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RING-CHAIN TAUTOMERISM OF SUBSTITUTED HYDRAZONES. 18.* SYNTHESIS OF 2-HYDRAZINO-1-PROPANETHIOL AND STRUCTURE OF ITS ALKYLIDENE DERIVATIVES

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1-Aminoaziridines react with hydrogen sulfide with ring opening to give vic-hydrazino thiols. In the case of 1-amino-2-methylaziridine the reaction proceeds regioselectively with the formation of 2-hydrazino-1-propanethiol. The products of condensation of the latter with carbonyl compounds exist in solution, depending on their structure, in the form of the corresponding perhydro-1,3,4-thiadiazines, (2-mercapto-1-methylethyl)hydrazones, or tautomeric mixtures of these compounds. The thermodynamic parameters of the tautomeric equilibria were determined for several systems from the ^{1}H NMR spectra.

In connection with the study of the ring-chain tautomerism of perhydro-1,3,4-thiadiazines, compounds that are not substituted in the 4 position are of special interest, since 4-alkylperhydrothiadiazines exist exclusively in the cyclic form in solutions in most cases [1]. The simplest method for the synthesis of such compounds consists in the condensation of aldehydes or ketones with hydrazino thiols. However, up until recently, the first representatives of the homologous series of vicinal hydrazino thiols were unknown. It was only recently that we described 2-hydrazinoethanethiol, which was isolated in low yield as a side product in the reaction of acetone hydrazone with thiirane [2]. N-Alkylhydrazino thiols are obtained by mercaptoalkylation of alkylhydrazines with thiiranes in nonpolar solvents [3] or in several steps under severe conditions with the aid of an S-benzyl protective group [4]. The latter method, which is extremely laborious, is hardly suitable for the preparative synthesis of the more labile N-unsubstituted hydrazino thiols. As regards the first method, our attempts to subject hydrazine hydrate or anhydrous hydrazine to the reaction with lower thiiranes with the use of a large number of solvents led to the formation of only products of the polymerization of the thiirane.

In order to develop a general preparative method for the production of vicinal hydrazino thiols with an unsubstituted hydrazo group we checked out the reaction of 1-aminoaziridines with hydrogen sulfide. It is known that hydrogen sulfide reacts smoothly with 1-alkyl- and 1-acylaziridines at low temperatures to give the corresponding amino thiols [5, p. 19].

Aminoaziridines I were synthesized by cyclization of β-hydrazinoalkyl sulfates under the conditions of the Wenker reaction [6]. We found that the use of pure aminoaziridines, which

*See [1] for Communication 17.

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TABLE 1. Derivatives of 2-Hydrazino-1-propanethiol

Compound	bp, °C (mm)	mp, °C (from hexane)	d_4^{20}*	n_D^{20}*	Found					Empirical formula	Calc.					Yield, %
					C, %	H, %	N, %	S, %	MR_D		C, %	H, %	N, %	S, %	MR_D	
IVb	76—77 (8)	62—64	—	—	40,7	8,5	—	27,2	—	$C_4H_{10}N_2S$	40,6	8,5	—	27,1	—	30
IVc	82—84 (10)	65,5—66,5	—	—	45,1	9,2	20,9	24,8	—	$C_5H_{12}N_2S$	45,4	9,1	21,2	24,2	—	72
IVd	91—92 (8)	70—70,5	—	—	52,6	10,2	17,4	20,0	—	$C_7H_{16}N_2S$	52,4	10,1	17,5	20,0	—	69
IIIe	120—150 (3)	97—98†	—	—	52,2	5,9	12,2	14,3	—	$C_{10}H_{13}ClN_2S$	52,5	5,7	12,2	14,0	—	38
IIIf ⇄ IVf	75—76 (8)	—	1,0035	1,5087	39,4	8,4	15,4	17,8	43,50	$C_6H_{14}N_2S \cdot HCl$‡	39,4	8,3	15,3	17,5	43,79**	64
IIIg ⇄ IVg	93—95 (11)	—	0,9910	1,5058	52,2	10,1	—	20,3	48,04	$C_7H_{16}N_2S$	52,4	10,1	—	20,0	48,44††	59
IIIh	100—102 (15)	—	0,9579	1,4956	55,2	10,4	—	18,3	53,12	$C_8H_{18}N_2S$	55,1	10,4	—	18,4	53,09	57
IIIi	88—91 (9)	—	0,9428	1,4903	57,5	10,9	—	16,8	57,76	$C_9H_{20}N_2S$	57,4	10,7	—	17,0	57,73	63

