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ALKYLIMINOMALONIC ACID AND 2-ALKYLOXAZIRIDINE-3,3-DICARBOXYLIC ACID ESTERS*

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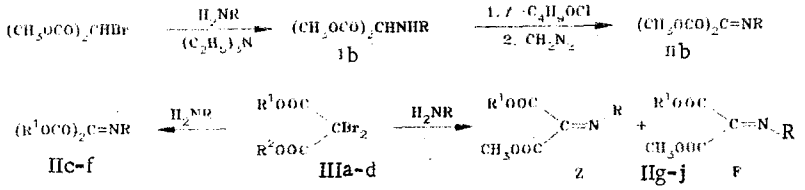
UDC 547.717.04:541.632:543.422

2-Alkyloxaziridine-3,3-dicarboxylic acid esters have been obtained by oxidizing alkylaminomalonic acid esters by monoperphthalic acid. The activation parameters for the inversion of the nitrogen atom have been obtained for a number of alkyliminomalonic acid and 2-alkyloxaziridine-3,3-dicarboxylic acid ester.

The introduction of geminal esteric groups in the α position to a configurationally stable nitrogen atom made it possible to develop a general method for the separation of 1-alkoxyaziridine-2,2- [2]-, 1-alkyldiaziridine-3,3- [3], and 2-alkoxyisoxazolidine-3,3-dicarboxylic acid esters [4], which contain only a nitrogen chiral center, into antipodes. It would be of interest to extend this method to other nitrogen-containing heterocycles, particularly to oxaziridines, whose chiral derivatives were previously obtained only by asymmetric reactions involving the oxidation of imines [5]. However, oxaziridines with electron-acceptor functional groups on the C atom were not known until very recently. The report of the syntheses of 2-phenyl-3,3-dibenzoyloxaziridine by the photoisomerization of N-phenyl-α,α-dibenzoylnitrone and the oxidation of the anil of diphenyl triketone in [6] proved to be erroneous [7]. We developed methods for the synthesis of alkyliminoamlonates and the first oxaziridines with functional groups on the C atom.†

Alkyliminomalonates IIa-j were obtained on the basis of mono- and dibromomalonates according to the schemes



I, II a R=CH_3, b R=C_2H_5; II c, d, g, i R=i-C_3H_7, d, f, h, j R=t-C_4H_9; c, d R^1=CH_3, e, f, g, h R^1=C_2H_5, i, j R^1=i-C_3H_7; III a, c, d R^1=CH_3, b R^1=C_2H_6; a R^2=CH_3, b, c R^2=C_2H_5; d R^2=i-C_3H_7

Imines IIa and b cannot be obtained by reacting n-alkylamines with dibromomalonic ester, since exhaustive amidation is observed in this case [8]. It must be noted that imines IIa and b, unlike the remaining imines, are unstable and polymerize completely during storage over the course of 1 month.

When imines IIa-j are oxidized by monoperphthalic acid, they form the corresponding oxaziridines IVa-j with good yields:

*Report 46 from a series entitled Asymmetric Nonbridging Nitrogen. For report 45 see [1].
†For the preliminary report see [8].

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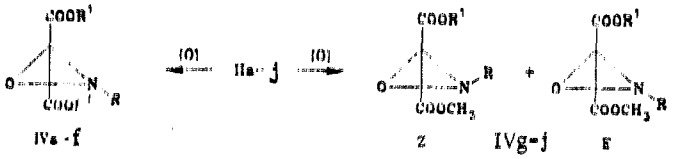
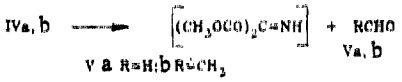


IV a R=CH$_3$, b R=C$_2$H$_5$, c, e, g, i R=*i*-C$_3$H$_7$, d, f, h, j R=*t*-C$_4$H$_9$; a – d R^1=CH$_3$, e – h R^1=C$_2$H$_5$, i, j R^1=*i*-C$_3$H$_7$

