REACTIVITY AND STEREOCHEMICAL STRUCTURE OF 4-HYDROXY- AND 4-ALKOXYHEXAHYDROPYRIMIDINE-2-THIONES

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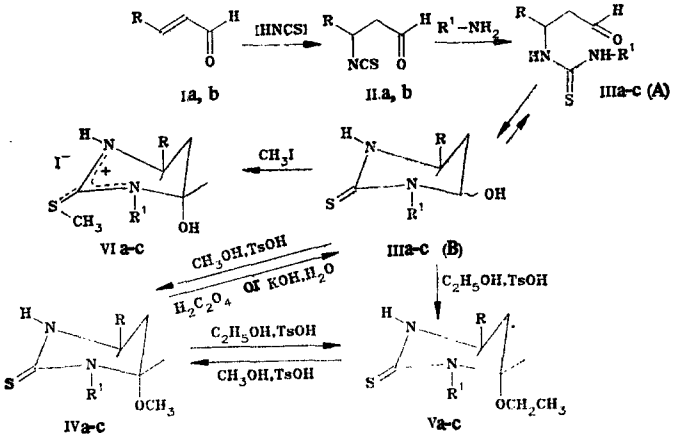
Substituted 4-hydroxyhexahydropyrimidine-2-thiones were obtained by the reaction of β-isothiocyanatoaldehydes with ammonia or methylamine. When heated with alcohols in the presence of p-toluenesulfonic acids, the synthesized compounds gave the corresponding 4-alkoxyhexahydropyrimidine-2-thiones, which were converted into other 4-alkoxy derivatives by the action of the respective alcohols and were hydrolyzed to the initial 4-hydroxyhexahydropyrimidine-2-thiones by the action of an aqueous solution of oxalic acid or potassium hydroxide. The reaction of the 4-hydroxyhexahydropyrimidine-2-thiones with methyl iodide led to the formation of 2-methylthio-4-hydroxy-3,4,5,6-tetrahydropyrimidine hydriodides. It was shown by PMR spectroscopy that the stereoisomers in which the hydroxyl (or alkoxyl) group has the axial orientation are thermodynamically more stable.

4-Hydroxyhexahydropyrimidine-2-thiones, which are readily formed during the reaction of β-isothiocyanatocarbonyl compounds with amines [1, 2] or by the addition of substituted thioureas to α,β-unsaturated carbonyl compounds [3, 4], have been the subject of intensive researches. This is due to the specific reactivity of these compounds, brought about both by the possibility of their conversion into acyclic systems (ring–chain isomerism) [2, 5] and by the presence of several reactive functional groups in their molecules. 1,2,3,6-Tetrahydropyrimidine-2-thiones [4,6], 2-methylthio-4-hydroxy-3,4,5,6-tetrahydropyrimidines [7], 2-alkyl(aryl)amino-4H-1,3-thiazines [8], 4-alkyl(aryl)amino-1,2,5,6-tetrahydropyridine-2-thiones [9, 10], and various condensed heterocyclic compounds [9, 11] have been obtained from 4-hydroxyhexahydropyrimidine-2-thiones.

Investigation of the reactivity of the "semiaminal" hydroxyl group at the $C_{(4)}$ carbon atom of the ring in the 4-hydroxyhexahydropyrimidine-2-thione molecules merits special attention. There are only fragmentary data in the literature on the substitution of this group by the action of certain nucleophilic reagents and, in particular, hydroxylamine and phenylhydrazine [4]. However, systematic investigation of the chemical behavior of the "semiaminal" fragment of the 4-hydroxyhexahydropyrimidine-2-thione molecules has not so far been undertaken, and there are no published data on the stereochemical structure of functionally 4-substituted hexahydropyrimidine-2-thiones. The present work was devoted to the solution of these problems.



I–VI a R=H, b R=CH_3; III–VI a, b R^1=H; c R=R^1=CH_3

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TABLE 1. The Characteristics of Compounds IIIa-c to VIa-c