*For the equilibrium tautomeric mixtures.
†From a mixture of hexane with ethanol (3:1).
‡The analytical characteristics are presented for the hydrochloride with mp 163-164°C (dec.).
**For hydrazone IIIf; the MR_D value calculated for perhydrothiadiazine IVf was 43.14.
††For hydrazone IIIg; the MR_D value calculated for hydrazone IVg was 47.79.

TABLE 2. Spectral Characteristics of the Products of Condensation of 2-Hydrazino-1-propanethiol with Carbonyl Compounds

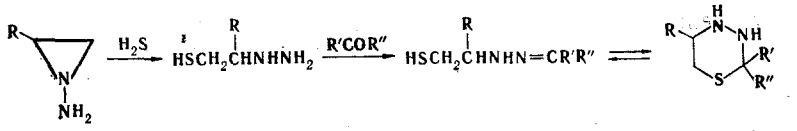
Compound	^{1}H NMR spectrum, δ, ppm (J, Hz)					ν, cm^{-1}		
	R	R′	R″	CH_2	CHN	C=N	S—H	N—H
IVb*	0,97 d (6,0)	3,74 dd (−12,9; 2,0)	4,17 d (−12,9)	2,4—3,0 m		—	—	3190, 3230
IVc†	0,97 d (6,0)	1,21 d (6,2)	4,18 q (6,2)	2,4—2,9 m		—	—	3175, 3220
IVd‡	0,96 d (6,7)	0,96 d 0,98 d (6,8)** 1,73 m	3,95 d (6,0)	2,5—2,9 m		—	—	3170, 3230
IIIe	1,22 d (7,0)	7,21 d 7,39 d (8,6)	7,47 s	2,69 dd (5,8; 8,0)	3,50 m	—	—	3190, 3230
IIIf†† ↓↑ IVf	1,14 d (6,6) 1,01 d (6,0)	1,69 s 1,29 s	1,86 s 1,60 s	2,3—3,5 m		1640	2560	3200, 3300
IIIg ↓↑ IVg	E: 1,14 d (6,7) Z: 1,13 d (6,7)	E: 1,00 t 2,18 g (7,5) 0,86 t (7,5)	E: 1,65 s Z: 1,83 s *e*: 1,24 s *a*: 1,54 s	2,63 d (6,0)‡‡ 2,5—2,9 m	3,31 m	1635	2555	3195, 3295
IIIh	1,15 d (6,5)	E: 1,01 d, 2,39 sep (7,0) Z: 1,05 d (7,0)	E: 1,63 s Z: 1,74 s	2,65 d‡‡ (5,5)	3,35 m	1635	2565	3275
IIIi	1,16 d (6,6)	1,04 s	1,65 s	2,65 dd (6,0; 6,0)‡‡	3,33 m	1625	2565	3270

Mass spectrum (here and subsequently, the m/z values are presented along with the relative intensities in percent, which are given in parentheses): 118 ($M^{+\cdot}$, 28), 115 (4), 84 (4), 75 (3), 74 (7), 73 (4), 72 (7), 71 (100), 69 (5), 60 (4), 59 (4), 57 (8), 56 (18), 47 (10), 46 (12), 45 (11), 44 (17), 43 (8), 42 (18), 41 (23); m 42.7, 37.1. †^{13}C NMR spectrum: 19.8 and 20.1 (methyl group C atoms), 35.6 (C_6), 51.9 (C_5), and 57.8 ppm (C_2). Mass spectrum: 132 ($M^{+\cdot}$, 11), 86 (6), 85 (100), 60 (3), 59 (3), 58 (6), 57 (3), 47 (6), 45 (4), 44 (51), 43 (5), 42 (16), 41 (12); m* 54.8, 37.1. ‡A signal of an azomethine proton of the acyclic IIId form is also observed in the ^{1}H NMR spectrum at 6.87 ppm (d, J = 5.0 Hz). ^{13}C NMR spectrum: 19.5 and 19.8 (methyl group C atoms), 32.9 (α-C atom of the isopropyl grouping), 35.5 (C_6), 52.8 (C_5), and 69.4 ppm (C_2). Mass spectrum: 160 ($M^{+\cdot}$, 7), 117 (9), 114 (8), 113 (100), 75 (3), 71 (3), 70 (3), 56 (4), 55 (4), 47 (5), 45 (3), 44 (45), 43 (3), 42 (7), 41 (16); m* 85.6, 79.8, 37.1. **Diastereotopic methyl groups. ††Mass spectrum: ($M^{+\cdot}$, 7), 100 (7), 72 (3), 58 (6), 57 (5), 56 (55), 47 (4), 44 (6), 42 (7), 41 (10); m* 67.1, 37.1, 31.7. ‡‡The signal is broadened.

