δ,[a] ppm									J,[a] Hz				
				T, °C	R		CH—R	CO_2Me	Ph	ring protons			AB	AC	BC	CHR	gem-CH_2
					CH_3	CH_2Ph				H_A	H_B	H_C					
I	MeO	Me	C_6F_6	100	1,21	—	2,38	3,59; 3,61	—	2,18	1,56	1,99	6,3	3,3	1,2	7,0	—
					1,19	—	2,41	3,59; 3,60	—	2,04	1,75	1,99	6,0	3,4	1,5	7,0	—
II	MeO	$PhCH_2$	C_6F_6	100	—	2,93	2,55	3,49; 3,56	7,00	1,72	1,30	1,83	6,0	3,3	0,8	7,0	12,5
					—	2,93	2,55	3,51; 3,54	7,05	2,10	1,65	1,83	6,0	3,3	1,5	7,0	12,5
			CH_2Cl_2	30	—	2,98	2,42	3,59; 3,61	7,13	1,96	1,22	1,68	6,3	3,3	0,5	6,6	12,5
					—	3,01	2,42	3,54; 3,59	7,00	2,13	1,67	2,01	6,0	3,3	0,5	6,6	12,5
			CD_3OD	30	—	3,10	2,64	3,65; 3,70	7,14	1,85	1,33	1,78	6,5	3,4	0,5	6,6	13,0
					—	3,10	2,64	3,60; 3,68	7,17	2,30	1,98	2,04	6,5	3,4	0,5	6,6	13,0
			CF_3CH_2OH	40	—	2,94	2,48	3,74; 3,77	7,16	1,98	1,28	1,66	6,6	3,5	0,5	6,6	13,0
					—	3,05	2,50	3,63; 3,73	7,15	2,19	1,70	2,00	6,6	3,6	0,5	6,6	13,0
VIIa	NH_2	Me	$CDCl_3$	50	1,32	—	2,34	3,65	6,30, 6,48 (NH)	2,15	1,63	1,95	7,0	3,0	0,5	7,0	—
			C_5D_5N	30	1,23	—	2,31	3,44	—	2,41	1,50	1,91	7,0	3,1	0,8	6,6	—
VIIb	NH_2	Me	$CDCl_3$	50	1,33	—	2,34	3,66	5,65, 6,28 (NH)	2,03	1,81	2,07	7,5	3,0	0,5	7,0	—
			C_5D_5N	30	1,25	—	2,35	3,53	—	2,31	1,78	2,10	7,0	3,1	0,8	6,6	—
VIII	NH_2	$PhCH_2$	C_5D_5N	30	—	3,10	2,68	3,49	7,10	2,18	1,73	2,00	6,6	3,0	0,5	6,5	12,5

[a]The parameters of the spectrum of the preponderant diastereomer (the ratio is 1.1: 1.2) are given in the upper lines.

therefore obtained amides VII and VIII in order to separate the diastereomers by crystallization (Table 1):



VII R = CH_3; VIII R = $C_6H_5CH_2$

VII, VIII

Signals of diastereomers (doubling of the signals of the MeC, CO_2Me, and Ph groups) are observed in the PMR spectra of I-VIII (Table 2) in nonpolar solvents (CCl_4, C_6F_6, C_6H_6, CH_2Cl_2, and $CDCl_3$) at 30°C. Analysis of the spectra of the ring protons is difficult in this case because of marked broadening of the signals, which is evidently due to the low magnitude of the diastereomeric anisochromicity and association of the compounds in nonpolar solvents. A study of the temperature (from −50 to +100°C) and concentration dependences of the spectra in various solvents showed that the most highly resolved spectra can be obtained for dilute solutions in polar solvents at elevated temperatures. This is explained by both a decrease in association and by an increase in the $\Delta\nu$ values of the signals at elevated temperatures. Analogies to this can be found in the literature [15-17].