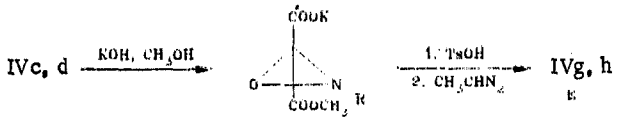
Oxaziridines IVc-j are thermally stable compounds, which can withstand many hours of heating in toluene at 110°C without showing signs of decomposition. At the same time, oxaziridines IVa and b are restrictedly stable during storage in the cold in solutions. Attempts to concentrate the reaction solutions of oxaziridines IVa and b resulted in their decomposition with the formation of the corresponding aldehydes:



V a R=H; b R=CH$_3$

In this case, acetaldehyde was identified in the form of the 2,4-dinitrophenylhydrazone (VI). Dimethyl iminomalonate could not be isolated, apparently due to its polymerization under the conditions of the reaction.

The oxidation of asymmetric imines IIg-j produces a practically equilibrium mixture of the Z and E isomers of oxaziridines IVg-j, which is not suitable for the determination of the activation parameters for the inversion of the nitrogen atom. For the purpose of synthesizing the individual E isomers of oxaziridines IVg and h, we investigated the deasymmetrization of oxaziridines IVc and d in analogy to other heterocycles containing geminal esteric groups [2-4]:



The saponification of oxaziridines IVc and d is trans-stereospecific, and the E configuration is maintained during the further conversions.

The composition and structure of the compounds obtained were confirmed by elemental analysis, as well as by the data from the IR and PMR spectra (Tables 1 and 2). The carbonyl bands of the esteric groups in the IR spectra of imines IIa-j and oxaziridines IVa-j were assigned in accordance with the 20-25-cm^{-1} displacement of the bands of the S-trans carbonyl groups to lower frequencies in comparison to the S-cis carbonyl groups [9].

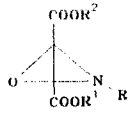
The signals of the protons of the esteric groups in the PMR spectra of imines IIa-j in benzene (Table 1) were assigned on the basis of the fact that in the case of acetone N-propylimine, the shift induced by an aromatic solvent is 0.28 ppm greater for the C-methyl group in the cis position to the substituent on the nitrogen atom [10]. The assignment was confirmed by an analysis of the shifts induced by the aromatic solvent for the esteric groups in the Z and E isomers of asymmetric imines IIg-j with consideration of the fact that the E isomer is predominant in the equilibrium due to the weak steric interaction of the substituent at the nitrogen atom with a cis-oriented esteric group.

It should be noted that in the PMR spectra of imines IIa-j in CCl_4 the protons of the esteric groups are always equivalent, while in the case of acetone N-propylimine, a deshielding influence of the lone pair of the nitrogen atom with respect to the cis substituent at the imino carbon atom in comparison to the substituent on the N atom was noted [10]. This fact is apparently caused by the influence of the effective conformations of the esteric groups.

The proton signals of the esteric groups in the PMR spectra of oxaziridines IVa-j in CCl_4 (Table 2) were assigned on the basis of the shielding effect of the lone pair of the nitrogen atom with respect to cis-oriented substituent, which was established by comparing the chemical shifts of the protons of the esteric groups in the Z and E isomers of oxaziridines IVg-j.

We determined the activation parameters of the thermal topomerization of imines IIa-d and the inversion of the nitrogen atom in oxaziridines E-IVg and h (Table 3). The lowering of the values of $\Delta G_{298\ K}^{\neq}$ as the size of the substituent at the imino nitrogen atom is increased is an indication of an inversion mechanism for the topomerization of imines IIa-d. The high barriers to the inversion of the nitrogen atom in the 2-alkyloxaziridine-3,3-dicarboxylic acid esters attest to the possibility of the synthesis of chiral derivatives of oxaziridines.