TABLE 3. Thermodyanmic Parameters of the Tautomeric (III⇄IV) and Stereoisomeric (Z⇄E) Equilibria*

Hydrazone	Type of equilibrium	K					ΔH^0, kJ/mole	ΔS^0, J/mole-°K
		30°	35°	50°	70°	90°		
IIIf	III⇄IV	—	1,59	2,18	3,59†	5,45	21,2±0,8	72±3
IIIg	III⇄IV	3,62	—	6,13	8,21	11,5	17,3±1,2	68±4
	Z⇄E	4,69	—	4,32	4,00	3,59	4,0±0,4	0,3±1

*Solutions in tetrachloroethylene (1 mole/liter).
†At 69°C.



I a,b II a,b III a-i IV a-i

I, II a R=H; b R=Me; III, IV a R=H, R′=R″=Me; b R=Me, R′=R″=H; c R=R′=Me, R″=H; d R=Me, R′=*i*-Pr, R″=H; e R=Me, R′=*p*-ClC$_6$H$_4$, R″=H; f R=R′=R″=Me; g R=R″=Me, R′=Et; h R=R″=Me, R′=*i*-Pr; i R=R″=Me, R′=*t*-Bu

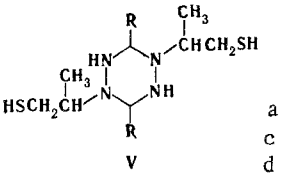
are extremely difficult to obtain in the individual state [6, 7], for the synthesis of hydrazino thiols is not absolutely necessary. Treatment of the products of the cyclization of hydrazino sulfates, which contain ∿40% aminoaziridine Ia in one case and ∿70% aminoaziridine Ib in the other [6, 7], with hydrogen sulfide in methanol under the conditions described for 1-methylaziridine [8] led to hydrazino thiols IIa, b in good yields.

The properties of hydrazino thiol IIa and the isopropylidene derivative (IIIa ⇄ IVa) obtained from it were in agreement with the properties of the previously described preparations [2]. The structure of hydrazino thiol IIb was confirmed by data from IR and PMR spectrsocopy. Its mass spectrum is similar to the mass spectra of N-alkyl-substituted hydrazino thiols [9]: the principal fragmentation pathway is β cleavage with respect to the nitrogen atom with splitting out of a CH_2SH particle (the 59 peak).* The presence of a low-intensity 45 peak could have been linked with similar fragmentation of the isomeric hydrazino thiol, which is formed as a result of opening of the three-membered ring in an alternative direction. However, it is much more likely that this peak corresponds to the product of partial decomposition of hydrazino thiol IIb, which is observed under the conditions of chromatographic mass-spectrometric analysis (hydrazino thiol IIa undergoes complete decomposition under these conditions). In this connection, it is important that peaks (and signals in their ^1H and ^{13}C NMR spectra) that could be assigned to the structural isomer with an alternative orientation of the methyl group are absent in the mass spectra of the alkylidene derivatives of hydrazino thiol IIb, which are completely stable under GLC conditions (see [2]). Thus it may be concluded that the opening of the 1-aminoaziridine ring by hydrogen sulfide is highly regioselective. Aziridines that do not have an amino group in the 1 position react completely regioselectively with hydrogen sulfide [10, 11].

Since alkylidene derivatives of hydrazino thiol IIa were previously obtained by treatment of hydrazones with thiirane [2], in the present research we studied only the derivatives of hydrazino thiol IIb. Its condensations with carbonyl compounds were carried out under conditions that are normal for similar reactions with other hydrazino thiols [1]. The properties of the reaction products are presented in Tables 1 and 2.