A selection of individual conditions for measuring the spectra made it possible to make the complete assignment of the signals of the diastereomers (Table 2). The assignment of the signals of the diastereomers of I and II was made with allowance for their different integral intensities. We were able to separate diastereomers VIIa,b by crystallization and to investigate the spectra of the individual isomers. The spectra of the ring protons of I, II, VII, and VIII are ABC systems. The assignment of the signals was made from the known (for monosubstituted aziridines) relationship between the spin-spin coupling constants (SSCC): $J_{cis} > J_{trans} > J_{gem}$ [18], as well as with allowance for the weak-field shift of the H_A signal under the influence of the adjacent electronegative substituent. It is known that the indicated SSCC depend not only on the nature of the substituents in the ring but also on their mutual orientation. Thus for trans-1-chloro-2-methylaziridine J_{AB} = 7.8 and J_{AC} = 5.8 Hz (ΔJ = 2 Hz), whereas J_{AB} = 6.3 and J_{AC} = 5.7 Hz (ΔJ = 0.6 Hz) for the cis isomer [19]. The J_{AB} and J_{AC} SSCC ($\Delta J \sim 3$ Hz) confirm the trans configuration of the investigated com-

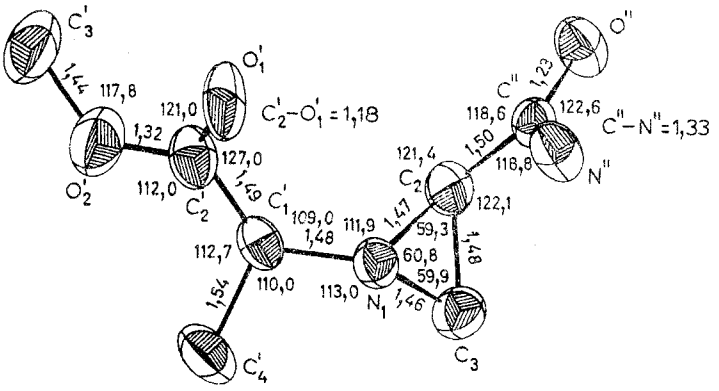


Fig. 1. Molecular structure of the VIIa isomer (1'S2R).

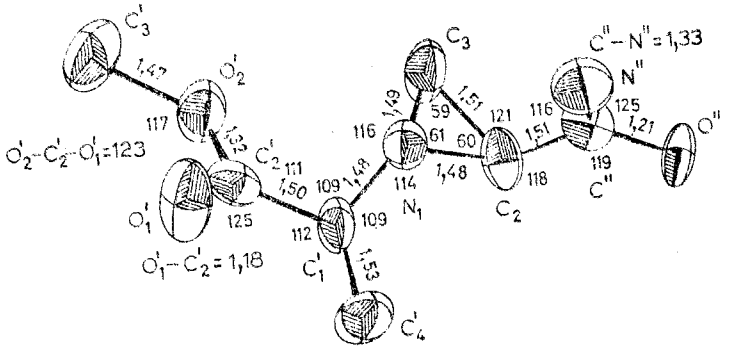


Fig. 2. Molecular structure of the VIIb isomer (1'S2S).

pounds (Table 2). The only PMR parameter with respect to which diastereomers VIIa,b differ significantly is $\Delta\nu_{AB}$ (Table 2). The use of this parameter for the determination of the absolute configuration requires additional study. As yet, one can only assume that the resulting single diastereomer VIII, judging from the $\Delta\nu_{AB}$ value, has the same configuration as VIIb.

The molecular and crystal structure, as well as the configuration of the $C_{(2)}$ center in the coordinates of the α-carbon center with a known S configuration, was determined by x-ray diffraction analysis of diastereomers VIIa,b. The absolute configuration of VIIa is 1'S2R, whereas that of VIIb is 1'S2S (Figs. 1 and 2).

The geometries of the molecules of both diastereomers coincide within the limits of the experimental error. The interatomic distances and bond angles of the amino acid fragment of the molecules are close to the values for the α-alanine molecule [20]. The N1—C1' bond is a single bond (1.48 Å). The deviations of the C1' and C'' atoms from the plane of the aziridine ring directed to the opposite sides are 1.32 and 1.19 Å for VIIa and 1.29 and 1.24 Å for diastereomer VIIb. The dihedral angles between the planar fragments of the C3', O2', C2', O1' and C2', C1', C4' atoms in the molecules of the diastereomers are 64 and 9°, respectively. The carbamoyl groups are turned at angles of 78 and 71° with respect to the aziridine ring.

The molecules in the VIIa crystal, due to N''—H...O'' hydrogen bonds of 2.89 Å, are joined together in chains along the b axis that are generated by the second-order helical axis (Fig. 3).

