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DERIVATIVES OF HETEROCYCLIC α-IMINOCARBOXYLIC ACIDS

2.* CONVERSION OF HYDRAZIDES OF HETEROCYCLIC α-IMINOCARBOXYLIC ACIDS INTO CONDENSED BICYCLIC SYSTEMS

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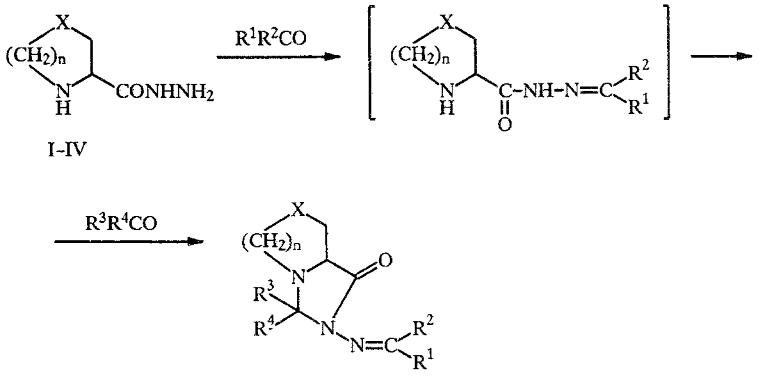
By the interaction of hydrazides of L-proline, L-thioproline, pipecolic acid, and tetrahydro-1,4-thiazine-3-carboxylic acid with an excess of a carbonyl compound, through a stage of hydrazone formation, the following compounds have been obtained: 2,3-substituted 1,3-diazabicyclo[3.3.0]octan-4-ones; 7,8-substituted 7-thia-1,7-diazabicyclo[3.3.0]octan-6-ones; and 8,9-substituted diazabicyclo[4.3.0]nonan-7-ones. Preferential trans-linkage of the rings is characteristic for these heterocycles in solutions; if the substitution is asymmetric, the E-isomers are predominant.

In an earlier communication [1] we showed that the interaction of hydrazides of five- and six-membered heterocyclic α-iminocarboxylic acids with equimolar quantities of carbonyl compounds results in the formation of the corresponding hydrazones.



I-IV

V-XXV

V—IX n = 1, X = CH_2; V $R^1 = R^2 = R^3 = R^4$ = Me; VI $R^1 = C_6H_5$, $R^2 = R^3 = R^4$ = Me; VII $R^1 = R^3$ = phenyl-2-, $R^2 = R^4$ = H; VIII $R^1 = R^3$ = 5-methylphenyl, $R^2 = R^4$ = H; IX $R^1 = R^3$ = p-MeO-C_6H_4, $R^2 = R^4$ = H; X—XV n = 1, X = S; X $R^1 = R^3 = C_6H_5$, $R^2 = R^4$ = H; XI $R^1 = R^3$ = p-Me-C_6H_4, $R^2 = R^4$ = H; XII $R^1 = R^3$ = p-MeO-C_6H_4, $R^2 = R^4$ = H; XIII $R^1 = R^3$ = phenyl2-, $R^2 = R^4$ = H; XIV $R^1 = R^3$ = 5-methyl.phenyl 2-, $R^2 = R^4$ = H; XV $R^1 + R^2 = R^3 + R^4$ = —$(CH_2)_5$—; XVI—XIX n = 2, X = CH_2; XVI $R^1 = R^2 = R^3 = R^4$ = Me; XVII $R^1 = R^3$ = p—MeO—C_6H_4, $R^2 = R^4$ = H; XVIII $R^1 = R^3$ = 2-phenyl, $R^2 = R^4$ = H; XIX $R^1 = R^3$ = 5-methylphenyl, $R^2 = R^4$ = H; XX—XXV n = 2, X = S; XX $R^1 = R^2 = R^3 = R^4$ = Me; XXI $R^1 = R^2 = R^3$ = Me, R^4 = H; XXII $R^1 = R^2$ = Me, $R^3 = R^4$ = H; XXIII $R^1 = R^3$ = Me; $R^2 = R^4$ = H; XXIV $R^1 = R^2$ = Me, $R^3 = C_6H_5$, R^4 = H; XXV $R^1 = R^3 = C_6H_5$, $R^2 = R^4$ = H

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*For Communication 1 see [1].