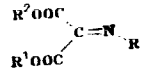
TABLE 2. Characteristics of 2-Alkyloxaziridines-3,3-dicarboxylic Acid Diesters IVa-j



Compound	n_D^{20}	IR spectrum, $\nu_{C=O}$, cm^{-1}		Equilibrium content of isomers, %		PMR spectrum (in CCl_4), δ*, ppm						Found: N, %	Empirical formula	Calculated: N, %	Yield, %
						R		R¹		R²					
		s-trans	S-cis	Z	E	CH_3	CH_2, CH	CH_3	CH_2, CH	CH_3	CH_2, CH				
IVa	—	1745	1760	—		2,85 (0,25)	— —	3,94 (0,50)	— —	3,87 (0,56)	— —	—	—	—	—
IVb	—	1748	1768	—		1,25 (0,24)	2,91† (0,24)	3,94 (0,51)	— —	3,88 (0,56)	— —	—	—	—	—
IVc	1,4397	1744	1766	—		1,12and1,25 (0,1?and0,16)	2,42 (−0,13)	3,91 (0,51)	— —	3,85 (0,61)	— —	6,81	$C_8H_{13}NO_5$	6,89	86
IVd	1,4504	1742	1768	—		1,15 (0,10)	— —	3,90 (0,50)	— —	3,85 (0,63)	— —	6,41	$C_9H_{15}NO_5$	6,44	89
IVe	1,4588	1739	1758	—		1,14and1,27 (0,10and0,15)	2,40 (−0,17)	1,38 (0,51)	4,33 (0,31)	1,33 (0,57)	4,27 (0,42)	6,03	$C_{10}H_{17}NO_5$	6,05	90
IVf	1,4441	1736	1760	—		1,16 (0,11)	— —	1,38 (0,51)	4,33 (0,31)	1,33 (0,59)	4,28 (0,45)	5,64	$C_{11}H_{19}NO_5$	5,71	87
IVg	1,4396	1739	1762	48	52	1,13and1,26 (0,08and0,12) 1,13and1,26 (0,08and0,12)	2,40 (−0,18) 2,40 (−0,18)	1,39 (0,48) 3,90 (0,54)	4,34 (0,27) —	3,84 (0,58) 1,34 (0,62)	— — 4,29 (0,44)	6,29	$C_9H_{15}NO_5$	6,44	91
IVh	1,4481	1740	1763	48	52	1,16 (0,11) 1,16 (0,07)	— — —	1,39 (0,45) 3,90 (0,50)	4,35 (0,26) —	3,85 (0,63) 1,33 (0,64)	— — 4,29 (0,49)	5,97	$C_{10}H_{17}NO_5$	6,05	89
IVi	1,4573	1744	1766	48	52	1,14and1,27 (0,10and0,13) 1,14and1,27 (0,10and0,13)	2,40 (−0,18) 2,40 (−0,18)	1,33 (0,34) 3,90 (0,54)	5,16 (0,12) —	3,85 (0,60) 1,30 (0,47)	— — 5,05 (0,16)	5,81	$C_{10}H_{17}NO_5$	6,05	86
IVj	1,4416	1743	1760	47	53	1,16 (0,11) 1,16 (0,06)	— — —	1,33 (0,36) 3,90 (0,52)	5,15 (0,12) —	3,85 (0,65) 1,30 (0,47)	— — 5,03 (0,17)	5,67	$C_{11}H_{19}NO_5$	5,71	93

*The values of the shifts induced by the aromatic solvent are given in parentheses: $J_{CH_3CH_2}$ = 7.0, J_{CH_3CH} = 6.0 Hz.
†$\Delta\delta$ = 12.5, J_{HH} = 13.5 Hz.

