B) A 2.66-g (10 mmole) sample of perchlorate Ia was dissolved in 40 ml of acetic acid after which 5-6 ml of 57% perchloric acid was added, and 2.62 g (10 mmole) of triphenylphosphine was added to the resulting precipitate. The mixture was refluxed for 3-3.5 h, after which it was cooled to room temperature. The resulting precipitate was removed by filtration and distilled in 20 ml of isopropyl alcohol, and the undissolved Va was crystallized from acetic acid to give 1.78 g (67%) of a product with mp 242-243°C.

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ABSOLUTE CONFIGURATIONS OF DIASTEREOMERIC ESTERS OF 1,4-TETRAHYDROTHIAZINE-3,5-DICARBOXYLIC ACID

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UDC 547.869.2:548.737:541.634

The reaction of dimethyl 1,4-tetrahydrothiazone-3,5-dicarboxylate with phenyl isocyanate and phenyl isothiocyanate leads to 2,4-dioxo-3-phenyl-9-methoxycarbonyl-7-thia-1,3-diazabicyclo[3.4.0]nonane and its thioxo analog. It is shown that only the trans isomer of the starting diester undergoes the reaction.

The reaction of methyl 1,2-dibromopropionate with L-cysteine methyl ester leads to the formation of a pair of SS and SR diastereomers of dimethyl 1,4-tetrahydrothiazone-3,5-dicarboxylate, which were separated into individual diastereomers by high-performance liquid chromatography (HPLC) [1]. The diastereomers are uncrystallizable liquids, which made it impossible to establish the absolute configuration of each of them by x-ray diffraction analysis. We therefore attempted to obtain crystalline derivatives of 1,4-tetrahydrothiazine-3,5-dicarboxylic acid for the subsequent determination of the absolute configurations by x-ray diffraction analysis.

We have previously shown that the reaction of methyl 1,4-tetrahydrothiazone-3-carboxylate with isocyanates and isothiocyanates leads to the formation of a two-ring system that consists of condensed thiazan and imidazolidine rings [2].

In order to obtain crystalline derivatives of diesters Ia, b we carried out their reaction with phenyl isocyanate and phenyl isothiocyanate; as expected, the corresponding two-ring derivatives were obtained as a result of this reaction. However, instead of the expected diastereomeric mixtures, we isolated monoesters VI and VII in the form of one diastereomer.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1056-1059, August, 1985. Original article submitted November 2, 1983; revision submitted September 3, 1984.

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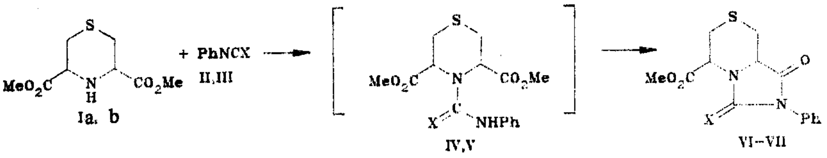

Ia — cis-isomer ; Ib — trans-isomer ; II, IV, VI X=O; III, V, VII X=S

An investigation of this reaction by analytical HPLC showed that only one diastereomer Ib undergoes the reaction and that the concentration of diastereomer Ia remains virtually unchanged. This was confirmed by an investigation of the reaction also by PMR spectroscopy. When phenyl isocyanate or phenyl isothiocyanate is added to diastereomer Ia, the spectrum of the starting diester remains unchanged for 3 days, whereas signals of only the reaction products are observed in the PMR spectrum 15 min after the addition of phenyl isocyanate or phenyl isothiocyanate to diastereomer Ib.

