DERIVATIVES OF HETEROCYCLIC α-IMINOCARBOXYLIC ACIDS.

1. SYNTHESES OF HYDRAZIDES OF HETEROCYCLIC α-IMINOCARBOXYLIC ACIDS AND THEIR HYDRAZONES

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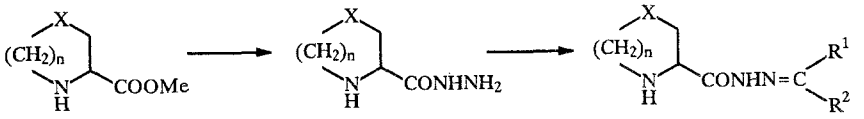
By the interaction of esters of L-proline, L-thioproline, pipecolic acid, and tetrahydro-1,4-thiazine-3-carboxylic acid with hydrazine, the corresponding hydrazides were obtained, which react with equimolar quantities of carbonyl compounds to form hydrazones consisting of mixtures of rotational isomers relative to the amide bond.

It is known that the hydrazide of aziridine-2-carboxylic acid is a convenient synthone for obtaining condensed heterocyclic systems as a result of its interaction with carbonyl compounds [1, 2]. It has been shown that the hydrazides of acyclic α-imino acids, in contrast, form only hydrazones or derivatives of α-iminopyrazolidine in this reaction [3]. We decided to investigate the possibility of obtaining condensed heterocycles by the interaction of carbonyl compounds with hydrazides of other cyclic α-iminocarboxylic acids, namely L-proline, L-thioproline, tetrahydro-1,4-thiazine-3-carboxylic acid, and pipecolic acid. We obtained the hydrazides of these compounds by hydrazinolysis of the corresponding methyl esters. It is known that the methyl ester of aziridine-2-carboxylic acid requires the use of anhydrous hydrazine to form a hydrazide [1]. Analogously, the esters of the five-membered α-iminocarboxylic acids proline and thioproline do not react with hydrazine hydrate, but do react with anhydrous hydrazine to give high yields of the hydrazides V and VI. At the same time, the corresponding derivatives of six-membered iminocarboxylic acids in alcohol solutions, even at 0°C, afford the hydrazides VII and VIII with nearly quantitative yields. Interaction of equimolar quantities of the hydrazides V-VIII with carbonyl compounds in alcohol or acetonitrile, or without solvent, gives 80-100% yields of the hydrazones IX-XXXIII (see also the next communication in this series):



I-IV V-VIII IX-XXXIII

III, V, IX—XIII n = 1, X = CH_2; IV, VI, XIV—XXV n = 1, X = S; I, VII, XXVI—XXX n = 2, X = CH_2; II, VIII, XXXI—XXXIII n = 2, X = S; IX, XV, XXVI, XXXII R^1 = C_6H_5, R^2 = H; X, XIX, XXVII R^1 = *p*-Br—C_6H_4, R^2 = H; XI, XVII, XXVIII R^1 = *p*-MeO-C_6H_4, R^2 = H; XII, XVIII, XXIX R^1 = 3,4,5-$(MeO)_3C_6H_2$, R^2 = H; XIII, XXX, XXXIII R^1 = C_6H_5, R^2 = Me; XIV, XXXI R^1 = R^2 = Me; XVI R^1 = *p*-Me-C_6H_4, R^2 = H; XX R^1 = *p*-NO_2—C_6H_4, R^2 = H; XXI R^1 = *p*-Me_2N-C_6H_4, R^2 = H; XXII R^1 = *o*-HO—C_6H_4, R^2 = H; XXIII $R^1 + R^2$ = -$(CH_2)_4$-; XXIV R^1 = 2-furyl, R^2 = H; R^1 = 4-Me-furyl-idene-2, R^2 = H

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TABLE 1. Characteristics of Hydrazones IX-XXXIII