TABLE 1. Characteristics of Alkylamino- and Alkylminiomalonates Ia, Ib, and IIa–j



Compound	bp, °C (mm Hg)	n_D^{20}	IR spectrum, ν, cm^{-1} C=O			Equilibrium content of isomers, %		PMR spectra (in C_6H_5), δ*						Found: N, %	Empirical formula	Calculated, N, %	Yield, %
			C=O S-trans	C=O S-cis	C=N (NH)	Z	E	R		R¹		R²					
								CH_3	CH_2, CH	CH_3	CH_2, CH	CH_3	CH_2, CH				
Ia	78 (4)	1,4342	1736	1752	(3381)	—		2,20	—	3,40	—	3,40	—	8,60	$C_6H_{11}NO_4$	8,69	33
Ib	70 (2)	1,4311	1739	1759	(3389)	—		0,86	2,45	3,40	—	3,40	—	7,90	$C_7H_{13}NO_4$	8,00	35
IIa	71 (3)	1,4456	1725	1745	1658	—		3,25	—	3,37	—	3,40	—	8,70	$C_6H_9NO_4$	8,80	77
								(0,25)	—	(0,52)	—	(0,49)	—				
IIb	84 (5)	1,4488	1724	1742	1656	—		1,05	3,45	3,37	—	3,40	—	8,01	$C_7H_{11}NO_4$	8,09	81
								(0,25)	(0,17)	(0,52)	—	(0,49)	—				
IIc	70 (2)	1,4406	1721	1744	1653	—		1,06	3,70	3,33	—	3,42	—	7,41	$C_8H_{13}NO_4$	7,48	65
								(0,14)	(−0,05)	(0,56)	—	(0,47)	—				
IId†	72 (2)	—	1722	1745	1655	—		1,18		3,32	—	3,42	—	6,91	$C_9H_{15}NO_4$	6,86	93
								(0,10)		(0,55)	—	(0,45)	—				
IIe	76 (1)	1,4362	1723	1740	1654	—		1,09	3,70	0,81	3,93	0,92	4,03	6,48	$C_{10}H_{17}NO_4$	6,50	78
								(0,12)	(−0,04)	(0,53)	(0,39)	(0,42)	(0,29)				
IIf	80 (1)	1,4451	1718	1741	1660	—		1,23	—	0,81	3,90	0,91	4,02	5,85	$C_{11}H_{19}NO_4$	6,11	87
								(0,06)	—	(0,53)	(0,40)	(0,43)	(0,28)				
IIg	70 (2)	1,4392	1723	1743	1655	48	52	1,10	3,70	0,80	3,93	3,40	—	6,79	$C_9H_{15}NO_4$	6,96	71
								(0,11)	(−0,04)	(0,54)	(0,38)	(0,46)	—				
								1,10	3,70	3,31	—	0,92	4,03				
								(0,11)	(−0,04)	(0,55)	—	(0,42)	(0,28)				
IIh	73 (2)	1,4403	1722	1739	1658	47	53	1,20	—	0,81	3,91	3,43	—	6,42	$C_{10}H_{17}NO_4$	6,50	86
								(0,09)	—	(0,54)	(0,41)	(0,45)	—				
								1,23	—	3,33	—	0,90	4,42				
								(0,06)	—	(0,55)	—	(0,45)	(0,30)				
IIi	76 (2)	1,4377	1726	1750	1655	47	53	1,10	3,70	0,92	5,09	3,38	—	6,39	$C_{10}H_{17}NO_4$	6,50	66
								(0,11)	(−0,04)	(0,41)	(−0,06)	(0,44)	—				
								1,10	3,70	3,29	—	1,03	(5,18)				
								(0,11)	(−0,04)	(0,53)	—	(0,28)	(−0,15)				
IIj	84 (2)	1,4395	1722	1740	1659	46	54	1,22	—	0,93	5,08	3,39	—	5,97	$C_{11}H_{19}NO_4$	6,11	84
								(0,06)	—	(0,39)	(−0,05)	(0,44)	—				
								1,25	—	3,29	—	0,95	5,17				
								(0,03)	—	(0,54)	—	(0,27)	(−0,14)				

*The values of the chemical shifts induced by the aromatic solvent are given in parentheses: $\Delta\delta = \delta_{CCl_4} - \delta_{C_6H_6}$; $J_{CH_2CH_3} = 7.0$, $J_{CH_3CH} = 6.0$ Hz.