The molecules in the VIIb crystal are joined together in layers by N''—H...O'' (2.96 Å) and N''—H...O'' (2.94 Å) hydrogen bonds formed with the participation of both hydrogen atoms attached to the N'' atom, as well as the O'' atom, which is an acceptor in the two hydrogen bonds (Fig. 4).

EXPERIMENTAL

The PMR spectra were measured with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with an MS-50E spectrom-

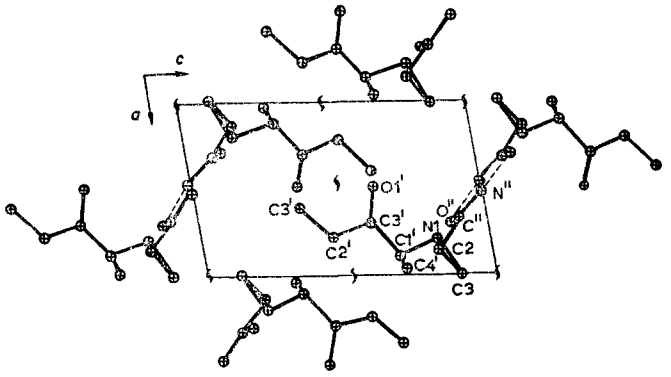


Fig. 3. Packing of the molecules of the VIIa isomer in the crystal.

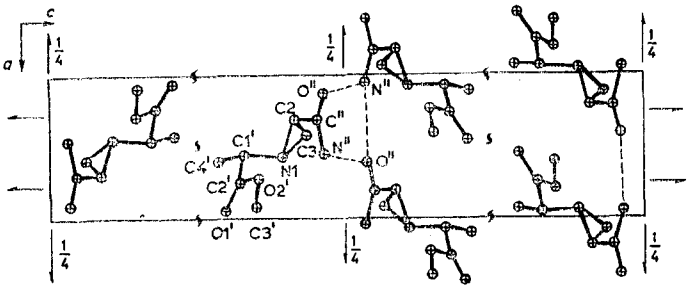


Fig. 4. Packing of the molecules of the VIIb isomer in the crystal.

eter. The IR spectra of mineral oil suspensions or molecular layers of the compounds were obtained with a UR-20 spectrometer. The optical rotation angles were obtained with a Perkin–Elmer 141 polarimeter.

X-Ray Diffraction Analysis. (1'S2R)-1,1-(1-Carbomethoxyethyl)-2-carbomoylaziridine (VIIa). Crystals of VIIa with the composition $C_7H_{12}O_3N_2$ were grown from alcohol and were monoclinic with a = 5.676(1), b = 8.315(2), c = 9.663(2) Å, β = 100.33(1)°, V = 448.7(2) Å^3, M = 172.2, d_{calc} = 1.27 g·cm^{-3}, μ(Cu K_α) = 8.5 cm^{-1}, Z = 2, space group $P2_1$, and F_{000} = 184. (1'S2S)-1-(1-Carbomethoxyethyl)-2-carbamoylaziridine (VIIb). Crystals of VIIb with the composition $C_7H_{12}O_3N_2$ were grown from alcohol and were rhombic with a = 5.210(1), b = 8.045(1), c = 22.383(5) A, V = 938.2(3) Å^3, M = 172.2, d_{calc} = 1.22 g·cm^{-3}, μ(Cu K_α) = 8.2 cm^{-1}, Z = 4, space group $P2_12_12_1$, and F_{000} = 368.

The intensities of 766 (VIIa) and 730 (VIIb) independent nonzero reflections were measured with a Syntex-$P2_1$ diffractometer with colorless single crystals with dimensions of 0.6 by 0.4 by 0.25 mm (VIIa) and 0.5 by 0.25 by 0.2 mm (VIIb) by the method of $\theta/2\theta$ scan in copper emission up to $2\theta_{max}$ = 150°. Models of the molecules were found by a direct method by means of the MULTAN program [21] of the XTL system. The VIIa structure was refined by the method of least squares within the fully matrix approximation up to R = 0.123 and then within the anisotropic approximation up to R = 0.073. The hydrogen atoms, which were found from differential Fourier synthesis, were refined isotropically. The final R factor was 0.041. The errors in the interatomic distances and bond angles were within the limits of 0.01 Å and 0.5°. The coordinates of the atoms are presented in Table 3.*

The VIIb structure was refined by the method of least squares within the anisotropic approximation with the weight scheme $W = 1/(\sigma_F + 0.01F^2)$. The position of the hydrogen atoms were obtained from differential synthesis with R = 0.086 and were not further refined (B_{isotr} = 6 Å^2). The final R value was 0.078. The errors in the interatomic distances and bond angles were within the limits of 0.01 A and 1°, respectively. The coordinates of the atoms and their temperature factors are presented in Table 3.