Compound	Empirical formula	mp, °C	M*	IR spectrum, cm^{-1}			Yield, %
				$\nu_{C=N}$	$\nu_{C=O}$	ν_{NH}	
IX	$C_{12}H_{15}N_3O$	79...82	217	1636	1662	3300	97
X	$C_{12}H_{14}N_3OBr$	100...107	395	1630	1680	3282	98
XI	$C_{13}H_{17}N_3O_2$	86...87	231	1620	1692	3314	93
XII	$C_{15}H_{21}N_3O_4$	174...175	307	1628	1696	3290	98
XIII	$C_{13}H_{17}N_3O$	106...107	231	1638	1690	3310	95
XIV	$C_7H_{13}N_3OS$	80...81	187	1636	1690	3290	97
XV	$C_{11}H_{13}N_3OS$	162...164	235	1640	1695	3280	98
XVI	$C_{12}H_{15}N_3OS$	194...195	249	1628	1710	3300	100
XVII	$C_{12}H_{25}N_3O_2S$	143...145	265	1630	1712	3310	98
XVIII	$C_{14}H_{19}N_3O_4S$	155...156	325	1648	1698	3296	100
XIX	$C_{11}H_{12}N_3OSBr$	210	313	1620	1692	3280	96
XX	$C_{11}H_{12}N_4O_3S$	198...200	280	1632	1695	3300	100
XXI	$C_{13}H_{18}N_4OS$	163...165	278	1638	1706	3310	90
XXII	$C_{11}H_{13}N_3O_2S$	146...148	251	1620	1712	3300	80
XXIII	$C_{10}H_{17}N_3OS$	90...91	227	1618	1690	3296	90
XXIV	$C_9H_{11}N_3O_2S$	120...121	225	1648	1694	3290	98
XXV	$C_{10}H_{13}N_3O_2S$	133...135	239	1636	1706	3286	100
XXVI	$C_{13}H_{17}N_3O$	96...98	207	1632	1660	3280	90
XXVII	$C_{13}H_{16}N_3OBr$	135...136	285	1630	1696	3290	96
XXVIII	$C_{14}H_{19}N_3O_2$	109...110	261	1640	1680	3300	96
XXIX	$C_{16}H_{23}N_3O_4$	144...146	321	1628	1690	3310	97
XXX	$C_{14}H_{19}N_3O$	168...171	245	1630	1692	3282	90
XXXI	$C_8H_{15}N_3OS$	120...121	201	1640	1692	3280	94
XXXII	$C_{12}H_{15}N_3OS$	143...144	249	1640	1698	3312	85
XXXIII	$C_{13}H_{17}N_3OS$	133...134	263	1648	1692	3300	80

*M denotes the molecular weight determined by mass spectrometry.

The most reactive compound proved to be the hydrazide of L-proline, which reacts even with ketones at room temperature. The other hydrazides are all very similar to each other in their rate of interaction with carbonyl compounds, the rate being determined mainly by the nature of the carbonyl component. With aldehydes, condensation usually proceeds to completion in 1 h at 20°C. The reaction of ketones requires either an extended holding period at 20°C or refluxing. The formation of the hydrazones IX-XXIII is confirmed by the presence of the molecular ion in their mass spectra, by the characteristic absorption of the azomethine bond at 1630-1648 cm^{-1} in the IR spectra, and by their NMR spectra (Tables 1-3).

The presence of the acylhydrazone fragment complicates the interpretation of the NMR spectra, since two types of isomers may exist: rotational isomers relative to the amide fragment, and Z,E isomers relative to the azomethine fragment. In the ^{1}H NMR spectra (Tables 2 and 3) we observe only signals corresponding to the two rotational isomers relative to the amide bond. As the temperature is raised, these signals coalesce (G = 12.7±0.3 kcal/mole for XXXI). Further increases of temperature do not simplify the spectrum, and this may be evidence of an increase in the rate of Z-E isomerization relative to the azomethine fragment. Our interpretation differs from that given in [4] for the dynamic processes observed in the NMR spectra of acylhydrazones, which were explained as a consequence of Z-E isomerization.

By observing the effect of an aromatic solvent on the chemical shift of proton signals [5], we determined the ratio of cis and trans isomers of the hydrazones XXXI-XXXIII (Table 4). Thus, with the cis orientation of the amide bond, an aromatic solvent displaces the resonance signals of only the 2-H and 3-H protons (either downfield or very slightly upfield). This is due to the nearness of an sp^2-hybridized nitrogen atom or oxygen atom of the carbonyl group to these protons. Thus we are able to calculate the ratio of rotational isomers in mixtures of the two.