†Mp 44°C.

TABLE 3. Activation Parameters* for the Inversion of the Nitrogen Atom in Imines IIa-d (in 1,2-$C_6H_4Cl_2$) and Oxaziridines IVg and h (in C_6H_6)

Compound	Δν, Hz	T_f,† K	k_f,‡ sec^{-1}	$\Delta G_f^{\neq}$, kJ/mole	$\Delta G_{298\ K}^{\neq}$, kJ/mole	lg $k_{298\ K}$
IIa	1,6	435	3,55	103,2	104,3	−5,49
IIb	2,2	429	4,90	100,6	101,7	−5,03
IIc	4,0	435	8,90	99,9	101,0	−4,91
IId	4,8	372	10,80	84,4	85,0	−2,10
IVg	—	383	$1,45 \cdot 10^{-4}$	122,9	123,6	−8,87
			$(1,57 \cdot 10^{-4})$	122,6	123,3	−8,81
IVh	—	353	$6,13 \cdot 10^{-4}$	108,4	109,0	−6,31
			$(6,51 \cdot 10^{-4})$	108,2	108,8	−6,13

*The values of the parameters at T_f were determined with the use of the formulas $k_f = \pi \cdot \Delta\nu/\sqrt{2}$ [11] and $\Delta G_f^{\neq} = 4.576 \cdot T_f \cdot (10.319 + \log T_f/k_f)$ [11] under the assumptions that $\Delta S^{\neq} = 0$ and $\Delta G_{298\ K} = \Delta G_f^{\neq} + R(T_f - 298)$ [12]. The values of log $k_{298\ K}$ were calculated from Eyring's equation [11] on the basis of the values of $\Delta G_{298\ K}^{\neq}$.

†The temperature at which the E,Z isomerization was carried out is given for compounds IVg and h.

‡In the case of compounds IVg and h, the rate constants of the forward (reverse) inversion reaction were calculated by the least-squares method from the kinetic data on the E,Z isomerization.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer in microlayers (in CCl_4 in the case of compounds IIa and b and in a KBr tablet in the case of IId), and the PMR spectra were recorded on an RYa-2305 spectrometer (60 MHz) with the use of 5 mole % solutions and with HMDS as an internal reference.

The activation parameters for the inversion of the nitrogen atom were determined from the temperature of fusion (T_f) of the proton signals of the methoxycarbonyl groups in the PMR spectra (imines IIa-d) or on the basis of the data on the kinetics of the thermal E,Z isomerization process (oxaziridines IVg and h). The isomerization kinetics were determined upon heating in sealed evacuated ampuls by measuring the integrated intensities of the PMR signals of the methoxycarbonyl groups. In the case of imines IIa and b, which are unstable at high temperatures, the value of T_f was determined after brief heating (10 min) in a pickup heated to T_f following the preliminary determination of T_f in other experiments on other samples of imines IIa and b. The error in the determination of T_f was ±1.0°C, and the error in the determination of Δν was ±0.1 Hz. Thus, the errors in the determination of the activation parameters of inversion were ±0.22 sec^{-1} for k_f, ±0.33 kJ/mole for $\Delta G^{\neq}$, and ±0.04 for log $k_{298\ K}$.

The characteristics of the compounds synthesized are presented in Tables 1-3.

Methyl Ethyl Malonate. A solution of 16 g (100 mmoles) of malonic ester in 50 ml of absolute ethanol is given an addition of a solution of 5.6 g (100 mmoles) of KOH in 100 ml of absolute ethanol, the mixture is held for 10 h, the ethanol is driven off, and the salt is washed with 100 ml of ether and dissolved in 30 ml of H_2O, given an addition of 10 ml of 36% hydrochloric acid, and extracted by ether (three 50-ml portions). The extract is given an addition of an excess of a solution of diazomethane in ether, the mixture is held for 15 min, the ether is distilled off, and the residue is vacuum-distilled. The yield is 13.6 g (93.5%), bp 58°C (3 mm Hg), n_D^{20} 1.4155. According to the data in [13], T_b 182°C.