The derivatives of aldehydes were of particular interest, since whereas N-(β-mercaptoalkyl)hydrazines of ketones can be obtained by the reaction of thiiranes with unsubstituted hydrazones of ketones, the reactions of unsubstituted aldohydrazones with thiiranes give 3-aminothiazolidines [2]. All of the products of the condensation of hydrazino thiol IIb with aldehydes were crystalline substances. It is known that monoalkylhydrazones of aldehydes undergo dimerization relatively easily to give crystalline perhydro-1,2,4,5-tetrazines [12, p. 7]], which in the case of the preparations that we investigated should have had structrues Va-d:

*Here and subsequently, the m/z values are given for all of the ion peaks.



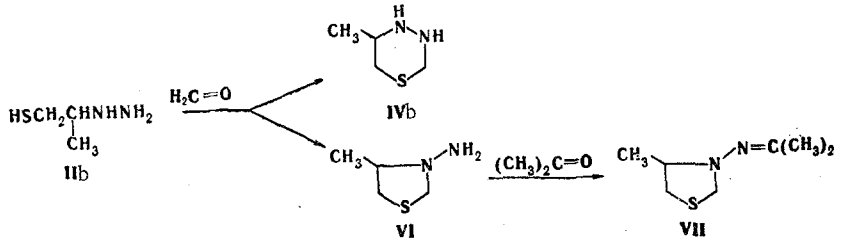
V

a R=H; b R=CH_3;
c R=*i*-C_3H_7;
d R=*p*-ClC_6H_4

However, the characteristic νS—H band is absent in the IR spectra of derivatives of aliphatic aldehydes at 2500-2600 cm^{-1}. Their mass spectra are in agreement with the monomeric structure of hydrazones IIIb-d or the corresponding potentially tautomeric perhydrothiadiazines [1, 2], although the possibility of monomerization of tetrazine derivatives V under the conditions of chromatographic mass-spectrometric analysis also cannot be excluded.

In the case of the formaldehyde derivative the PMR spectroscopic data are not in agreement with structure Va. The signals of the protons of the alkylidene fragment form an AB system (Table 2), which should be expected for perhydrothiadiazine IVb, which exists primarily in only the chair conformation, but not for perhydrotetrazine Va. Conversion of the ring of N-alkylperhydro-1,2,4,5-tetrazines at ∿30°C takes place at a rather high rate, and the signal of the methylene protons is observed in the form of a singlet [13]. In the case of IVa even raising the temperature does not lead to changes in the ^1H NMR spectrum. The splitting of the high-field doublet of the AB system observed in the PMR spectra of IVa obtained for solutions in tetrachloroethylene or d_4-methanol is due in all likelihood to spin-spin coupling between the equatorially oriented 2- and 5-H protons) this coupling of the W type has been noted for other perhydrothiadiazines [1], but it cannot occur in tetrazine structure Va.

It must be noted that, in contrast to other alkylidene derivatives of hydrazino thiol IIb, which are individual substances according to the GLC data, 5-methylperhydro-1,3,4-thiadiazine (IVb), even when it was purified by crystallization, contained an admixed isomer, to which a singlet (4.08 ppm) and a doublet (1.12 ppm, J = 6.8 Hz) correspond in the PMR spectrum. The singlet signal remains unchanged when the temperature is raised to 90°C (in C_2Cl_4) or when it is lowered to -56°C (in $CDCl_3$); however, it is converted to two singlets with Δδ 5.2 Hz on passing to a solution in d_4-methanol. An important difference between the mass spectrum of this impurity and the mass spectrum of perhydrothiadiazine IVb is the presence of an intense $(M-CH_2S)^+$ ion (72, metastable ion 43.7) in place of the typical $(M-CH_2SH)^+$ ion (71, metastable ion 42.7), which corresponds to β cleavage relative to the amide nitrogen atom of the molecular ion of chain form IIIb (see [1, 2]). Treatment of the contaminated IVb preparation with acetone leads to the appearance in the PMR spectrum of the reaction mixture of two singlets of methyl groups with chemical shifts corresponding to the substituents attached to the azomethine carbon atom (1.85 and 1.95 ppm; the position and multiplicity of the remaining signals remain virtually unchanged in this case). The set of data presented above makes it possible to conclude that the impurity is 3-amino-4-methylthiazolidine (VI), which is converted to hydrazone VII on treatment with acetone. Tetrazine structure Va is excluded, since changes in the PMR spectrum in the region of the resonance of the methylene protons of the ring should be observed as the temperature is lowered as a result of slowing down of the conversion of the perhydrotetrazine ring [13].