Compound	mp,[a] °C	UV spectrum[b] λ_{max}, nm (lg ε)	Found, %				Molecular formula	Calculated, %				R_f	Yield, %[c]
			C	H	N(I)	S		C	H	N(I)	S		
IIIa	138—138,5	245 (4,13)	—	—	—	24,4	$C_4H_8N_2OS$	—	—	—	24,3	0,18	48,2
cis-IIIb	138,5—139,5	246 (4,19)	41,1	7,0	—	21,8	$C_5H_{10}N_2OS$	41,1	6,9	—	21,9	0,31	87
trans-IIIb	138—138,5	247 (4,21)											
cis-IIIc	147—147,5	247 (4,20)	—	—	17,7	20,1	$C_6H_{12}N_2OS$	45,0	7,6	17,5	20,0	0,40	80,5
trans-IIIc	146,5—147,5 (143—144 [2])	247 (4,20)	45,0	7,9	17,6	—							
IVa	133—133,5	247 (4,16)	41,2	6,6	19,2	21,9	$C_5H_{10}N_2OS$	41,1	6,9	19,2	21,9	0,24	89,5
IVb	164—165	247 (4,20)[d]	45,1	7,7	17,3	20,4	$C_6H_{12}N_2OS$	45,0	7,6	17,5	20,0	0,47	85,2
IVc	126,5—128	248 (4,19)	—	—	16,4	18,3	$C_7H_{14}N_2OS$	—	—	16,1	18,4	0,35	80,0
Va	145,5—146	245 (4,18)	—	—	—	20,0	$C_6H_{12}N_2OS$	—	—	—	20,0	0,43	77,5
Vb	163,5—164	247 (4,18)	—	—	16,5	18,0	$C_7H_{14}N_2OS$	—	—	16,1	18,4	0,59	82,3
Vc	138—139	248 (4,17)	50,9	8,9	—	17,1	$C_8H_{16}N_2OS$	51,0	8,6	—	17,0	0,45	75,0
VIa	116—117,5	221 (4,30)	—	—	10,0	11,9	$C_5H_{10}N_2OS \cdot HI$	—	—	10,2	11,7	—	68,2
VIb	122,5—123,5	220 (4,36)	—	—	(44,0)	11,1	$C_6H_{12}N_2OS \cdot HI$	—	—	(44,0)	11,1	—	87,5
VIc	144,5—145	222 (4,36)	—	—	—	10,2	$C_7H_{14}N_2OS \cdot HI$	—	—	—	10,6	—	90,7

Note. a) Compounds (IIIa, trans-IIIb, IVa, b) were crystallized from acetone; cis-(IIIb), cis- and trans-(IIIc), and (IVc) from methanol; (Va-c) from ethanol. b) The band of the $\pi \rightarrow \pi^*$ transition. c) For compounds (IIIa-c), starting from compounds (IIa, b); for (IV to VIa-c), starting from (IIIa-c). d) λ_{max} 255 (in acetonitrile), 258 (in ether), 254 nm (in dioxane).

4-Hydroxyhexahydropyrimidine-2-thiones (IIIa-c) are formed in the reaction of 3-isothiocyanatopropanal (IIa) with ammonia and of 3-isothiocyanatobutanal (IIc) with ammonia or methylamine in ether at 0°C. The β-isothiocyanatoaldehydes (IIa,b) in turn are obtained by the addition of thiocyanic acid to the multiple bonds of acrolein (Ia) or crotonaldehyde (Ib). It should be noted that the yield of (IIIa), obtained from isothiocyanatopropanal (IIa), is not greater than 50%. This is clearly due to the presence of a significant amount (up to 30%) of the isomeric addition product 3-cyanatopropanal in compound (IIa) [12].

Compounds (IIIa-c) can exist in two isomeric forms, i.e., the acyclic form of the oxoalkylthioureas (A) and the cyclic form of 4-hydroxyhexahydropyrimidine-2-thiones (B). By IR and PMR spectroscopy it was established that compounds (IIIa-c) have the cyclic structure B exclusively both in the crystalline state in solutions. Thus, the IR spectra of (IIIa-c) do not contain a band for the stretching vibrations of the carbonyl group of the acyclic form A. In the PMR spectra of solutions of the pyrimidines (IIIa, b) in DMSO-D_6 there are signals for three mobile protons, i.e., two signals for the protons of the N—H groups in the downfield region (7.6-8.4 ppm) and signals for the proton of the O—H group (a doublet, δ 5.7-5.8 ppm). In the PMR spectra of (IIIc) there is a singlet for the proton of the N—H group and a doublet for the proton of the O—H group. In addition, the PMR spectra of (IIIa-c) do not contain signals for the aldehyde proton of the acyclic isomers (IIIA).

During investigation of the stereochemical structure of the molecules of the thiones (IIIa-c) we started from published data [13], in which the crystal structure of hexahydropyrimidine-2-thione was studied by x-ray crystallographic analysis. It was shown that the thioamide group is planar but the $C(_4)$, $C(_5)$, and $C(_6)$ carbon atoms do not lie in the same plane, so that the six-membered ring approximates to a chair form.

We established that a mixture of two diastereomeric products (IIIb, c) with the cis and trans arrangement of the 4-OH and 6-CH_3 groups is formed in the reaction of (IIb) with ammonia or methylamine in ether at 0°C (see below). The cis and trans stereoisomers of compounds (IIIb, c) are easily separated by crystallization from methanol. The cis stereoisomers are thermodynamically less stable and readily change into the corresponding trans isomers when heated in various solvents (water, acetone). The analogous transformation into the individual trans isomers takes place when a mixture of the cis and trans stereoisomers of (IIIb, c) is heated in water. Thus, we have obtained individual cis and trans isomers of (IIIb, c), the constants and spectral parameters of which are given in Tables 1 and 2.