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TABLE 1. Characteristics of 4-Oxo-1,3-diazabicyclo[3.3.0]octanes (V-IX), 6-Oxo-3-thia-1,3-diazabicyclo[3.3.0]octanes (X-XV), 7-Oxo-1,8-diazabicyclo[4.3.0]nonanes (XVI-XIX), and 7-Oxo-4-thia-1,8-diazabicyclo[4.3.0]nonanes (XX-XXV)

Compound	Empirical formula	mp, °C	$M^{+\cdot}$	IR spectrum (cm^{-1})		Yield, %
				$\nu_{C=N}$	$\nu_{C=O}$	
V	$C_{11}H_{19}N_3O$	47...48	209	1640	1716	96
VI	$C_{15}H_{15}N_3O_3$	170...172	285	1642	1700	98
VII	$C_{17}H_{19}N_3O_3$	183...185	313	1630	1710	95
VIII	$C_{16}H_{20}N_3O$	154...156	270	1635	1712	92
IX	$C_{21}H_{23}N_3O_3$	110...112	365	1632	1718	95
X	$C_{18}H_{17}N_3OS$	137...138	223	1632	1710	95
XI	$C_{20}H_{21}N_3OS$	182...183	352	1628	1720	100
XII	$C_{20}H_{21}N_3O_3S$	168...170	383	1640	1698	94
XIII	$C_{14}H_{13}N_3O_3S$	132...133	303	1638	1714	95
XIV	$C_{16}H_{17}N_3O_3S$	144...146	331	1632	1718	90
XV	$C_{16}H_{25}N_3OS$	95...97	307	1620	1730	80
XVI	$C_{12}H_{21}N_3O$	88...89	223	1642	1716	98
XVII	$C_{22}H_{25}N_3O_3$	121...123	379	1635	1710	95
XVIII	$C_{16}H_{17}N_3O_3$	158...159	299	1630	1700	94
XIX	$C_{18}H_{21}N_3O_3$	161...162	327	1636	1718	100
XX	$C_{11}H_{19}N_3OS$	103...104	241	1640	1695	90
XXI	$C_{10}H_{17}N_3OS$	127...128	227	1620	1696	97
XXII	$C_9H_{15}N_3OS$	76...78	213	1642	1706	94
XXIII	$C_9H_{15}N_3OS$	108...109	213	1628	1718	91
XXIV	$C_{19}H_{19}N_3OS$	130...131	337	1630	1712	96
XXV	$C_{15}H_{19}N_3OS$	177...178	289	1632	1710	95

Previously, however, in the reaction of the hydrazide of aziridine-2-carboxylic acid with excess aldehyde or ketone, 1,3,4-triazabicyclo[4.1.0]heptan-5-ones were obtained [2, 3]. One of us had reported that in an analogous reaction, from the hydrazide of 1,4-thiazinecarboxylic acid and acetone, or in the reaction of the isopropylidene derivative of the acid and benzaldehyde, derivatives of 7-oxa-4-thia-1,8-diazabicyclo[4.3.0]nonane can be obtained [4]. We have now investigated in more detail the applicability of this condensation to the synthesis of a number of condensed heterosystems. And indeed, through the interaction of an excess of the carbonyl component with hydrazides of proline (I), thioproline (II), pipecolic acid (III), or thiazanecarboxylic acid (IV), the expected condensed heterocycles V-XXV are formed. This reaction proceeds through a stage of hydrazone formation [1], the hydrazone subsequently reacting with the next molecule of aldehyde or ketone.

Thus, we obtain 2,3-substituted 1,3-diazabicyclo[3.3.0]octan-4-ones (V-IX), 7,8-substituted 3-thia-1,7-diazabicyclo[3.3.0]octan-6-ones (X-XV), 8,9-substituted 1,8-diazabicyclo[4.3.0]nonan-7-ones (XVI-XIX), and 8,9-substituted 4-thia-1,8-diazabicyclo[4.3.0]nonan-7-ones (XX-XXV), consisting of condensed rings of the corresponding cyclic imino acids and 1,3-imidazolidine (Tables 1-3).