IIb IVb VI VII

The reaction of hydrazino thiol IIb with formaldehyde leads to the formation of approximately equal amounts of perhydrothiadiazine IVb and aminothiazolidine VI. The development of the latter may be associated with cyclization of the intermediate carbinol amine, which arises as a result of competitive attack on the carbonyl group by the substituted nitrogen atom of the hydrazino alcohol series, the possibility that the monothiohemiacetal [5, p. 81] that is formed by attack on the carbonyl group by the sulfur atom — the third nucleophilic center of the hydrazino thiol molecule — and undergoes subsequent cyclization to perhydro-

thiadiazine IVb or aminothiazolidine VI may act as an intermediate in the reaction of the hydrazino thiol with formaldehyde also is not excluded.

We have previously observed that 4-alkylperhydro-1,3,4-thiadiazines that contain only one alkyl group in the 2 position exist entirely in the ring form [1]. The absence of a substituent in the 4 position, like an increase in the volume of the substituent in the 2 position in the 2,2-dialkylperhydrothiadiazine series [1, 2], shifts the tautomeric equilibrium to favor the chain form. 5-Methylperhydro-1,3,4-thiadiazine (IVb) in solutions exists exclusively in the ring form even when the temperature is raised to 90°C. When there is a methyl group in the 2 position (IVc), even though signals of chain form IIIb are not observed in the PMR spectrum at room temperature (Table 2), these signals [particularly a quartet at 6.96 ppm (J ≈ 5.0 Hz) due to CH = N] do appear as the temperature is raised, and K_T (III/IV) = 0.14 at 90°C. The presence in the strong-field region of the spectrum of two doublets at 1.65 and 1.78 ppm (J = 5.0 Hz), which correspond to the methyl group attached to the azomethine bond of hydrazone IIIc, indicates the presence of the E and Z isomers of this compound in a ratio of 1.2:1 (see [14]).

The signal of the azomethine proton of chain form IIId is noticeable in the PMR spectra of 2-isopropyl-5-methylperhydro-1,3,4-thiadiazine (IVd) even at room temperature; K_T = 0.06 at 30°C, whereas $K_T \sim 1$ at 150°C (in decalin). According to ^{1}H NMR spectroscopic data, hydrazone form IIId is represented only by the E isomer) a substantial shift of the stereoisomeric equilibrium on passing from acetaldehyde derivatives to isobutyraldehyde derivatives is also known for other monosubstituted hydrazones [14].

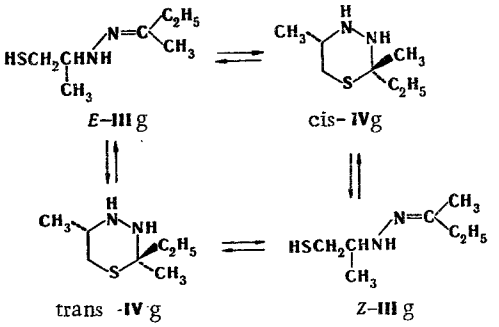
In contrast to 2,6-disubstituted compounds [15], the NMR spectra in the case of 2,6-dialkylperhydrothiadiazines IVc, d, make it possible to detect the presence of a single stereoisomer, which evidently has a trans configuration with a diequatorial orientation of both alkyl groups.

As regards the p-chlorobenzylidene derivative, signals that could be assigned to ring form IVe are completely absent in the PMR spectrum of a solution of this compound (Table 2). This should have been expected, considering the structure of arylidene derivatives of N-alkylhydrazino thiols [15], which exist in solutions in the form of tautomeric mixtures, and the absence of an N-alkyl substituent, which shifts the equilibrium to favor the chain form [1].

In the crystalline state all of the derivatives of aldehydes obtained probably have ring structure IVb-e: the characteristic νS—H band is absent in their IR spectra (in mineral oil) (Table 2).