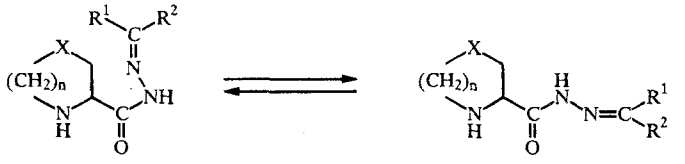


TABLE 2. ^1H NMR Spectra of Hydrazones IX-XXX in $CDCl_3$

Compound	Isomer	Chemical shift δ, ppm				Contents of isomers, %
		-C(O)-NH-	H_{R^1}	H_{R^2}	other protons	
IX	cis	9,23	7,1...7,6	8,17	1,51...3,20 (8H, m, protons	70
	trans	10,27		7,73	of pyrollidine ring)	30
X	cis	9,40	7,2...7,53	8,20	1,48...3,09 (8H, m, protons	65
	trans	10,61		7,87	of pyrollidine ring)	45
XI	cis	10,84	7,17...7,36	8,15	1,60...3,18 (8H, m, protons	90
	trans			7,75	of pyrollidine ring)	10
XII	cis	10,64	7,0; 7,23	8,10	1,64...3,22 (8H, m, protons of pyrollidine ring)	85
	trans			7,69	3,88 (9H, s, OMe)	15
XIII	cis	10,80	7,73	8,46	1,77...3,14 (8H, m, protons	80
	trans	9,96	7,65	8,12	of pyrollidine ring)	20
XIV	cis	8,48	2,00	1,83	2,75...4,71 (6H, m, protons	40
	trans	9,73	2,08	1,87	of thiazolidine ring)	60
XV	cis	9,25	5,38	7,71	2,17...4,60 (6H, m, protons	55
	trans	10,0	7,60		of thiazolidine 8.17 ring)	45
XVI	cis	9,48	7,13	7,73	2,33 (3H, s, CH_3), 2,60...4,58	62
	trans	9,95	7,51	8,17	(6H, m, protons of thiazolidine ring)	38
XVII	cis	9,11	6,85; 7,48	7,73	3,82 (3H, s, OCH_3), 2,49...4,58	55
	trans	9,91	6,94; 7,60	8,08	(6H, m, protons of thiazolidine ring)	45
XVIII	cis	9,52	6,96	7,71	3,91 (9H, s, OCH_3), 2,55...4,61	40
	trans	10,13	7,04	8,15	(6H, m, protons of thiazolidine ring)	60
XIX	cis	9,46	7,53	7,73	2,4...4,57 (6H, m, protons	48
	trans	10,0	8,07	8,17	of thioazolidine ring)	52
XX	cis	9,42	7,15	7,70	2,15...4,55 (6H, m, protons	40
	trans	9,90	7,61	8,10	of thiazolidine ring)	60
XXI	cis	9,18	7,21	7,83	3,15 (6H, s, Me_2N), 2,28...4,60	60
	trans	9,95	7,50	8,21	(6H, m, protons of thiazolidine ring)	40
XXII	cis	9,27	6,86	7,74	2,13...4,50 (7H, m, OH	55
	trans	10,06	7,63	8,25	and protons of thiazolidine ring)	45
XXIII	cis	9,38	1,42		2,28...4,13 (6H, m, protons	60
	trans	9,85	1,48		of thiazolidine ring)	40
XXIV	cis	10,1	6,49; 6,78	8,36	2,1...4,62 (6H, m, protons	46
	trans	9,76	7,48	7,69	of thiazolidine ring)	54
XXV	cis	10,0	6,1; 6,67,	8,40	2,15...4,50 (6H, m, protons	43
	trans	9,00	2,37 (CH_3)	7,22	of thiazolidine ring)	57
XXVI	cis	9,71	6,98...7,24	8,10	1,26...3,48 (10H, m, protons	85
	trans			7,69	of piperdine ring) 3.87 (9H, s, OMe)	15
XXVII	cis	9,67	7,10...7,35	8,38	1,30...3,42 (10H, m, protons	90
	trans			7,70	of piperdine ring)	10
XXVIII	cis	9,70	6,94...7,60	8,18	3,80 (3H, s, OCH_3), 1,27...3,50	80
	trans			7,73	(10H, m, protons of piperdine ring)	20
XXIX	cis	9,83	7,2...7,53	8,10	3,91 (9H, m, OCH_3), 1,25...3,41	76
	trans			7,70	(10H, m, protons of piperdine ring)	24
XXX	cis	9,74	7,1...7,40	8,15	1,48...3,51 (10H, m, protons	30
	trans			7,71	of piperdine ring) 2.26 (3H, s, CH_3)	70