The chemical shifts of the 5- and 9-H protons in the PMR spectra of VI and VII indicate their trans orientation. This was confirmed by x-ray diffraction analysis of VII, according to which the ester group and the $C_{(4)}$ atom of the imidazolidine ring are located on different sides of the thiazan ring. Consequently, diastereomer Ib, which does undergo the reaction, is the trans isomer. Chromatographic monitoring indicates the rapid formation of final products VI and VII. Intermediate products of the addition of phenyl isocyanate and phenyl isothiocyanate, viz., urea and thiourea derivatives IV and V, were not detected; this can be explained by the ease of intramolecular cyclization of the latter with the participation of the equatorially oriented methoxycarbonyl group (according to the results of x-ray diffraction analysis of VII, the methoxycarbonyl group in its molecule is pseudoaxially oriented). At the same time, monitoring of the reaction of cis isomer Ia with phenyl isocyanate and phenyl isothiocyanate by HPLC did not reveal the presence of either final products (VI, VII) or intermediates (IV, V). The different reactivities of diastereomers Ia and Ib can evidently be explained by the fact that a diequatorial orientation of the methoxycarbonyl groups is sterically suppressed in the transition state of the cis isomer, and the conformer with a diaxial orientation is destabilized because of the existence of a steric 1,3 interaction [3], which can lead to retrodecomposition to the starting components of the reaction.

The molecular and crystal structures of two-ring compound VII and the absolute configuration of the asymmetric $C_{(5)}$ and $C_{(9)}$ atoms were determined by X-ray diffraction analysis. A three-dimensional model of the VII molecule with designation of the atoms and the dihedral angles between the planar fragments of the molecule is shown in Fig. 1; the interatomic distances and the bond angles are presented in Tables 1 and 2.

As in the case of the chondrin molecule [4], the thiomorpholine ring in the VII molecule has a chair conformation. The deviations of the $S_{(7)}$ and $N_{(1)}$ atoms from the plane of the remaining four atoms of the heteroring are 0.942 Å and 0.573 Å, respectively. The imidazolidine ring is planar within the limits of 0.01 Å. Both nitrogen atoms have planar coordination. The ester group (plane V in Fig. 1) forms angles of 67.8° and 72° with the II and III planes, respectively, and is pseudoaxially oriented. The $C_{(4)}$ and $C_{(10)}$ atoms deviate 0.179 Å and 1.333 Å, respectively, to opposite sides relative to the III plane. Thus the ester group is trans oriented with respect to the $C_{(4)}$ atom. The dihedral angle between the planes of the phenyl and imidazolidine rings is 68.3°. The average value of the C—S bond lengths in the thiomorpholine ring (1.812 Å) is close to their values in the condrin molecule [4] and corresponds to the length of the C—S single bond [5]. The lengths of the C—N bonds in the thiomorpholine ring are close to the length of the C—N single bond (1.472 Å) [6]. The C—N bonds in the imidazolidine ring are sesquibonds. The shortening of the length of the $C_{(2)}=S_{(2)}$ bond (1.633 Å) as compared with its value in the thiourea and ethylenethiourea molecules (1.71 Å) [5] can also be explained by conjugation in the chain of $O_{(4)}$, $C_{(4)}$, $N_{(3)}$, $C_{(2)}$, $N_{(1)}$, and $S_{(2)}$ atoms. It is apparent from Fig. 1 that the ellipsoids of the thermal vibrations increase in the direction of the periphery of the molecule; the phenyl ring of the VII molecule participates in significant librational vibrations. The shortening of the $C_{(17)}$—$C_{(18)}$ bond (1.320 Å) of the phenyl ring can be explained by this fact, which is associated with the refinement model [6]. In the crystals the molecules are packed at distances that are no less than the sums of the van der Waals radii of the corresponding atoms [7].

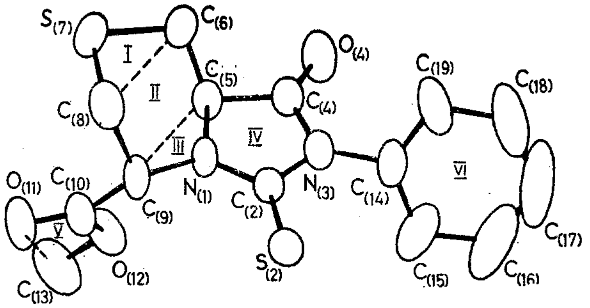

Fig. 1. Three-dimensional structure of VII. Angles between the planes: I-II 52.4°, I-III 2.6°, II-III 50.1°, II-IV 56.9°, III-IV 7.3°, II-V 67.8°, III-V 72.0°, and IV-VI 68.3°.