Methyl Isopropyl Malonate. This compound is obtained in an analogous manner from diisopropyl malonate, but the reaction with KOH is carried out in tert-butanol. The yield is 81.5%, bp 63°C (3 mm Hg), n_D^{20} 1.4145. Found: C 52.6; H 7.7%. Calculated for $C_7H_{12}O_4$: C 52.5; H 7.6%.

Dimethyl dibromomalonate (IIIa) is obtained according to [14]. The yield is 95%, mp 65°C. According to the data in [14], mp 63-65°C.

Methyl ethyl dibromomalonate (IIIc) [93% yield, T_b 108°C (2 mm Hg), n_D^{20} 1.4393. Found: C 23.8; H 2.8%. Calculated for $C_6H_8Br_2O_4$: C 23.7; H 2.6%] and methyl isopropyl dibromomalon-

ate (IIId) [94% yield, bp 110°C (2 mm Hg), n_D^{20} 1.4357. Found: C 25.6; H 3.2%. Calculated for $C_7H_{10}Br_2O_4$: C 26.4; H 3.2%] are obtained in a similar manner.

Dimethyl Ethylaminomalonate (Ib). A solution of 4.5 g (100 mmoles) of ethylamine and 10.1 g (100 mmoles) of triethylamine in 150 ml of acetonitrile is given an addition of 21.0 g (100 mmole) of dimethyl bromomalonate, the mixture is stirred for 2 h, the acetonitrile is distilled off, and the residue is extracted with 150 ml of absolute ether. The extract is saturated with dry HCl, the precipitate formed is separated and dissolved in 20 ml of absolute methanol, 10.1 g (100 mmoles) of triethylamine are added to the solution, the mixture is stirred for 5 min, the methanol is distilled off under a vacuum, and the residue is extracted with ether (two 100-ml portions). The ether is evaporated, the residue is vacuum-distilled, and 6.1 g (35%) of amine Ib are obtained.

Compound Ia is obtained in a similar manner.

Dimethyl Ethyliminomalonate (IIb). A solution of 1.75 g (10 mmole) of Ib in 30 ml of asbolute ether at 0°C is given an addition of 1.09 g (10 mmoles) of tert-butyl hypochlorite in 5 ml of absolute ether, the mixture is held for 5 min, and a solution of diazomethane is added until the evolution of nitrogen ceases. The ether is distilled off, the residue is vacuum-distilled, and 1.4 g of imine IIb are obtained.

Compound IIa is obtained in a similar manner.

Dimethyl tert-butyliminomalonate (IId) is obtained according to [8]. The yield is 93%.

Compounds IIc and e-j are obtained in a similar manner.

Dimethyl 2-tert-Butyloxaziridine-3,3-dicarboxylate (IVd). A solution of 2.01 g (10 mmoles) of imine IId in 5 ml of ether is given an addition of an ethereal solution of monoperphthalic acid containing 10 mmoles of active oxygen, the mixture is held for 3 h and then filtered, and the filtrate is washed with a 5% solution of Na_2CO_3 to pH 7 for the ethereal solution and dried over Na_2SO_4. The ether is evaporated, and the residue is chromatographed in a column (Silica Gel L100/160 μ with chloroform as the eluent). This gives 2.93 g (89%) of oxaziridine IVd.

Oxaziridines IVa-c and e-j are obtained in a similar manner.