TABLE 3. Parameters of ^1H NMR Spectra of Hydrazones XXXI-XXXIII

Compound	Isomer	Chemical shift, δ, ppm								$J_{H^2H^2}$	$J_{H^3H^2}$	$J_{H^6H^5}$	$J_{H^5H^5}$	$J_{H^6H^6}$	$J_{H^{2e}H^{6e}}$	Content of isomer, %
		H_2	H_3	H_5	H_6	N_4H	NH	H_{R^1}	H_{R^2}							
XXXI	cis-	2,68 *a* 2,72 *e*	4,38	3,10 *a* 3,45 *e*	2,72 *a* 2,37 *e*	1,8	8,4	2,01		13,2	8,8(*aa*) 4,0(*ae*)	11,8(*aa*) 2,8(*ee*) 3,0(6*a*5*e*) 2,5(5*a*6*e*)	13,4	13,2	1,5	30
	trans	2,74 *a* 2,96 *e*	3,67	3,06 *a* 3,36 *e*	2,64 *a* 2,44 *e*	1,8	9,5	2,11	1,85	13,5	9,5(*aa*)	10,3(*aa*) 3,5(*ee*) 2,9(6*a*5*e*) 2,5(5*a*6*e*)	13,2	13,2	1,5	70
XXXII	cis	2,77 *a* 2,82 *e*	4,51	3,16 *a* 3,49 *e*	2,76 *a* 2,40 *e*	1,8	8,9	7,65 (H*o*) 7,41 (H*m,p*)	7,78	12,6	9,8(*aa*) 3,4(*ae*)	11,3(*aa*) 2,8(*ee*) 2,5(6*a*5*e*) 2,6(5*a*6*e*)	13,2	13,3	1,4	37
	trans	2,78 *a* 2,97 *e*	3,71	3,08 *a* 3,37 *e*	2,64 *a* 2,45 *e*	1,8	9,2	7,73 (H*o*) 7,38 (H*m,p*)	8,20	13,5	9,2(*aa*) 2,8(*ae*)	10,2(*aa*) 4,0(*ee*) 3,0(6*a*5*e*) 2,6(5*a*6*e*)	13,2	13,4	1,5	63
XXXIII	cis	2,75 *a* 2,81 *e*	4,53	3,15 *a* 3,48 *e*	2,75 *a* 2,39 *e*	1,8	8,7	7,73 (H*o*) 7,41 (H*m,p*)	2,26	12,8	9,8(*aa*) 3,1(*ae*)	11,5(*aa*) 2,8(*ee*) 2,8(6*a*5*e*) 2,5(5*a*6*e*)	13,2	13,2	1,3	56
	trans	2,78 *a* 3,01 *e*	3,74	3,10 *a* 3,39 *e*	2,65 *a* 2,45 *e*	1,8	9,8	7,82 (H*o*) 7,36 (H*m,p*)	2,23	13,0	9,2(*aa*) 2,8(*ae*)	10,3(*aa*) 4,0(*ee*) 3,0(6*a*5*e*) 2,7(5*a*6*e*)	13,1	13,3	1,4	44

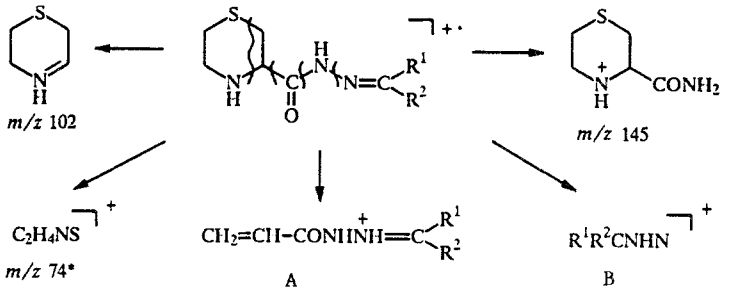
TABLE 4. Influence of Aromatic Solvent on Chemical Shift (ppm) $H_i = H_i(CDCl_3) - H_i(C_6D_6)$

