passed through the contact tube in the course of 2.5 h. A total of 3.1 liters of gas was collected (at 757 mm and 28°C; H_2 81%, CH_4 16.9%, C_nH_{2n} 1.66%, and CO_2 0.43%). A total of 0.12 g of a polymer gradually precipitated as a white amorphous substance from the residue after distillation from the catalyzate of the benzene and 8.5 g of starting XXVI. The polymer decomposed at 256°C.

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THREE-DIMENSIONAL STRUCTURE OF 3-IMINOQUINUCLIDINES

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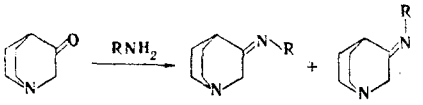
UDC 541.63:547.834.4

The syn—anti isomerism of some 3-iminoquinuclidines was studied by means of ^1H and ^{13}C NMR spectroscopy with a paramagnetic-shift reagent [Eu(DPM)$_3$]. The conformations and configurations of these compounds were established, and the differences in the free energies of the isomers and the free energies of activation of the isomerization were calculated.

In connection with the search for antihistamine preparations among quinuclidine derivatives we synthesized 3-iminoquinuclidines by reaction of 3-quinuclidone with alkyl-, aryl-, and heteroarylamines in toluene or xylene in the presence of p-toluenesulfonic acid with removal of the water by azeotropic distillation.



I R = $C_6H_4CH_3$-*m*; II R = $C_6H_4CH_3$-*p*; III R = C_6H_4Cl-*o*; IV R = C_6H_4Cl-*p*; V R = $C_6H_4COOC_2H_5$-*p*; VI R = (C_5H_4N)-α; VII R = (α'-$CH_3C_5H_3N$)-α; VIII R = (C_5H_4N)-β; IX R = $CH_2C_6H_5$; X R = CH_2CH_2OH; XI R = CH_2CH_3

Since the 3-iminoquinuclidine molecules contain an exocyclic C=N bond, one might have assumed that these compounds would exist in the form of syn and anti isomers. The present paper is devoted to the study of this isomerism and the conformations of the indicated compounds by NMR spectroscopy.

Two sets of signals — multiplets of the β protons of the quinuclidine ring at 1.7-1.9 ppm, quintets of the γ protons at 2.4-2.7 ppm, multiplets of the α protons at 2.7-3.0 ppm, and singlets of the α' protons (attached to the 2-C atom of the quinuclidine ring) at 3.0-3.6 ppm, and a multiplet of the protons of the aryl substituents at 6.5-7.5 ppm (Fig. 1a and Table 1) — are observed in the ^1H NMR spectra of I-XI recorded at room temperature. This confirms the assumption of the existence of the investigated compounds in the form of a mixture of syn and anti isomers that undergo interconversion relatively slowly. Depending on the substituents, the isomer ratio ranges from 1.2:1 to 5:1. (See scheme on following page.)

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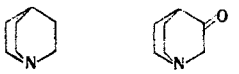
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1241-1247, September, 1978. Original article submitted December 6, 1977.



A B

A study of the ^1H NMR spectra of quinuclidine (A) and 3-quinuclidone (B) recorded in the presence of a paramagnetic-shift reagent (PSR) — tris(dipivaloylmethanato)europium [Eu(DPM)$_3$] — made it possible to conclude that the unshared pair of electrons of the nitrogen atom of the quinuclidine ring has high coordinating capacity with respect to the lanthanide ion. Thus the specific shifts (Δ_{Eu}) of the α, β, and γ protons of quinuclidine were found to be higher than the corresponding values for other tertiary amines, particularly triethylamine and pyridine:

Compound	Δ_{Eu}, ppm			Compound	Δ_{Eu}, ppm		
	α	β	γ		α	β	γ
$(CH_3CH_2)_3N$	15.3	9.0		A	37.5	14.7	14.3
C_5H_5N	26,0	9,0	8.0	B	35,3	13,5	13.5

The specific shifts of the protons of the quinuclidine ring are extremely close in the spectra of quinuclidine and 3-quinuclidone, and this indicates that coordination of the europium ion with the nitrogen atom of the quinuclidine ring clearly predominates over coordination with the oxygen atom of the carbonyl group.