In the case of acetophenone, however, the reaction stops in the stage of formation of the corresponding hydrazone. The structures of the bicyclics V-XXV were confirmed by a combination of spectroscopic data. In particular, the presence of absorption bands at 1700-1710 cm^{-1}, which are characteristic for cyclic hydrazides, together with the nonequivalence of signals in the PMR spectra from identical substituents of the imidazolidine ring in comparison with those in the hydrazone fragment, confirms the presence of a condensed ring system in these structures.

The structure of the bicyclics V-XXV suggests the possible existence of several types of isomerism: cis–trans linking of the heterocycles with each other [5, 7], Z,E isomerism relative to the C=N azomethine bond (when $R^1 \neq R^2$), and optical isomerism when $R^3 \neq R^4$. However, the PMR spectra of the asymmetric bicyclics XXI, XXIV, and XXV do not exhibit the signals that would be expected with different orientations of the substituents (Z- or E-orientation) relative to the azomethine bond. We can conclude tentatively that these compounds exist exclusively in the E-form. The measured values of the SSCC between protons of the six-membered ring show very little difference among all of the bicyclics XX-XXV, indicating a similar conformation of the heterocycle in their molecules.

Values calculated by the K-factor method [8] for the $S-C_{(5)}-C_{(6)}-N$ dihedral angles are $60 \pm 2°$ for all of the compounds. Judging from the values of the SSCC between the $C_{(6)}H$ and $C_{(5)}H_2$ protons, the $C_{(6)}-C=O$ bond in the tetrahydrothiazine ring is equatorially oriented.

TABLE 2. PMR Spectra of 1,3-Diazabicyclo[3.3.0]octan-4-ones (V-IX), 3-Thia-1,7-diazabicyclo[3.3.0]octan-6-ones (X-XV), and 1,8-Diazabicyclo[4.3.0]nonan-6-ones (XVI-XIX), in $CDCl_3$

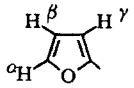
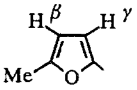
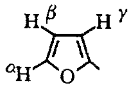
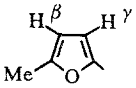
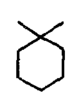
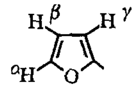
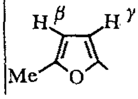
Compound	Chemical shift, δ, ppm						
	of protons of substituents in imidazolidine ring						of protons of condensed ring
	$R^1 = R^3$	$R^2=R^4$	H_{R1}	H_{R2}	H_{R3}	H_{R4}	
1	2	3	4	5	6	7	8
V	CH_3	CH_3	1,87	2,13	1,33	1,56	1,90...2,66(4H, m, β-CH_2 & γ-CH_2), 3,00(2H, m, δ-CH_2), 3,86(1H,q, α-CH)
VI	C_6H_5	CH_3	7,2...7,6	2,21	1,37	1,64	1,93(2H, m, γ-CH_2), 2,73(2H, м, β-CH_2), 3,02(2H, m, δ-CH_2), 3,96(1H, q., α-CH)
VII	 	H	6,48(Hβ) 6,75(Hγ) 7,44(Hα)	9,00	6,37(Hβ) 6,51(Hγ) 6,71(Hα	5,62	1,75...2,28(2H, m, γ-CH_2), 2,77(2H, m, β-CH_2), 2,42(2H, m, δ-CH_2), 4,08(1H,t, α-CH)
VIII	 	H	2,33(CH_3) 6,20(Hβ) 6,44(Hγ)	8,56	2,26(CH_3) 5,91(Hβ) 6,02(Hγ)	5,55	1,77...2,17(2H, m, γ-CH_2), 2,8(2H, m β-CH_2), 3,37(2H, m, δ-CH_2), 4,11(1H,t, α-CH)
IX	p-MeO-C_6H_5	H	3,76(OCH_3) 6,82...7,53	8,00	3,76(OCH_3) 6,82...7,53	5,51	1,73...2,31(2H,m, γ-CH_2), 2,84(2H, m, β-CH_2), 3,40(2H, m, δ-CH_2), 3,98(1H,t, α-CH)
X	C_6H_5	H	7,2...7,5	8,10	7,2...7,5	5,40	3,08(β-CH_a), 3,35(β-CH_e), 4,48(δ-CH_a), 4,50(α-CH), 5,36(δ-CH_e)
XI	p-Me-C_6H_4	H	2,30(CH_3) 7,3...7,7	8,15	2,30(CH_3) 7,3...7,7	5,80	3,16(β-CH_a), 3,41(β-CH_e), 4,49(δ-CH_a), 4,67(α-CH), 5,45(δ-CH_e)
XII	p-MeO-C_6H_4	H	3,81(OCH_3) 7,0...7,5	8,10	3,81(OCH_3) 7,0...7,5	5,76	3,20(β-CH_a), 3,41(β-CH_e), 4,60(δ-CH_a), 4,65(α-CH), 5,58(δ-CH_e)
XIII	 	H	6,50(Hβ) 6,81 (Hγ) 7,60 (Hα)	9,03	6,41(Hβ) 6,59(Hγ) 6,75(Hα)	5,71	3,15(β-CH_a), 3,48(β-CH_e), 4,47(δ-CH_a(, 4,71(α-CH), 5,50(δ-CH_e)
XIV	 	H	2,30(CH_3) 6,20(Hα) 6,55(Hβ)	8,41	2,30(CH_3) 5,96(Hα) 6,10(Hβ)	5,62	3,19(β-CH_a), 3,47(β-CH_e), 4,58(δ-CH_a), 4,70(α-CH), 5,36(δ-CH_e)