On passing to the derivatives of ketones, the tautomeric equilibrium is shifted to favor the corresponding hydrazone III, so that the cyclic form cannot be detected in the case of the derivatives of methyl isopropyl ketone (IIIh) and pinacolone (IIIi). At the same time, the ^{1}H NMR spectra of the derivatives of acetone ($III_f \rightleftarrows IV_f$) and methyl ethyl ketone ($III_g \rightleftarrows IV_g$) indicate the presence of both the ring and chain forms and change reversibly as the temperature is changed. The refractometric characteristics of the freshly distilled preparations change, reaching the equilibrium values in a few hours. The thermodynamic parameters for the equilibria of tautomeric mixtures determined by ^{1}H NMR spectroscopy are presented in Table 3. A comparison with the data in [2] indicates that on passing from 2,2,6-trimethylperhydro-1,3,4-thiadiazine (ΔH° = 15.8 ±2.1 kJ/mole, ΔS° = 57.6 ±6.4 J/mole·°K [2]) to 2,2,5-trimethyl-substituted IVf (Table 3) the thermodynamic parameters of the tautomeric equilibrium increase appreciably. In our opinion, this may be due to weakening of the intramolecular hydrogen bonds in which the NH and SH groupings of the chain form participate. This weakening is due to steric hindrance that develops when a methyl group is introduced in the α position relative to the sp^3-hybridized nitrogen atom. The introduction of a substituent in the α position relative to the sulfur atom has a smaller effect as a consequence of the considerable length of the C—S bond.

In the case of the derivative of methyl ethyl ketone ($III_g \rightleftarrows IV_g$) it is apparent that even a very slight increase in the volume of the substituent in the 2 position of the ring shifts the equilibrium markedly to favor the open form. In this case four isomers, viz., the E and Z forms of hydrazone IIIg and cis- and trans-perhydrothiadiazines IVg, exist in equilibrium:



The thermodynamic equilibrium parameters were determined for the E,Z isomerization of the open form (Table 3). This sort of determination for the cis,trans isomerization of the cyclic form could not be made because of lowering of the equilibrium concentration of the ring isomer as the temperature was raised. At 30°C, equilibrium constant $K_{trans/cis} \approx 5$ ($\Delta G^\circ \approx 4$ kJ/mole). It is difficult to explain such a significant difference in the conformational energies of the methyl and ethyl groups in the 2 position of the perhydrothiadiazine ring on the basis of the available experimental data.

The data in Table 3 show that the shift of the equilibrium on passing from the derivative of acetone to the derivative of methyl ethyl ketone is subject to enthalpy control. The destabilizing nonvalence interactions between the β-CH_3 group and the closest fragments of the heteroring in tautomer IVg probably constitute the deciding factor in this case. As the volume of the substituent in the 2 position is increased further, the role played by this factor increases to an even greater extent, and this leads to a marked shift of the equilibrium to favor the acyclic structure in the case of derivatives of methyl isopropyl ketone and pinacolone.

EXPERIMENTAL

The PMR spectra of 20% solutions of the compounds in tetrachloroethylene were recorded with a Varian HA-100D-15 spectrometer at 25-30°C with hexamethyldisiloxane as the internal standard. The temperature dependence of the equilibrium constants was determined from the spectra of solutions in tetrachloroethylene (1 mole/liter) with hexamethyldisiloxane as the external standard. The establishment of equilibrium was monitored by successive recording of the spectra. The intensities of the signals of the methyl groups of the alkylidene fragment were used to estimate the equilibrium constants. The results were treated by the method of least squares. The ^{13}C NMR spectra of 20% solutions of the compounds in benzene (with the chemical shifts presented on the δ scale) were obtained with a CFT-20 spectrometer at 35-40°C. The IR spectra of thin layers (for the liquid compounds) or mineral oil suspensions (for the crystalline samples) were recorded with a UR-20 spectrometer. The mass spectra were obtained under the conditions described in [2]; the peaks with m/z values lower than 41 or with intensities below 3% were not presented. The individuality of alkylidene derivatives III (IV) was monitored by GLC (see [1] for the conditions).