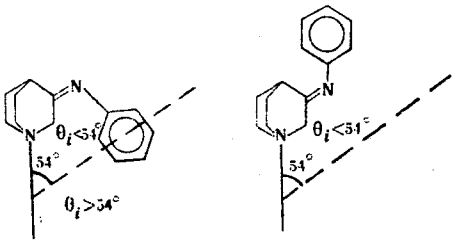
In the case of retention of the preferred coordination at the same nitrogen atom in 3-iminoquinuclidines one might have expected a different effect of the PSR on the chemical shifts of the protons of the substituent in the syn and anti isomers.

A difference of this type was actually observed (Fig. 1). Thus, as the Eu(DPM)$_3$ concentration increases, the signals of the protons of the aryl substituent of one of the isomers are shifted only to weak field, whereas those of the other isomer are shifted to both weak and strong field; the signals of the protons of the quinuclidine rings of both isomers are shifted only to weak field.

It is known [1] that in the general case the dependence of the shift of the H_i proton due to the PSR on the geometry of the molecule is expressed approximately in the form

$$\delta_i = \text{const}\frac{3\cos^2\theta_i - 1}{r_i^3}, \quad (1)$$

where r_i is the length of vector $\bar{r}_i$ between the center of the paramagnetic ion and the i ring, and θ_i is the angle between vector $\bar{r}_i$ and the major magnetic axis of the complex. According to expression (1), the sign of δ_i depends on the θ_i value and, as θ_i increases, changes from positive to negative when $\theta_i \approx 54°$.*



An examination of the molecular models of the aryliminoquinuclidines that we investigated shows that in the syn isomers of these compounds θ_i angles greater than 54° and, consequently, negative values of the specific shifts are possible for at least some of the protons of the aryl substituent, whereas in the anti isomers $\theta_i < 54°$ for all of the protons, and the expected values of the specific shifts are positive. The negative specific shifts observed

*The constant is greater than zero in the complexes with Eu(DPM)$_3$.

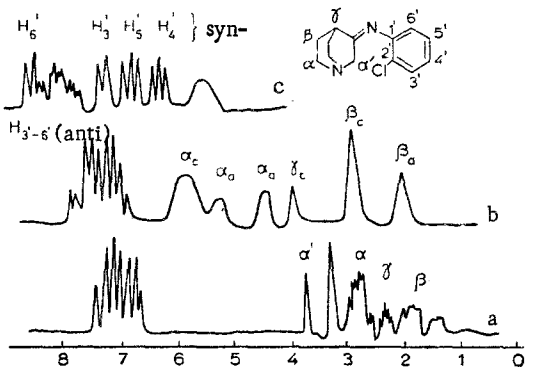


Fig. 1. ^{1}H NMR spectra of 3-(o-chlorophenyl)-iminoquinuclidine recorded with added Eu(DPM)$_3$ for ratios of the molar concentrations of the reagent and substrate (c_r/c_s) of 0.00 (a), 0.05 (b), and 0.32 (c).

TABLE 1. Chemical Shifts in the ^{1}H NMR Spectra of 3-Iminoquinuclidines (δ, ppm)

Compound	Form[a]	α	α′	β	γ	N=CH$_2$-, N=CH$_2$CH$_3$	2′	3′	4′	5′	6′
I	syn-	3,0	3,30	2,0	2,7		6,6	2,3	6,8	7,2	6,6
	anti-		3,56	1,7							
II	syn-	2,9	3,29	1,9	2,7		6,7	7,1	2,3	7,1	6,7
	anti-		3,62	1,7							
III	syn-	3,0	3,18	2,0	2,75		6,8				7,4
	anti-	2,9	3,66	1,8	2,44		6,8				7,4
IV	syn-	3,0	3,28	2,0	2,7		6,7	7,3	—	7,3	6,7
	anti-		3,58	1,8	2,7						
V	syn-	2,9	3,26	2,00	2,7		6,8	8,0	CH$_3$-1,4 CH$_2$-4,4	8,0	6,8
	anti-		3,59	1,72	2,6						
VI	syn-	3,0	3,53	2,1	2,73			8,4	6,9	7,7	6,9
	anti-		3,64	1,8	2,62						
VII	syn-	3,0	3,57	2,0	2,72			2,52	6,8	7,54	6,7
	anti-		3,64	1,8	2,61			2,57	6,8	7,51	6,53
VIII	syn-	3,0	3,29	2,0	2,7		8,1	—	8,4	7,1—7,3	
	anti-		3,62	1,8							
IX	syn-	2,9	3,50	1,9	2,6	CH$_2$-4,4, -4,6			7,3		
	anti-	2,8	3,45	1,9							
XI	syn-	2,9	3,47	1,8	2,5	CH$_3$-1,3 CH$_2$-3,2					

[a]The solvent was deuterochloroform.