TABLE 2. (Continued)

1	2	3	4	5	6	7	8
XV		H	1,42...1,48		1,42...1,48		3,20(β-CH$_a$), 3,41(β-CH$_e$), 5,50(δ-CH$_a$), 4,69(α-CH), 5,42(δ-CH$_e$)
XVI	CH_3	CH_3	1,90	2,15	1,38	1,61	1,20...3,48 (9H, m)
XVII	p-MeO-C_6H_4	H	3,80(OCH_3) 7,2...7,6	8,12	3,80(OCH_3) 7,2...7,6	5,63	1,51...4,0 (9H, m)
XVIII		H	6,42(Hβ) 6,70(Hγ) 7,64(Hα)	8,87	6,31(Hβ) 6,40(Hγ) 6,60(Hα)	5,50	1,24...3,56 (9H, m)
XIX		H	2,38(CH_3) 6,10(Hα) 6,51(Hβ)	8,65	2,32(CH_3) 5,90(Hα) 6,00(Hβ)	5,55	1,28...3,50 (9H, m)

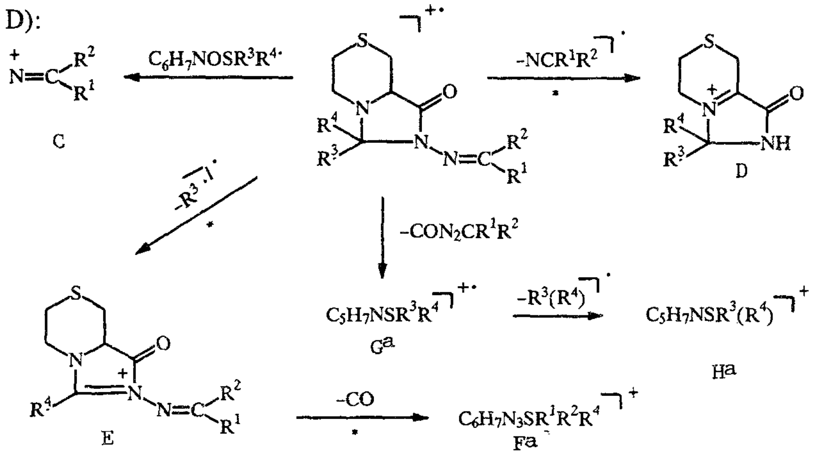
The large value of the SSCC (J for $H_R{}^3H_R{}^5$ = 4.3 Hz) in compound XXII, according to [9, 10] indicates preferential trans-linking of the two rings in solutions.