Compound	Isomer	H_2	H_3	H_5	H_6	H_{R1}	H_{R2}
XXXI	cis	+0,04(*a*) +0,12(*e*)	+0,12	-0,18(*a*) -0,37(*e*)	-0,32 (*a*) -0,41(*e*)	-0,39	-0,33
	trans	-0,03(*a*) -0,14(*e*)	+0,15	-0,34(*a*) -0,42(*e*)	-0,32(*a*) -0,42(*e*)	-0,28	-0,46
XXXII	cis	+0,01(*a*) -0,03(*e*)	+0,08	-0,21(*a*) -0,46(*e*)	-0,46(*a*) -0,54(*e*)		-0,93
	trans	-0,21(*a*) -0,16(*e*)	-0,42	-0,62(*a*) -0,74(*e*)	-0,61(*a*) -0,67(*e*)		-0,65
XXXIII	cis	-0,09(*a*) -0,09(*e*)	0	-0,26(*a*) -0,52(*e*)	-0,52(*a*) -0,58(*e*)		-0,46
	trans	-0,37(*a*) -0,25(*e*)	-0,57	-0,68(*a*) -0,80(*e*)	-0,65(*a*) -0,70(*e*)		0,23

TABLE 5. Characteristics Ions of Mass Spectra of 3-Alkylidene-(arylidene)hydrazinocarbonyltetrahydro-1,4-thiazines (XXXI-XXXIII)

Compound	R^1	R^2	M^+	*m/z* 74	A	*m/z* 102	B	*m/z* 145
XXXI	CH_3	CH_3	201(10)	(62)	127(35)	(100)	—	(11)
XXXII	C_6H_5	H	249(11)	(23)	175(4)	(100)	119(4)	(2)
XXXIII	C_6H_5	CH_3	263(23)	(23)	189(6)	(100)	133(6)	(4)

The mass-spectrometric decomposition of the hydrazones IX-XXXIII is characterized by rupture of N—N and CO—N single bonds in the substituent, and also destruction of the ring system; this is demonstrated graphically in the example of the derivatives of 1,4-thiazinecarboxylic acid (Table 5):



The hydrazones IX-XXXIII that have been obtained are accessible synthones for the preparation of bicyclic heterosystems.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were obtained in Bruker WH-90/OS (90 MHz) and Bruker WH-360 (360 MHz) instruments, with TMS internal standard. The mass spectra were taken in an MS-50 AEI spectrometer (ionizing voltage 70 eV). The IR spectra were taken in UR-20 and Perkin—Elmer 580-B spectrophotometers in white mineral oil, in a thin layer.

The results of elemental analyses of all of the synthesized compounds for C, H, N, and S corresponded to the calculated values.

General Procedure for Obtaining Hydrazides V-VIII. To a solution of 0.1 mole of freshly prepared ester I-IV in 20-50 ml of methanol at −20°C (for esters I and II) or at +20°C (for esters III and IV), there was added a solution of 0.11-0.12 mole of hydrazine hydrate (for esters I and II) or anhydrous hydrazine (for esters III and IV) in 5-10 ml of methanol. The mixture was stirred for 12 h at room temperature, the solvent was cautiously taken off under vacuum, and the residue was washed with absolute ether and crystallized from methanol (V-VII) or from a 10:1 ethanol—water mixture (VIII).

Hydrazide of L-Proline (V). Yield 10 g (80%); colorless, extremely hygroscopic crystals, mp 22-25°C. IR spectrum, cm^{-1}: 1650 (CO), 3230 (NH_2). ^1H NMR spectrum, ppm ($CDCl_3$): 2.10-4.1 (8H, m, ring protons); 7.9-8.1 ppm (3H, br.s, $NHNH_2$). Mass spectrum: 129 (M^+) (9%), 99[$M-NHNH_2$]$^+$ (10%).

Hydrazide of 1,3-Thiazolidine-4-carboxylic Acid (VI). Yield 14.4 g (98%); colorless crystals, mp 112-114°C. IR spectrum, cm^{-1}: 1650 (CO), 3212 (NH), 3308 (NH_2). ^1H NMR spectrum ($CDCl_3$), ppm: 2.18 (1H, s, ring NH); 3.01 (1H, d, 5-H_a, J = 7.4 Hz); 3.12 (1H, d, 5-H_e, J = 7.0 Hz); 3.96 (1H, m, 4-H); 4.10 (2H, s, S—CH_2—N); 7.5-7.7 ppm (3H, br.s, $NHNH_2$). Mass spectrum: 147 [M]$^+$ (5), 116 [$M-NHNH_2$]$^+$ (7).