TABLE 2. Specific Shifts (Δ_{Eu}, ppm) of the Protons of the Substituents of the syn Isomers of 3-Aryliminoquinuclidines

	I	II	III	IV	VI	VII
H-2′	2,6	4,4	—	5,0	—	—
H-3′	−1,4 (CH$_3$)	−0,4	−1,0	−1,0	−1,6	−4,0 (CH$_3$)
H-4′	−1,7	−2,0 (CH$_3$)	−1,8	—	−0,4	−2,0
H-5′	−1,5	−0,4	−1,2	−1,0	0,0	−1,0
H-6′	4,0	4,4	5,6	5,0	1,0	6,0

TABLE 3. Chemical Shifts of the ^{13}C Atoms of Some 3-Iminoquinuclidines (Δ_{Eu}, ppm)

Compound	Isomer[a]	α	α′	β	β′	γ	1′	2′,6′	3′,5′	4′	Others
Quinuclidine A[b]		48,7		27,7		21,9					
IV	syn	47,2	55,5	26,5	181,9[c]	35,6	149,5[d]	120,6	129,2	132,7	
	anti	47,2	59,5	26,1	181,0[c]	28,6	149,0[d]	121,1	129,0		
II	syn	47,2	55,2	27,1	177,2[c]	35,7	145,7[d]	117,2	127,3	130,2	21,3 (4′-CH_3)
	anti	47,2	59,2	26,7	176,3[c]	28,6	146,7[d]	117,6	127,1		
IX	syn	47,2	55,2[c]	26,6	178,2	35,4	140,2	127,6	128,2	126,4	53,4[c] CH_2R
	anti	47,2	59,7	25,6	177,2	26,6					54,2

[a]The solvent was deuterochloroform. [b]According to the data in [2]. [c,d]The assignment of the signals with identical letter superscripts is possibly reversible.

for the 3'-H, 4'-H, and 5'-H protons* of the aryl substituent† in the preferred isomer of 3-aryliminoquinuclidines (Table 2) therefore constitute evidence for the syn configuration of this isomer.

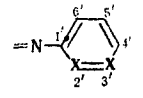
The less favorable isomer, all of the signals of the protons of which are shifted only to weak field under the influence of $Eu(DPM)_3$, is consequently the anti isomer.

The assignment of the signals to the syn and anti isomers of 3-benzyliminoquinuclidine and the independent confirmation of the preferableness of the syn isomer in 3-aryliminoquinuclidines were realized by ^{13}C NMR spectroscopy. The signals at strong field (∿ 25-60 ppm) in the spectra of both isomers of the 3-iminoquinuclidines (Table 3) belong to the carbon atoms of the quinuclidine ring; signals of the imine atoms of the 3-C carbon atom are observed at weak field (∿ 180 ppm). The assignment of the signals of the α and β carbon atoms of the unsubstituted bridges of the quinuclidine ring follows unambiguously from a comparison of the ^{13}C NMR spectra of 3-iminoquinuclidines with one another and with the spectrum of unsubstituted quinuclidine [2]. The signals of the carbon atoms in the γ (4-C) and α' (2-C) positions of the substituted bridge of 3-iminoquinuclidines are shifted to weak field relative to the corresponding signals in unsubstituted quinuclidine because of the deshielding effect of the adjacent C=N bond.

A characteristic feature of the ^{13}C NMR spectra of 3-iminoquinuclidines is a significant difference in the chemical shifts of the 2-C and 4-C atoms of the quinuclidine ring in the syn and anti isomers. Considering the similarity in the electronic effects in the geometrical isomers of the investigated compounds, the indicated difference can be explained by steric effects. In particular, it is known that a carbon atom that experiences the effect of the closeness of other atoms gives resonance at stronger field than structurally unhindered carbon atoms [3].