Acetaldehyde 2,4-Dinitrophenylhydrazone (VI). The reaction mass remaining after the thermolysis of oxaziridine IVb is treated in analogy to [15]. This gives hydrazone VI, mp 146°. According to the data in [16], mp 147°C.

cis-Methyl trans-Ethyl 2-tert-Butyloxaziridine-3,3-Dicarboxylate (E-IVh). A solution of 0.43 g (2 mmoles) of oxaziridine IVd in 10 ml of absolute methanol is given an addition of a solution of 0.11 g (2 mmoles) of KOH in 10 ml of absolute methanol. The mixture is held for 24 h, 0.34 g (2 mmoles) of p-toluenesulfonic acid in 5 ml of absolute methanol is added at 0°C, the mixture is stirred for 5 min, and a solution of diazoethane in ether is added until the evolution of nitrogen ceases. The reaction mixture is held for 10 min, the solvents are removed at a reduced pressure, the residue is extracted with ether (two 50-ml portions), and the ether is evaporated. The product is chromatographed in a column (Silica Gel L100/160μ with chloroform as the eluent). This gives 0.39 g (85%) of oxaziridine E-IVh.

Oxaziridine E-IVg is obtained in a similar manner.

LITERATURE CITED

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OXAZOLIDINES.

1. BASIC CATALYTIC DISPROPORTIONATION OF CYCLOHEXANOSPIRO-2-OXAZOLIDINES: SYNTHESIS OF N-SUBSTITUTED 4,5,6,7-TETRAHYDROINDOLES

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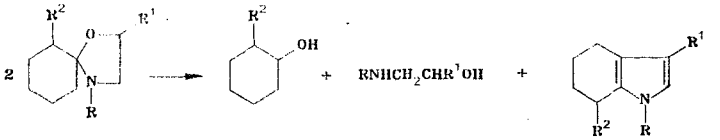
UDC 547.787.3'752:543.422.25

It has been shown that the basic catalytic disproportionation of cyclohexanospiro-2-oxazolidines in the presence of potassium hydroxide or sodium methylate leads to N-substituted 4,5,6,7-tetrahydroindoles with a yield of up to 73%. The influence of the character of substituents at the nitrogen atom of oxazolidine on the course of the reaction has been established.

The cyclohexanospiro-2-oxazolidines disproportionate in the presence of potassium tert-butylate to form tetrahydroindole derivatives with yields of up to 20% [1]. In order to develop a procedure for the preparation of 1-substituted tetrahydroindoles from readily available cyclohexanospiro-2-oxazolidines we have investigated the disproportionation of 3-(2-hydroxyethyl)-cyclohexanospiro-2-oxazolidine (I) under the influence of the hydroxides and alcoholates (C_1-C_4) of potassium, sodium, lithium, calcium, barium, and aluminum. The highest activity (at a high selectivity) was shown among the catalysts of this series by potassium hydroxide and sodium methylate, while the aluminum hydroxide and alcoholates did not catalyze the process at all. The highest yields of 1-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole (IIa) (63-73%) were obtained by refluxing 1 mole of oxazolidine I with 0.2-0.5 mole potassium hydroxide or sodium methylate. The duration of the reaction, determined by GLC from the time required for the complete decomposition of the oxazolidine Ia, was 2.5-4 h.

The disproportionation of the oxazolidines Ib-m was also performed under the conditions found.



I a-m IIa-m

I, II **a**,**k** R = CH_2CH_2OH, **b**,**m** R = CH_3, **c** R = $CH(CH_3)_2$, **d** R = C_4H_9-*n*, **e** R = C_4H_9-*i*, **f** R = C_4H_9-*s*, **g** R = C_6H_5, **h** R = $CH_2C_6H_5$, **i** R = C_6H_{11}-*cyclo*, **l** R = $CH_2CH(OH)CH_3$; **a**-**k** R^1 = H, **l**,**m** R^1 = CH_3; **a**-**i**,**l**,**m** R^2 = H, **k** R^2 = CH_3

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 533-535, April, 1986. Original article submitted December 3, 1984.

0009-3122/86/2204-0437$12.50