Hydrazide of Pipecolic Acid (VII). Yield 14.0 g (97%); colorless crystals, mp 98°C (from methanol). IR spectrum, cm^{-1}: 1660 (CO), 3200-3310 ($NHNH_2$). ^1H NMR spectrum ($CDCl_3$), ppm: 2.30 (1H, br.s, ring NH); 2.35-4.20 (9H, m, ring protons); 7.8 (2H, br.d, NH_2); 8.1 (1H, br.s, CONH).

Hydrazide of Tetrahydro-1,4-thiazine-3-carboxylic Acid (VIII). Yield 15.5 g (96%); colorless crystals, mp 117-118°C (from 10:1 ethanol—water mixture). IR spectrum, cm^{-1}: 1652 (CO), 3120 (NH), 3310 (NH_2). ^1H NMR spectrum (360 MHz, $CDCl_3$), ppm: 2.25 (1H, br.s, ring NH); 2.46 (1H, m, 6-H_e, J = 13.0, 3.0, and 4.6 Hz); 2.70 (1H, m, 6-H_a, J = 13.0, 8.8, and 2.5 Hz); 2.82 (1H, m, 2-H_e, J = 13.3 and 2.9 Hz); 2.95 (1H, d.d, 2-H_a, J = 13.3 and 8.0 Hz); 3.10 (1H, m, 5-H_a, J = 11.8, 8.8, and 3.3 Hz); 3.42 (1H, m, 5-H_e, J = 11.8, 4.6, and 2.6 Hz); 3.66 (1H, d.d, 3-H_a, J = 8.0 and 2.9 Hz); 6.37 (2H, br.d, NH_2); 8.8 (1H, br.s, CONH). Mass spectrum: 161 (5), 130 (8), 103 (8), 102 (100), 86 (5), 74 (24), 71 (7), 69 (5), 58 (12), 56 (10), 45 (9).

General Procedure for Obtaining Hydrazones of L-Proline (IX-XIII), 1,3-Thiazolidine-4-carboxylic Acid (XIV-XXV), and Pipecolic Acid (XXVI-XXX). To a solution of 0.01 mole of the hydrazine V-VII in 20 ml of ethanol at 20°C, an equimolar quantity of the carbonyl component was added slowly with stirring. After completion of the reaction (as determined by (TLC), the solvent was removed, and the residue was treated with dry ether and then dried in a desiccator. The product was purified by crystallization from ethanol. The characteristics of the hydrazones IX-XXX are listed in Tables 1-3.

Isopropylidenehydrazinocarbonyltetrahydro-1,4-thiazine (XXXI). A solution of 1.61 g (0.01 mmoles) of the hydrazide VIII in 50 ml of acetone was held for 1 h at 40°C. The solvent was removed under vacuum, obtaining 1.90 g (94%) of colorless crystals of the hydrazone XXXI, with mp 120-121°C (ethanol). Mass spectrum: 73 (40), 61 (47), 41 (63).

3-(Benzylidenehydrazinocarbonyl)tetrahydro-1,4-thiazine (XXXII). To a solution of 1.61 g (0.01 mole) of the hydrazine VIII in 10 ml of acetonitrile, 1.06 g (0.01 mole) of benzaldehyde was added. The reaction mixture was refluxed for 30 min. The solvent was removed, and the residue was chromatographed in a 30 × 3-cm column with silica gel, with 4:1 chloroform—hexane eluent. Obtained 2.21 g (85%) of colorless crystals of the hydrazone XXXII. Mass spectrum: 232 (11), 90 (7), 77 (12), 55 (14) (see Tables 1 and 5).

3-(Methylbenzylidenehydrazinocarbonyl)tetrahydro-1,4-thiazine (XXXIII). To a solution of 1.61 g (0.01 mole) of the hydrazine VIII in 50 ml of acetonitrile, 30 g (0.25 mole) of acetophenone was added, and the mixture was refluxed for 40 h. The solvent was removed, and the residue was chromatographed in a 30 × 3-cm column with silica gel (column 30 × 3.0 cm), with 1:1 ethyl acetate—hexane eluent. Obtained 2.0 g (80%) of the hydrazone XXXIII. Mass spectrum: 134 (6), 120 (28), 77 (33), 56 (10), 51 (5), 42 (5) (see Tables 1 and 5).

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