An examination of the molecular models of the syn and anti isomers of iminoquinuclidines makes it possible to conclude that a substituent will give rise to steric hindrance of the 2-C atom in the syn isomer and the 4-C atom in the anti isomer. The 2-C and 4-C signals, which are found at relatively stronger field, should therefore be assigned to, respectively, the syn and anti isomers. A comparison of the intensities of these signals for the two iso-

*In the present paper for convenience we used the numbering of the carbon atoms and the aromatic substituent protons attached to them in which the carbon atom bonded directly or through the CH_2 group to the nitrogen atom of the imino group is designated C'_1, regardless of whether the substituent is a phenyl ring or a pyridine ring.



X = C—H; N

†Or the protons of the methyl group in these positions.

TABLE 4. Difference in the Chemical Shifts of the Methylene Protons in the 2 Position of the Quinuclidine Ring in the syn and anti Isomers ($\Delta\delta = \delta_{anti} - \delta_{syn}$), Isomer Ratios ($C_{syn}/C_{anti}$), Differences in the Free Energies of the Isomers (ΔG), and Free Energies of Activation of the Isomerization (ΔG^*) of 3-Aryliminoquinuclidines and 3-Benzyliminoquinuclidine

	I	II	III	IV	VI	VII	VIII	IX
$\Delta\delta_{CH_2}$, ppm	0,26	0,24	0,46	0,31	0,09	0,12	0,32	0.05
C_{syn}/C_{anti}	1,32	1,27	1,9	1,25	2,07	2,41	1,1	4,7
ΔG, kcal/mole	0,17	0,15	0,39	0,13	0,43	0,53	0,06	0,93
ΔG^*, kcal/mole	20,6	20,9	19,2	20,3	18,7	18,9	19,6	>25.0

TABLE 5. 3-Iminoquinuclidine Derivatives

Compound	bp, °C (mm)	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
I	128—129 (1)	78,6	8,5	13,1	$C_{14}H_{18}N_2$	78,5	8,4	13,1	56
II	148—150 (2)	78,8	8,6	13,0	$C_{14}H_{18}N_2$	78,5	8,4	13,1	63
III	130—132 (0,6)	66,5	6,5	11,9	$C_{13}H_{17}ClN_2$	66,5	6,4	11,9	50
IV	—[a]	66,4	6,3	11,9	$C_{13}H_{17}ClN_2$	66,5	6,4	11,9	71
V	171—173 (1)	70,4	7,3	10,3	$C_{16}H_{20}N_2O_2$	70,6	7,4	10,3	54
VI	—[b]	71,5	7,4	21,0	$C_{12}H_{15}N_3$	71,6	7,5	20,9	71
VII	134—136 (0,8)	72,2	7,9	—	$C_{13}H_{17}N_3$	72,5	7,9	—	37
VIII	129—131 (0,5)	71,1	7,4	20,7	$C_{12}H_{15}N_3$	71,6	7,5	20,9	63
IX	142—143 (1)	78,7	8,5	13,4	$C_{14}H_{18}N_2$	78,5	8,4	13,1	87
X	105—107 (1,5)	64,3	9,6	17,0	$C_9H_{16}N_2O$	64,3	9,6	16,7	83
XI	119—120 (10)	70,7	10,4	—	$C_9H_{16}N_2$	71,0	10,6	—	75

[a]This compound had mp 81-83°C (from heptane). [b]This compound had mp 90-92°C (from heptane).

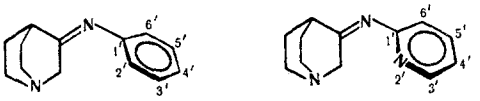
mers indicates that the syn isomer is preferred in both 3-benzyliminoquinuclidine and 3-aryliminoquinuclidines. For the latter this is in complete agreement with the above ^1H NMR spectral data recorded with shift reagents.

We also used the PMR spectra to establish the conformations of the investigated 3-iminoquinuclidines. It follows from Table 4 that the signals of the protons attached to 2-C in the syn isomers of 3-phenyl- and 3-(β-pyridyl)iminoquinuclidines are shifted appreciably to strong field (0.24-0.46 ppm) as compared with the signals of the anti isomers. This constitutes evidence for their location in the region of shielding by the aryl rings.