General Method for the Preparation of Aziridines I-IV. A 10.1 g (0.1 mole) sample of triethylamine was added at 5°C to a solution of 24.6 g (0.1 mole) of methyl 2,3-dibromopro-

*The anisotropic temperature factors can be obtained from the authors.

TABLE 3. Coordinates of the Atoms of Isomers VIIa,b

Atom	VIIa			VIIb		
	x	*y*	*z*	*x*	*y*	*z*
O1′	0,5002 (7)	0,0800 (0)	0,3691 (4)	0,5511 (14)	0,3563 (8)	0,2060 (3)
O2′	0,7684 (6)	0,1755 (9)	0,5392 (3)	0,7822 (15)	0,5114 (8)	0,1454 (3)
O″	0,7022 (6)	−0,3592 (8)	0,1212 (3)	1,3908 (9)	−0,0994 (7)	0,0364 (2)
N1	0,8078 (6)	0,0725 (8)	0,1829 (3)	0,9394 (12)	0,1843 (6)	0,1073 (2)
N″	0,5141 (8)	−0,1549 (9)	−0,0038 (4)	0,9589 (12)	−0,0942 (7)	0,0334 (3)
C1′	0,8900 (8)	0,1447 (9)	0,3226 (4)	0,9455 (15)	0,2494 (8)	0,1690 (3)
C2′	0,6962 (8)	0,1302 (9)	0,4075 (4)	0,7343 (16)	0,3740 (8)	0,1760 (3)
C3′	0,6012 (13)	0,1625 (12)	0,6346 (6)	0,5910 (26)	0,6450 (11)	0,1496 (5)
C4′	0,9681 (15)	0,3196 (9)	0,3064 (5)	0,9138 (24)	0,1042 (10)	0,2122 (3)
C″	0,6811 (7)	−0,2144 (9)	0,0972 (3)	1,1877 (15)	−0,0358 (7)	0,0491 (3)
C2	0,8531 (7)	−0,1014 (9)	0,1832 (3)	1,1890 (14)	0,1204 (8)	0,0862 (3)
C3	1,0033 (9)	0,0114 (9)	0,1182 (4)	1,0848 (18)	0,2816 (7)	0,0617 (3)
H1N″	0,422 (8)	−0,229 (5)	−0,044 (4)	0,770	−0,044	0,040
H2N″	0,476 (8)	−0,053 (6)	−0,0-9 (4)	0,929	−0,198	0,007
H1C3	1,181 (8)	0,041 (6)	0,145 (4)	1,180	0,401	0,073
H2C3	0,975 (8)	0,024 (5)	0,004 (5)	1,022	0,289	0,015
HC2	0,937 (8)	−0,164 (6)	0,281 (4)	1,369	0,086	0,107
HC1′	1,039 (8)	0,079 (6)	0,376 (4)	1,129	0,313	0,178
H1C4′	0,988 (10)	0,383 (10)	0,432 (6)	0,766	0,059	0,226
H2C4′	1,088 (10)	0,356 (10)	0,267 (10)	1,022	0,020	0,215
H3C4′	0,853 (10)	0,399 (9)	0,271 (7)	0,967	0,211	0,238
H1C3′	0,453 (10)	0,234 (10)	0,587 (9)	0,534	0,705	0,192
H2C3′	0,657 (10)	0,187 (10)	0,754 (9)	0,536	0,727	0,113
H3C3′	0,519 (10)	0,052 (9)	0,625 (6)	0,473	0,532	0,146

pionate in ethanol, the mixture was allowed to stand for 30 min, and 0.1 mole of the amino acid methyl ester hydrochloride and 25.3 g (0.25 mole) of triethylamine in 200 ml of ethanol were added. The mixture was maintained at room temperature for 5 h and then at 70°C for 5 h, after which the solvent was removed, and the reaction product was extracted with ether. The extract was filtered and evaporated, and the residue was distilled under high vacuum.