However, the very slight differences in values of the SSCC in the PMR spectra for the bicyclics XXI and XXIII-XXV, which are unsymmetrically substituted in position 9, are not in themselves a sufficient basis for any reasonably reliable assignment of the signals to cis- or trans-linking; hence we are unable to establish the configuration of these compounds. Certain differences are observed only for the long-range SSCC $C_{(9)}H-C_{(6)}H$ (Table 3).

One of us had previously accomplished the separation of 8-(N-benzylideneamino(9-phenyl-7-oxo-4-thia-1,8-diazabicyclo[4.3.0]nonane (XXV) into isomers with respect to the asymmetric atom $C_{(9)}$, by means of high-performance liquid chromatography [4]. The chromatographic data indicated that the ratios of isomers were XXIVa:XXIVb = 15:1 and XXVa:XXVb = 10:1, values very close to those determined from the signal intensities for the R^3 and R^4 groups in the PMR spectra of these compounds.

Previously, x-ray structure analysis was used to investigate the molecular and crystal structure of the predominant isomer of 8-(N-isopropylideneamino)-9-phenyl-7-oxo-4-thia-1,8-diazabicyclo[4.3.0] nonane (XXIVa), and also, for comparison, structure of 9,9-dimethyl-3-(N-isopropylideneamino)-7-oxo-4-thia-1,8-diazabicyclo[4.3.0]nonane (XX). As a result it was established that the bicyclics XXIVa and XXV are trans-linked and that the tetrahydrothiazine ring in these molecules has the chair conformation, the imidazolidine fragment the half-chair conformation. It is characteristic that the isomer of the bicyclic XXIVa, the same as for compounds XXI, XXIII, and XXV, has a large value of the long-range SSCC in the PMR spectra. Therefore, for bicyclics XXIVb and XXVb, which have small values of the long-range SSCC, we have assigned the cis-structure.

The mass spectra of the bicyclics XX-XXV are characterized by medium-intensity molecular ions (Table 4). In the decomposition of the molecular ions, in general, three parallel processes are observed. One of them is homolytic cleavage of the N–N bond of the hydrazine fragment with localization of the charge on one of the parts of the original ion (preferential formation of cation C or D):



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*Decomposition paths were confirmed by metastable transitions. The compositions of the ions that are denoted by the superscript "a" were established with high resolution.

TABLE 3. Parameters of PMR Spectra of 4-Thia-1,8-diazabicyclo[4.3.0]nonan-7-thiones (XX-XXV), in $CDCl_3$