It follows from an examination of molecular models that this sort of shielding effect is possible only in the case of considerable noncoplanarity of the aryl rings and the C=N bond. The angle of rotation of the phenyl ring relative to the plane of the C=N bond is particularly large (close to 90°) for 3-(o-chlorophenyl)iminoquinuclidine, as indicated by the very large $\Delta\delta_{CH_2}$ value and the virtually equal values of the specific shifts of the 3'-H and 5'-H protons, which are symmetrical relative to the axis of rotation of the ring. This conformation of the substituent in the syn isomers of 3-phenyl-substituted iminoquinuclidines is evidently due to the closeness of the 2' and 6' protons (or other residues) of the aryl substituent and the protons attached to the 2-C atom of the quinuclidine ring.

The difference in the chemical shifts of the protons attached to 2-C is considerably less for 3-(α-pyridyl)iminoquinuclidines than for other 3-aryliminoquinuclidines and amounts to ∿ 0.09-0.12 ppm. This can be explained by a decrease in the angle of rotation of the pyridine ring relative to the plane of the C=N bond (the plane of the 3-C=N—C atoms). In this connection, the existence of two energetically nonequivalent conformations of the heteroatomic ring relative to the 1'-C—4'-C axis with different orientations of the pyridine nitrogen atom relative to the quinuclidine ring becomes possible.

An analysis of the specific shifts of the protons of the substituent in these compounds (Table 2) confirms the assumption advanced above and shows that the conformer in which 3'-H and, consequently, the pyridine nitrogen atom are drawn close to the quinuclidine ring is more favorable. In fact, the specific shifts of the 3'-H and 5'-H protons of 3-(α-pyridyl)-iminoquinuclidine, which are symmetrical relative to the axis of rotation of the 1'-C—4'-C bond, are, respectively, −1.6 ppm (3'-H) and 0.0 ppm (5'-H), i.e., 3'-H is found at a greater angle relative to the axis of the complex. An analysis of the specific shifts for the corresponding α-methyl derivative also gives similar results.



The indicated conformation is preferred, probably because of the smaller interactions of the protons attached to 2-C of the quinuclidine ring with the unshared pair of electrons of the nitrogen atom than with the proton in the 3' position of the pyridine substituent. The $\Delta\delta_{CH_2}$ value for the remaining 3-aryliminoquinuclidines, which is intermediate between the values for 3-(α-pyridyl)iminoquinuclidine and 3-(o-chlorophenyl)iminoquinuclidine, probably indicates an intermediate value for the angle of rotation of the aromatic ring of the substituent relative to the plane of the C=N bond.

Changes that attest to an increase in the rate of syn and anti isomerization are observed in the PMR spectra of 3-iminoquinuclidines recorded as the temperature is raised: the signals become broader, coalesce, and merge.* The ratio of the intensities of the sets of signals remained identical before and after heating, and the isomer ratios found from the PMR spectra therefore correspond to the thermodynamic equilibrium (Table 4).

The differences in the free energies (ΔG), which characterize the energetic advantageousness of the syn isomer as compared with the anti isomer, were determined from the ratio of the isomers. An examination of the molecular models shows makes it possible to conclude that pronounced overlapping of the van der Waals radii of the H atom attached to 4-C and the first carbon atom of the substituent exists in the anti isomers of 3-iminoquinuclidines because of the coplanarity of the proton attached to 4-C and the 3-C=N—1'-C grouping. Overlapping of the van der Waals radii and steric strain are less in the syn isomers, in which the protons attached to 2-C are remote from the plane of the double bond.

Steric interactions are particularly strong in the anti isomer of 3-benzyliminoquinuclidine, in which the proton attacted to 4-C and one of the protons of the CH_2 group of the benzyl substituent are coplanar. This leads to a significant decrease in the relative concentration of the anti isomer and to an appreciable strong-field shift of the 4-C signal in the ^{13}C NMR spectra of the anti isomer of 3-benzyliminoquinuclidine as compared with the anti isomers of 3-aryliminoquinuclidines.

The calculated energy of activation of isomerization (ΔG*) [4] also is a maximum for 3-benzyliminoquinuclidine, in which delocalization of the electrons is absent, and the order of the C=N bond is a maximum. Conjugation of the π electrons of the C=N bond with the phenyl ring leads to a decrease in the order of this bond, and, correspondingly, to a decrease in the energy of activation. The greater coplanarity of the heteraryl ring and the C=N bond in 3-(α-pyridyl)iminoquinuclidine is responsible for further delocalization of the electrons of the C=N bond, the decrease in its order, and the lowering of the barrier to syn—anti isomerization.