1-(1-Carbomethoxyethyl)-2-carbamoylaziridine (VII). A 10.1 g (0.1 mole) sample of triethylamine was added at 5°C to a solution of 23.1 g (0.1 mole) of 2,3-dibromopropionamide in 300 ml of ethanol, and the mixture was allowed to stand for 30 min. It was then treated with 0.1 mole of α-alanine methyl ester hydrochloride and 25.3 ml (0.25 mole) of triethylamine in 200 ml of ethanol, and the mixture was maintained at 20°C for 5 h and then at 70°C for 10 h. The solvent was then removed, and the residue was diluted with a small amount of water and extracted three times with ethyl acetate. The extracts were combined and dried with magnesium sulfate, the ethyl acetate was evaporated, and the dark viscous residue was dissolved by heating in 30 ml of ethanol. The solution was allowed to stand in a refrigerator for a few days, and the resulting crystalline reaction product was separated and dried in vacuo. Three crystallizations from ethanol gave diastereomerically pure amide VIIa. A residue was isolated from the combined mother liquors and was crystallized two to three times from ethanol to give amide VIIa. The residue was 70% enriched in the second diastereomer. Three crystallizations from ethyl acetate gave diastereomerically pure VIIb.

1-(1-Carbomethoxy-2-phenylethyl)-2-carbamoylaziridine (VIII). A 10.1 g (0.1 mole) sample of triethylamine was added at 5°C to a solution of 23.1 g (0.1 mole) of 2,3-dibromopropionamide in 300 ml of ethanol, the mixture was allowed to stand for 30 min, and 21.5 g (0.1 mole) of α-phenylalanine methyl ester hydrochloride and 25.3 g (0.25 mole) of triethylamine in 200 ml of ethanol were added. The mixture was then maintained at 20°C for 5 h and at 70°C for 10 h. The solvent was removed, 50 ml of water was added to the residue, and the resulting crystalline product was separated and dried in vacuo to give a product with mp 164-166°C in 91% yield. Recrystallization from ethanol gave a product with mp 172-174°C.

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REACTION OF THE FISCHER BASE WITH 8-HYDROXY-1-NAPHTHALDEHYDES. INVESTIGATION OF THE REACTION PRODUCTS BY ^{13}C NMR SPECTROSCOPY

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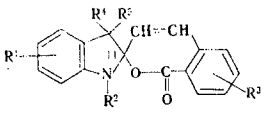
The product of the condensation of the Fischer base with unsubstituted 8-hydroxy-1-naphthaldehyde is a bisindolinespirooxepine. 5,7-Dinitro-8-hydroxy-1-naphthaldehyde reacts with the Fischer base to give a merocyanine that does not display a tendency to undergo conversion to the cyclic form. 2H-Naphtho[1,8-bc]furan derivatives are formed in the reaction of the Fischer base with 5-nitro-, 5-bromo-, and 5,7-dibromo-8-hydroxy-1-naphthaldehydes. The structures of the compounds obtained were established on the basis of data from the PMR and ^{13}C NMR spectra. It was shown by means of the ^{13}C NMR spectra that the product of the condensation of phthalic monoaldehyde with the Fischer base is not a seven-membered spirolactone, as previously assumed, but rather a phthalide derivative.

The search for photochromic substances in series of indoline spiro compounds is being conducted in various directions. One of the most important directions is the synthesis of spiro derivatives that do not contain a six-membered pyran ring as in spiropyrans but rather a seven-membered oxepine ring as, for example, in spirolactones with the I structure [1] or an eight-membered oxacine ring [2-4]. Quantum-chemical calculations [5] that showed that spirooxepine II should exist primarily in the closed form, whereas its mercyanine form should have a long-wave absorption maximum between the visible and IR regions of the spectrum, were published in 1980 for spirooxepine II, the formation of which might be expected in the reaction of the Fischer base with 8-hydroxy-1-naphthaldehyde. These calculated data indicate that it is expedient to search for new photochromic compounds among indolinespirooxepines of the II type. In the present research we made at attempt to obtain these compounds.



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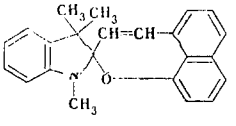

II

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