TABLE 1. Coordinates of the Atoms of the VII Molecule

Atom	x	y	z	Atom	x	y	z
$S_{(2)}$	0,1302 (3)	0,8157 (2)	0,48882 (8)	$C_{(17)}$	0,049 (4)	1,003 (2)	0,6921 (5)
$S_{(7)}$	−0,4983 (4)	0,9694 (3)	0,35252 (8)	$C_{(18)}$	−0,133 (3)	0,962 (2)	0,6770 (5)
$O_{(4)}$	−0,359 (1)	1,1924 (6)	0,5299 (2)	$C_{(19)}$	−0,195 (2)	0,962 (1)	0,6192 (4)
$O_{(11)}$	−0,012 (1)	0,9541 (6)	0,2829 (2)	$HC_{(5)}$	−0,26 (2)	1,20 (1)	0,405 (4)
$O_{(12)}$	0,042 (1)	1,1161 (5)	0,3494 (2)	$H_{(1)}C_{(6)}$	−0,56 (2)	0,95 (1)	0,440 (4)
$N_{(1)}$	−0,133 (1)	0,9744 (6)	0,4314 (2)	$H_{(2)}C_{(6)}$	−0,58 (2)	1,14 (1)	0,420 (4)
$N_{(3)}$	−0,118 (1)	1,0197 (6)	0,5228 (2)	$H_{(1)}C_{(8)}$	−0,37 (1)	0,755 (7)	0,390 (3)
$C_{(2)}$	−0,7040 (1)	0,9348 (7)	0,4798 (3)	$H_{(2)}C_{(8)}$	−0,30 (1)	0,777 (9)	0,324 (4)
$C_{(4)}$	−0,264 (1)	1,1105 (8)	0,5027 (3)	$HC_{(9)}$	−0,01 (1)	0,801 (8)	0,387 (3)
$C_{(5)}$	−0,282 (1)	1,0827 (8)	0,4391 (3)	$H_{(1)}C_{(13)}$	0,02 (2)	1,24 (1)	0,275 (5)
$C_{(6)}$	−0,491 (2)	1,036 (1)	0,4244 (3)	$H_{(2)}C_{(13)}$	0,21 (2)	1,179 (9)	0,280 (4)
$C_{(8)}$	−0,308 (2)	0,8386 (9)	0,3601 (3)	$H_{(3)}C_{(13)}$	0,21 (2)	1,26 (1)	0,322 (4)
$C_{(9)}$	−0,107 (1)	0,9005 (7)	0,3779 (3)	$HC_{(16)}$	0,36 (2)	1,12 (1)	0,660 (5)
$C_{(10)}$	−0,019 (2)	0,9936 (8)	0,3311 (3)	$HC_{(17)}$	0,14 (2)	1,01 (1)	0,730 (5)
$C_{(13)}$	0,122 (3)	1,208 (1)	0,3069 (6)	$HC_{(18)}$	−0,23 (2)	0,91 (1)	0,716 (5)
$C_{(14)}$	−0,057 (1)	1,0128 (8)	0,5813 (3)	$HC_{(15)}$	0,25 (2)	1,13 (1)	0,575 (4)
$C_{(15)}$	0,135 (2)	1,0541 (9)	0,5952 (4)	$HC_{(19)}$	−0,34 (1)	0,936 (9)	0,604 (3)
$C_{(16)}$	0,187 (3)	1,049 (1)	0,6530 (7)				

TABLE 2. Interatomic Distances (Å) in the VII Molecule

Bond	Length (standard deviation)	Bond	Length (standard deviation)	Bond	Length (standard deviation)
$N_{(1)}$—$C_{(2)}$	1,356 (8)	$C_{(4)}$—$C_{(5)}$	1,534 (10)	$C_{(10)}$—$O_{(12)}$	1,332 (10)
$N_{(1)}$—$C_{(5)}$	1,459 (11)	$C_{(5)}$—$C_{(6)}$	1,498 (14)	$C_{(12)}$—$C_{(13)}$	1,443 (16)
$N_{(1)}$—$C_{(9)}$	1,466 (8)	$C_{(6)}$—$S_{(7)}$	1,822 (8)	$C_{(14)}$—$C_{(15)}$	1,378 (15)
$C_{(2)}$—$S_{(2)}$	1,633 (7)	$S_{(7)}$—$C_{(8)}$	1,801 (10)	$C_{(15)}$—$C_{(16)}$	1,412 (19)
$C_{(2)}$—$N_{(3)}$	1,408 (8)	$C_{(8)}$—$C_{(9)}$	1,528 (13)	$C_{(16)}$—$C_{(17)}$	1,381 (26)
$N_{(3)}$—$C_{(4)}$	1,398 (10)	$C_{(9)}$—$C_{(10)}$	1,544 (10)	$C_{(17)}$—$C_{(18)}$	1,320 (30)
$N_{(3)}$—$C_{(14)}$	1,442 (9)	$C_{(10)}$—$O_{(11)}$	1,203 (8)	$C_{(18)}$—$C_{(19)}$	1,430 (15)
$C_{(4)}$—$O_{(4)}$	1,201 (9)				