Compound	Chemical shift, δ, ppm								Spin-spin coupling constants, J. Hz						
	H_2	H_3	H_5	H_6	R^1	R^2	R^3	R^4	$J_{H_2H_2}$	$J_{H_2H_3}$	$J_{H_3H_3}$	$J_{H_{2e}H_{6e}}$	$J_{H_5H_5}$	$J_{H_5H_6}$	$J_{H_9H_6}$
XX	3,20(*e*) 3,70(*a*)	2,93(*a*) 2,51(*e*)	2,87(*e*) 2,71(*a*)	3,27	2,14	1,91	1,35	1,24	11,0	11,3(*aa*) 3,0(*ee*) 3,0(2*e*3*a*) 2,2(2*a*3*e*)	12,9	1,0	12,2	10,5(*aa*) 2,5(*ee*)	—
XXI	3,36(*e*) 2,55(*a*)	2,98(*a*) 2,53(*e*)	2,87(*e*) 2,77(*a*)	3,10	2,13	1,97	1,15	4,23	10,8	11,4(*aa*) 2,8(*ee*) 3,0(3*a*2*e*) 2,9(2*a*3*e*)	13,6	1,6	12,7	10,4(*aa*) 2,4(*ee*)	2,0
XXII	3,25(*e*) 2,73(*a*)	2,98(*a*) 2,50(*e*)	2,83(*e*) 2,78(*a*)	3,13	2,15	1,98	4,32	4,19	11,1	11,1(*aa*) 2,6(*ee*) 3,2(3a2e) 2,6(2*a*3*e*)	13,1	1,2	12,6	9,5(*aa*) 3,2(*ee*)	2,3
XXIII	3,33(*e*) 2,51(*a*)	2,95(*a*) 2,50(*e*)	2,83(*e*) 2,75(*a*)	3,06	2,02	8,58	1,35	4,16	11,0	11,3(*aa*) 3,0(*ee*) 3,0(2*e*3*a*) 2,2(2*a*3*e*)	12,9	1,0	12,2	10,5(*aa*) 2,5(*ee*)	2,0
XXIVa	2,99(*e*) 2,61(*a*)	2,86(*a*) 2,42(*e*)	2,96(*e*) 2,90(*a*)	3,30	1,94	1,85	7,35...7,45	5,0	11,1	11,1(*aa*) 3,0(*ee*) 3,3(3*a*2*e*) 2,9(2*a*3*e*)	13,2	1,5	12,2	10,0(*aa*) 2,9(*ae*)	2,2
XXIVb	2,96(*e*) 2,71(*a*)	2,86(*a*) 2,22(*e*)	2,80(*e*) 2,84(*a*)	3,38	1,99	1,90	5,56	7,3...7,4	12,7	11,7(*aa*) 2,7(*ee*) 2,8(3*a*2*e*) 2,5(2*a*3*e*)	13,2	1,8	13,1	11,0(*aa*) 3,3(*ae*)	1,7
XXVa	3,05(*e*) 2,63(*a*)	2,87(*a*) 2,42(*e*)	2,98(*e*) 2,93(*a*)	3,38	7,50(H_o) 7,39($H_{m,p}$)	9,17	7,48(H_o) 7,30($H_{m,p}$)	5,13	10,9	11,2(*aa*) 3,0(*ee*) 3,2(3*a*2*e*) 2,3(2*a*3*e*)	13,2	1,1	12,6	8,9(*aa*) 3,9(*ae*)	2,1
XXVb	3,05(*e*) 2,30(*a*)	2,94(*a*) 2,35(*e*)	2,89(*e*) 2,85(*a*)	3,71	7,58(H_o) 7,3($H_{m,p}$)	8,37	5,79	7,42(H_o) 7,3($H_{m,p}$)	11,5	11,8(aa) 2,7(ee) 3,2(3a2e) 2,3(2a3e)	13,3	1,0	12,6	9,7(*aa*) 3,6(*ae*)	1,2

TABLE 4. Characteristic Ions of Mass Spectra of 7-Oxo-4-thia-1,8-diazabicyclo-[4.3.0]nonanes (XX-XXV)

Compound	R^1	R^2	R^3	R^4	$M^{+\cdot}$	m/z (and intensity, in % of maximum ion)					
						C	D	E	F	G	H
XX	CH_3	CH_3	CH_3	CH_3	241 (16)	56 (54)	185 (1)	226 (100)	198 (7)	143 (7)	128 (13)
XXI	CH_3	CH_3	CH_3	H	227 (25)	56 (78)	171 (14)	212 (100)	184 (11)	129 (39)	144 (94)
XXII	CH_3	CH_3	H	H	213 (30)	56 (27)	157 (100)	212 (3)	184 (2)	115 (73)	114 (23)
XXIII	CH_3	H	CH_3	H	213 (20)	42 (48)	171 (18)	198 (100)	170 (28)	129 (10)	114 (20)
XXIV	C_6H_5	H	C_6H_5	H	337 (35)	104 (46)	223 (32)	260 (23)	232 (11)	191 (61)	190 (100)
XXV	CH_3	CH_3	C_6H_5	H	289 (40)	56 (32)	233 (30)	212 (17)	184 (5)	191 (89)	190 (100)

The second characteristic process of molecular ion decomposition is elimination of the substituent from position 9 in the form of a radical. The formation of the ion F^a with subsequent breakdown of the five-membered ring through ejection of a CO molecule is confirmed by the presence of the corresponding metastable peaks and by high-resolution determination of the elemental composition of the final fragment.