EXPERIMENTAL

The ^1H NMR spectra were recorded with a JNM-4H-100 spectrometer. Deuterochloroform and d_5-bromobenzene were used as the solvents, and tetramethylsilane was the internal standard. The chemical shifts and the specific shifts of the protons were determined from spectra recorded at a sample temperature of ∿ 22°C. The temperature measurements were made in d_5-bromobenzene at 22-160°C (with hexamethyldisiloxane as the internal standard, δ = 0.05 ppm). The specific shifts were determined by the method described in [5]. The ^{13}C NMR spectra were recorded with WP-60 and CFT-20 spectrometers. Chloroform was used as the solvent and

*In the case of 3-benzyliminoquinuclidine only a certain broadening of the signals was observed even in the case of the maximum temperature of ∿ 170°C.

the internal standard (δ = 76.9 ppm). The spectra were recorded at a sample temperature of 50°C with complete suppression of the spin—spin coupling with the protons.

3-(p-Chlorophenyl)iminoquinuclidine (IV). A mixture of 12.5 g (0.1 mole) of 3-quinuclidone, 12.75 g (0.1 mole) of 4-chloroaniline, and 150 ml of toluene was heated in the presence of a catalytic amount of p-toluenesulfonic acid in a Dean—Stark apparatus until the liberation of water ceased (10-12 h). The reaction mixture was then treated with charcoal, and the toluene was removed by distillation. The residue was fractionated in vacuo at 2 mm. Two fractions were collected: the first fraction had bp 84-132°C (1.8 g), and the second fraction had bp 162-163°C (16.65 g). The second fraction was identified as IV. Redistillation of the first fraction gave 0.8 g of a product with bp 118-119°C (25 mm), which was identified as an azeotropic mixture of the starting components in an equimolar ratio. Found: C 61.9; H 6.7; Cl 14.3; N 11.1%. $C_7H_{11}NO + C_6H_6ClN$. Calculated: C 61.8; H 6.7; Cl 14.1; N 11.1%.

An azeotropic mixture of the above composition was also obtained by distillation of equimolar amounts of 3-quinuclidone and 4-chloroaniline.

The formation of azeotropic mixtures was also observed in the preparation of azomethines I and VI-VIII. Compounds I-III and VI-XI were synthesized by the method used to prepare IV (see Table 5).

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REACTION OF 2,3-DIOXO-4-(N,N-DIMETHYLAMINOMETHYLENE)HEXAHYDROAZEPINE WITH HYDRAZINE AND ITS DERIVATIVES*

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UDC 547.779.1'891

8-Oxo-8H-4,5,6,7-tetrahydropyrazolo[5,4-c]azepine and a mixture of 2-phenyl-8-oxo-8H-4,5,6,7-tetrahydro[3,4-c]azepine and 2,3-dioxo-4-formylhexahydroazepine 4-phenylhydrazone were obtained in the reactions of 2,3-dioxo-4-(N,N-dimethylaminomethylene)-hexahydroazepine with hydrazine and phenylhydrazine, respectively. Cyclization of 2,3-dioxo-4-formylhexahydroazepine 4-phenylhydrazone gave 1-phenyl-8-oxo-8H-4,5,6,7-tetrahydropyrazolo[5,4-c]azepine. The reaction of 2,3-dioxo-4-(N,N-dimethylaminomethylene)hexahydroazepine with semicarbazide and thiosemicarbazide gives 2,3-dioxo-4-formylhexahydroazepine 4-semicarbazone and 4-thiosemicarbazone.

In order to synthesize some condensed heterocyclic compounds, in the present research we studied the reactions of 2,3-dioxo-4-(N,N-dimethylaminomethylene)hexahydroazepine (I) [2] with hydrazine and its derivatives — phenylhydrazine, thiosemicarbazide, and semicarbazide.

The reaction of enamino ketone I with hydrazine leads to the formation of pyrazole II in close to quantitative yield. The reaction of enamino ketone I with phenylhydrazine proceeds

*Communication XXX from the series "Research on Lactams." See [1] for communication XXIX.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1248-1251, September, 1978. Original article submitted October 25, 1977.