According to x-ray diffraction analysis, the absolute configuration of the asymmetric carbon atoms in VII and, consequently, in diastereomer Ib is SS. Thus the absolute configuration of the asymmetric carbon atoms of diastereomer Ia is SR.

EXPERIMENTAL

The PMR spectra of 10% solutions of the compounds in $CDCl_3$ were recorded with a Bruker WH-90 spectrometer (90 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of suspensions of the compounds in Nujol were obtained with a UR-20 spectrometer. The mass spectrum was obtained with an MS-50 AEI spectrometer. Analytical HPLC was accomplished with an EAK chromatograph (Special Design Office of the Academy of Sciences of the Estonian SSR) with a column packed with Silasorb 7μ silica gel (250 by 5) and a refractometric Waters detector by elution with 2-propanol—hexane (1:2).

TABLE 3. Bond Angles (deg) in the VII Molecule (standard deviation in parentheses)

Angle	Bond	Angle	Bond	Angle	Bond
$N_{(1)}—C_{(2)}—N_{(3)}$	106,0 (6)	$C_{(5)}—C_{(6)}—S_{(7)}$	110,5 (6)	$C_{(10)}—O_{(12)}—C_{(13}$	116,0 (8)
$C_{(2)}—N_{(3)}—C_{(4)}$	112,4 (6)	$C_{(6)}—S_{(7)}—C_{(8)}$	98,1 (4)	$C_{(2)}—N_{(3)}—C_{(14)}$	124,3 (6)
$N_{(3)}—C_{(4)}—C_{(5)}$	106,0 (6)	$S_{(7)}—C_{(8)}—C_{(9)}$	111,3 (6)	$C_{(4)}—N_{(3)}—C_{(14)}$	123,4 (6)
$C_{(4)}—C_{(5)}—N_{(1)}$	101,4 (6)	$N_{(1)}—C_{(9)}—C_{(8)}$	109,2 (6)	$N_{(3)}—C_{(14)}—C_{(15)}$	118,4 (8)
$C_{(2)}—N_{(1)}—C_{(5)}$	114,2 (6)	$C_{(5)}—N_{(1)}—C_{(9)}$	122,8 (6)	$C_{(14)}—C_{(15)}—C_{(16)}$	116,7 (11)
$N_{(1)}—C_{(2)}—S_{(2)}$	128,8 (5)	$C_{(2)}—N_{(1)}—C_{(9)}$	122,4 (6)	$C_{(15)}—C_{(16)}—C_{(17)}$	119,8 (15)
$N_{(3)}—C_{(2)}—S_{(2)}$	125,1 (5)	$N_{(1)}—C_{(9)}—C_{(10)}$	112,1 (6)	$C_{(16)}—C_{(17)}—C_{(18)}$	121,7 (17)
$N_{(3)}—C_{(4)}—O_{(4)}$	126,9 (7)	$C_{(8)}—C_{(9)}—C_{(10)}$	111,3 (7)	$C_{(17)}—C_{(18)}—C_{(19)}$	121,4 (15)
$C_{(5)}—C_{(4)}—O_{(4)}$	127,0 (7)	$C_{(9)}—C_{(10)}—O_{(11)}$	120,5 (7)	$C_{(18)}—C_{(19)}—C_{(14)}$	115,8 (10)
$C_{(4)}—C_{(5)}—C_{(6)}$	110,7 (7)	$C_{(9)}—C_{(10)}—O_{(12)}$	114,0 (7)	$C_{(15)}—C_{(14)}—C_{(19)}$	124,4 (9)
$N_{(1)}—C_{(5)}—C_{(6)}$	112,5 (7)	$O_{(11)}—C_{(10)}—O_{(12,}$	125,5 (8)	$C_{(19)}—C_{(14)}—N_{(3)}$	117,2 (8)