As the third path of molecular ion decomposition we observe breakdown of the five-membered ring — most characteristic for the bicyclics XXIV and XXV, which contain phenyl substituents. This process is accomplished by successive ejection of the fragment $CONHN{=}CR^1R^2$ (formation of the hypothetical ion G) and one of the substituents R^3 or R^4 (primarily the phenyl substituent).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were obtained in Bruker WH-90/OS and WH-360 instruments (90 and 360 MHz, respectively), with internal standards TMS and hexamethyldisilazane for the ^1H NMR, and cyclohexane and $CDCl_3$ for the ^{13}C NMR. The mass spectra were taken in an MS-50 AEI spectrometer (ionizing voltage 70 eV). The chromatograph/mass spectra were obtained in a Kratos MS-25 instrument (ionizing voltage 70 eV).

The IR spectra were taken in UR-20 and Perkin-Elmer 580-B spectrometers, either in white mineral oil or in pure form. The analytical chromatography was performed in a Chrom 5 instrument in columns with SE-30 stationary phase.

The analytical and preparative high-performance liquid chromatography was carried out in a Du Pont-830 Prep instrument, UV detector (λ = 229, 254, and 334 nm), analytical column Zorbax-Sil (250 × 4.6 mm), preparative column Zorbax-Sil (250 × 22.4 mm). Silica gel L 40/100 was used for the column chromatography. The course of the reaction and the purity of the products were monitored by means of TLC on Silufol UV-254 plates with detection in UV light at 254 nm, and also by development of the spots in iodine vapor.

The hydrazides of the heterocyclic iminocarboxylic acids I-IV were obtained by procedures given in [1].

General Method for Preparation of 2,3-Substituted 1,3-Diazabicyclo[3.3.0]octan-4-ones (V-IX), 7,8-Substituted 7-Thia-1,7-diazabicyclo[3.3.0]octan-6-ones (X-XV), and 8,9-Substituted Diazabicyclo[4.3.0]nonan-7-ones (XVI-XIX). To a solution of 10 mmoles of the hydrazide of L-proline (1,3-thiazolidine-4-carboxylic acid or pipecolic acid) in 25 ml of ethanol at 20°C, 11 mmoles of the carbonyl component was added while stirring. When the reaction was completed, the solvent was driven off, and the residue was treated with dry ether, filtered, and dried in a desiccator. The product was recrystallized from ethanol (Tables 1-4).

9,9-Dimethyl-3-(N-isopropylideneamino)-7-oxo-4-thia-1,8-diazabicyclo[4.3.0]nonane (XX). A solution of 1.61 g (10 mmoles) of the hydrazide of 1,4-tetrahydrothiazine-3-carboxylic acid in 50 ml of acetone was refluxed for 15 h. The solvent was evaporated, and the residue was chromatographed in a silica gel column with ethyl acetate eluent. Obtained 2.1 g (90%) of colorless crystals of compound XX. Mass spectrum: 171 (6), 143 (7), 115 (9), 113 (5), 85 (10), 70 (18), 56 (54), 42 (18) (Tables 1-3).

8-Isopropylideneamino-9-methyl-7-oxo-4-thia-1,8-diazabicyclo[4.3.0]nonane (XXI). To a solution of 1.0 g (5 mmoles) of the isopropylidenehydrazide of 1,4-tetrahydrothiazine-3-carboxylic acid in 5 ml of ethanol, at 20°C, 2.0 ml (35 mmoles) of acetaldehyde was added dropwise with stirring, and the mixture was held for 30 min. After removing the solvent, obtained 1.1 g (97%) of colorless crystals of the bicyclic XXI. Mass spectrum: 170 (8), 128 (22), 102 (39), 98 (14), 96 (11), 83 (11), 82 (25), 71 (11), 69 (17), 55 (18), 54 (17), 42 (28) (Tables 1-3).

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