2-Hydrazino-2lpropanethiol (IIb). A 20-g (0.59 mole) sample of dry hydrogen sulfide was dissolved in 70 ml of cooled (to −60°C) anhydrous methanol, and a solution of 11.4 g of the product of cyclization of 1-hydrazino-2- propyl sulfate [6] (bp 99-102°C, n_D^{20} 1.4435; the ^1H NMR spectrum was identical to the spectrum described for 1-amino-2-methylaziridine [16]) containing 0.11 mole of aziridine Ib in 70 ml of methanol was added dropwise with stirring to this solution. The reaction mixture was then stirred vigorously for another 3 h while passing a stream of gaseous hydrogen sulfide through it and maintaining the temperature at -60°C. The temperature was then raised with stirring to room temperature in the course of 1 h, and the mixture was allowed to stand overnight. The reaction product was isolated by fractionation with a column to give 7.6 g (63%) of a product with bp 90-92°C (10 mm), d_4^{20} 1.0640, n_D^{20} 1.5279, and MR_D 30.73 (calculated value 30.90). PMR spectrum (in CD_3OD): δ 1.07 (d, J = 6.2 Hz, CH_3) and 2.5-3.0 ppm (m, $CHCH_2$). IR spectrum: 1615 (δ NH_2) 2550 (νSH) 3190 and 3330 cm^{-1} (νNH). Mass spectrum: 106 (M^+, 2), 78 (8), 60 (3), 59 (100), 57 (5), 47 (8), 45 (5), 44 (12), 43 (4), 42 (21), 41 (17); m* 37.1, 32.8, 29.9. The picrolonate had mp 208-209°C (dec.). Found: C 42.3; H 4.8; N 22.6; S 8.4%. $C_3H_{10}N_2S \cdot C_{10}H_8N_4O_5$. Calculated: C 42.2; H 4.9; N 22.7; S 8.6%. The hydrochloride was extremely hygroscopic.

2-Hydrazinoethanethiol (II) was similarly obtained in 61% yield. Its constants and the ^{1}H NMR spectrum obtained from its isopropylidene derivative IIIa were in agreement with the constants and spectrum described in [2].

5-Methylperhydro-1,3,4-thiadiazine (IVb). A flask equipped with a Dean–Stark adapter was charged with 5.2 g (0.049 mole) of hydrazino thiol IIb, 25 ml of benzene, and 1.5 g (0.016 mole) of paraformaldehyde, and the mixture was refluxed for 1.5 h. It was then distilled in vacuo, and the reaction product was crystallized from the minimum amount of hexane. The physicochemical, analytical, and spectral characteristics of perhydrothiadiazine IVb are presented in Tables 1 and 2. The reaction product contained admixed 3-amino-4-methylthiazolidine (VI), the percentage of which in the unrecrystallized preparation reached 50%. Mass spectrum of the impurity: 120 (5), 119 (6), 118 ($M^{+\cdot}$, 100), 117 (4), 103 (17), 75 (7), 74 (17), 73 (6), 72 (70), 71 (8), 60 (10), 59 (9), 58 (4), 57 (32), 56 (60), 55 (4), 47 (17), 46 (12), 45 (24), 44 (31), 43 (20), 42 (9), 41 (44); m* 89,9, 43.7, 37.1.

Pinacolone (2-Mercapto-1-methylethyl)hydrazone (IIIi, Tables 1 and 2). This compound was similarly obtained (after refluxing for 17 h).

2,5-Dimethylperhydro-1,3,4-thiadiazine (IVc). A 4.0-g (0.09 mole) sample of acetaldehyde was added with stirring and cooling with water in the course of 15 min to a solution of 9.2 g (0.087 mole) of hydrazino thiol IIb in 30 ml of benzene, and the mixture was maintained at room temperature for 1 h. It was then refluxed for 1 h, after which the organic layer was separated, dried with sodium sulfate, and distilled. The reaction product was recrystallized from hexane.

Compounds IVd and IVe were similarly obtained (Tables 1 and 2).

2,2,5-Trimethylperhydro-1,3,4-thiadiazine (IVf). A 3.5-g (0.06 mole) sample of acetone was added in the course of 15 min with stirring and cooling with water to 5.3 g (0.05 mole) of hydrazino thiol IIb, after which the mixture was maintained at room temperature until spontaneous heating ceased. Benzene (30 ml) was then added, and the mixture was refluxed for 2 h. The organic layer was separated, dried with sodium sulfate, and distilled.

Compounds IVg and IIIj were similarly obtained (Tables 1 and 2).

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