For the x-ray diffraction analysis of 2-thioxo-3-phenyl-4-oxo-9-methoxycarbonyl-7-thia-1,3-diazbicyclo[3.4.0]nonane (VII) rhombic crystals with the composition $C_{14}H_{14}N_3O_3S_2$ and the following parameters were grown from ethyl acetate: a = 6.644 (1), b = 9.727 (2), c = 23.660 (4) Å, V = 1529.1 (5) Å, M 322.42, d_{calc} = 1.40 g/cm^3, μ(Cu K$_\alpha$) = 31.5 cm^{-1}, Z = 4, space group $P2_12_12_1$, and F_{000} = 672. The intensities of 1525 independent nonzero reflections were measured with a Syntex $R2_1$ diffractometer by θ/θ scanning in copper emission up to $2\theta_{max}$ = 150°. The model of the molecule was found by the direct method. The structure was refined by the method of least squares within the total-matrix approximation, anisotropically for the nonhydrogen atoms and isotropically for the hydrogen atoms up to R = 0.057. The coordinates of the atoms are presented in Table 1.

2,4-Dioxo-3-phenyl-9-methoxycarbonyl-7-thia-1,3-diazabicyclo[3.4.0]nonane (VI). A solution of 120 mg (1.0 mmole) of phenyl isocyanate in 1 ml of dry tetrahydrofuran (THF) was added dropwise with stirring at room temperature to a solution of 220 mg (1.0 mmole) of dimethyl 1,4-tetrahydrothiazine-3,5-dicarboxylate in 1 ml of dry THF. The course of the reaction was monitored by HPLC. Diastereomer IB vanished completely in the course of 15 min, after which the solvent was removed at reduced pressure. The resulting crystals were washed with cold dry ether, removed by filtration, and dried to give 200 mg (65%) of colorless crystals of VI. In the case of individual diastereomer Ib the reaction was complete after a few minutes, and a product with mp 142-143°C (from ethyl acetate) and $|\alpha|_D^{20}$ = –19.1° (c 1.13, MeOH), was obtained in 95% yield. IR spectrum: 1595 (aromatic $\nu_{C=C}$), 1718 (ring $\nu_{C=O}$), and 1740 cm^{-1} (ester $\nu_{C=O}$). PMR spectrum: 2.75 (1H, dd, J = 11.4 and 13.3 Hz, 6-H$_a$), 2.89 (1H, dd, J = 3.9 and 13.3 Hz, 8-H$_a$), 3.09 (1H, dd, J = 3.9 and 13.3 Hz, 6-H$_e$), 3.26 (1H, dd, J = 3.0 and 13.3 Hz, 8-H$_e$), 3.90 (3H, s, OMe), 4.62 (1H, dd, J = 3.9 and 11.4 Hz, 5-H$_a$), 5.33 (1H, dd, J = 3.0 and 3.9 Hz, 9-H$_e$), and 7.3-7.5 ppm (5H, m, Ph). Found: C 55.0; H 4.7; H 9.0%. $C_{14}H_{14}N_2O_4S$. Calculated: C 54.9; H 4.6; N 9.1%. M 306 (by mass spectrometry).

2-Thioxo-3-phenyl-4-oxo-9-methoxycarbonyl-7-thia-1,3-diazabicyclo[3.4.0]nonane (VII). This compound was similarly obtained in 66% yield from a mixture of the diastereomers and in quantitative yield from individual diastereomer Ib by reaction with phenyl isothiocyanate. The product had mp 190-192°C (from ethyl acetate) and $|\alpha|_D^{20}$ = –11.0° (c 1.0, MeOH). IR spectrum: 1195 ($\nu_{C=S}$), 1600 (aromatic $\nu_{C=C}$), 1735 (ring $\nu_{C=O}$), and 1746 cm^{-1} (ester $\nu_{C=O}$). PMR spectrum: 2.82 (1H, dd, J = 3.9 and 13.0 Hz, 6-H$_a$), 3.06 (1H, dd, J = 3.9 and 13.2 Hz, 8-H$_a$), 3.16 (1H, dd, J = 3.9 and 13.9 Hz, 6-H$_e$), 3.24 (1H, dd, J = 3.0 and 13.2 Hz, 8-H$_e$), 3.84 (3H, s, OMe), 4.69 (1H, dd, J = 3.9 and 11.0 Hz, 5-H$_a$), 6.11 (1H, dd, J = 3.6 and 3.0 Hz, 9-H$_e$), and 7.2-7.6 ppm (5H, m, Ph). Found: C 52.4; H 4.5; N 8.8%. $C_{14}H_{14}N_2O_3S_2$. Calculated: C 52.2; H 4.3; N 8.7%. M 322 (by mass spectrometry).

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SYNTHESIS OF PYRIDINIUM SALTS BY THE REACTION OF α, β-UNSATURATED KETONES, PRIMARY AMINES, AND COMPOUNDS WITH LABILE HYDROGEN ATOMS

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UDC 547.835.2'821.3.07

The reaction of α, β-unsaturated ketones or Mannich bases of ketones with primary aromatic amines and ketones (monoketones or dimedone) in the presence of polyhaloalkanes leads to pyridinium, 5,6,7,8-tetrahydroquinolinium, or sym-octahydroacridinium salts. The reaction of benxalcyclohexanone with primary aromatic amines and malonodinitrile makes it possible to obtain 2-amino-3-cyano-5,6,7,8-tetrahydroquinolinium salts.

Examples of the synthesis of nitrogen-unsubstituted pyridine derivatives by the reaction of α, β-unsaturated ketones with ketones and ammonia (in the form of ammonium acetate) are known [1, 2]. A similar reaction of α, β-unsaturated ketones, ammonium acetate, and malonodinitrile gives 2-amino-3-cyanopyridine derivatives [3, 4]; 2-hydroxy-3-cyanopyridine derivatives are formed when malonodinitrile is replaced by cyanoacetic ester [5]. The preparation of N-substituted pyridinium salts via analogous schemes with primary amines in place of ammonia has not been described.

It has been previously shown that the reaction of 1,5-diketones with primary amines in the presence of oxidizing agents, viz., polyhaloalkanes, leads to N-substituted pyridinium salts [6, 7]; the one-step synthesis of 4-aryl-1-R-pyridinium salts by the reaction of ketones, aromatic aldehydes, and primary amines in the presence of CCl has also been described [8, 9].

We have shown that the reaction of α, β-unsaturated ketones with primary amines and compounds with a labile hydrogen atom in the presence of an oxidizing agent, viz., carbon tetrachloride or hexachloroethane, makes it possible to obtain a number of pyridinium salts. The use of C_2Cl_6 is preparatively more convenient and gives better yields of the salts than the use of CCl_4. The corresponding N-substituted dihydropyridines (products of a reaction of the type in the Hantzsch synthesis), which are subsequently oxidized by polyhaloalkanes, are possible intermediates in the reaction.

Benzalacetophenone, benzalpinacolone, and benzalcyclohexanone were used as the α, β-unsaturated ketones. As demonstrated in the case of β-dimethylaminopropiophenone (IIIa) and 2-(α-phenylamino-benzyl)cyclohexanone (IIIb), Mannich bases can be the source of α, β-unsaturated ketones. Monoketones, dimedone, and malonodinitrile were used as compounds with a labile hydrogen atom; cyanoacetic ester does not participate in the formation of pyridinium salts. The use of aromatic primary amines gives satisfactory results. In the case of aliphatic amines (benzylamine, cyclohexylamine, and ethanolamine) pyridinium salts were obtained in insignificant amounts; nitrogen-unsubstituted pyridines with corresponding structures are formed during the reaction, most likely as a consequence of aromatization of the intermediate N-alkyl-dihydropyridines with splitting out of a hydrocarbon [10, 11]. The reaction of IIIb with cyclohexanone or malonodinitrile without the addition of an amine was also carried out; the aniline formed in the deamination of amino ketone IIIb participated in the reaction.

Far Eastern State University, Vladivostok 690652. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1060-1064, August, 1985. Original article submitted October 12, 1984.

0009-3122/85/2108-0883$09.50