On the basis of the high value (8.6-12.0 Hz) of one of the spin—spin coupling constants of the 6-H proton with the 5-H protons (Table 2) in the PMR spectra of the cis and trans isomers of (IIIb) we concluded that the methyl group at the $C(_6)$ atom of the ring has the equatorial orientation. The 4-H protons in the PMR spectra of (IIIa) and the trans stereoisomers of (IIIb, c) in DMSO-D_6 + D_2O solution appear in the form of a triplet (1:2:1), the distance between the end lines of which is 5-6 Hz. This indicates that the spin—spin coupling constants of the 4-H proton with the 5-H protons have low and approximately equal values which indicates the axial orientation for the hydroxyl groups in the molecules of (IIIa) and trans-(IIIb, c). This conclusion is confirmed by examination of the multiplets of the signals for the 5-H_a and 5-H_e protons (doublets of quartets). On the other hand, in the PMR spectra of the cis isomers of (IIIb,c) the 4-H protons give a quartet with spin—spin coupling constants J_{45} of 4.5-4.9 and 6.5-7.2 Hz. From this follows that the hydroxyl group in the molecules of compounds cis-(IIIb,c) has the equatorial orientation.

Thus, the most stable in the series of investigated compounds are the stereoisomers with the axial orientation of the hydroxyl group at the $C(_4)$ position of the ring. This evidently results from the appearance of the anomeric effect in the $N(_3)$—C—OH system [14, 15].

The specific reactivity of the hydroxyl group in compounds (IIIa-c) was studied for the case of their reaction with alcohols. When solutions of compounds (IIIa-c) in alcohols (methanol, ethanol) were boiled in the presence of p-toluenesulfonic acid, the corresponding 4-methoxyhexahydropyrimidine-2-thiones (IVa-c) and 4-ethoxyhexahydropyrimidine-2-thiones (Va-c) were formed with yields of 75-90% (Table 1). It should be noted that identical products are formed from the cis and trans isomers of (IIIb,c). The obtained methoxy and ethoxy derivatives are converted into each other when boiled in the respective alcohol in the presence of p-toluenesulfonic acid. According to the data from the PMR spectra (Table 2), we established that all the synthesized 4-alkoxyhexahydropyrimidine-2-thiones (IVa-c, Va-c) have

the axial orientation of the alkoxy group (spin–spin coupling constants J_{45} 2-3 Hz). It is known [16] that the nature and polarity of the solvent have a large effect on the magnitude of the anomeric effect. However, in the PMR spectra of (IVa) in various solvents (benzene-D_6, acetone-D_6, pyridine-D_5, DMSO-D_6, methanol-D_4) no spectral indications of a conformer with an equatorial ethoxy group were found.

When solutions of the thiones (IVa-c) were heated in water in the presence of potassium hydroxide or oxalic acid, the alkoxy groups were readily exchanged by a hydroxyl group with the formation of compounds (IIIa) or trans-(IIIb, c) (with yields of up to 80%).

The transformations described above evidently take place by a nucleophilic substitution mechanism at the $C(_4)$ electrophilic center.

In the reaction of (IIIa-c) with methyl iodide in acetone at 20°C the corresponding 2-methylthio-4-hydroxy-3,4,5,6-tetrahydropyrimidine hydriodides (VIa-c) are formed, while the cis and trans stereoisomers of (IIIb,c) give one and the same product. According to PMR spectroscopy (Table 2), the hydroxyl group in the molecules of (VIa-c) has the axial orientation.

The UV spectra of compounds (IIIa-c to Va-c) contain two strong absorption bands with maxima in the regions of 206–210 (log ε 3.9–4.1) and 245–247 nm (log ε 4.13–4.21). On the basis of published data [17] we assigned the low-frequency absorption band to the π–π* transition of the thioureide chromophore. For the case of 6-methyl-4-methoxyhexahydropyrimidine-2-thione (IVb) it was shown that change in the dielectric constant of the solvent has little effect on the position of the low-frequency absorption band. At the same time, the nature of the spectrum is strongly affected by the transition from an aprotic to a protic solvent (Table 1). Thus, the transition from acetonitrile to methanol shifts the band of the π–π* transition toward short wavelengths by 8 nm, which agrees well with published data on the nature of the effect of the solvent on this band [18].

In the UV spectra of compounds (VIa-c) in the region of 220–222 nm there is a strong absorption band due to the $\pi \rightarrow \pi^*$ transition of the thiouronium chromophore [18].

In the IR spectra of compounds (IIIa-c to VIa-c) in the region of 3000–3600 cm^{-1} there are broad bands for the stretching vibrations of the N–H and O–H groups, while in the range of 1500–1600 cm^{-1} for compounds (IIIa-c to Va-c) there are two strong absorption bands due to the vibrations of the atoms of the thioureide fragment of the molecules.† On the basis of published data [19] we assigned the low-frequency band (1520-1550 cm^{-1}) to the $\nu_{as}CN$ vibration and the high-frequency band (1530–1580 cm^{-1}) to the mixed vibration $\delta_S NH + \nu_S CN$. In the spectra of compounds (VIa-c) the indicated vibrations appear in the regions of 1603–1610 and 1532–1571 cm^{-1} respectively. The short-wave shift of the maximum of the $\nu_{as}CN$ band is clearly due to the increase in the orders of the $C(_2)–N(_1)$ and $C(_2)–N(_3)$ bonds in compounds (VIa-c) compared with compounds (IIIa-c to Va-c).

EXPERIMENTAL

The IR spectra were recorded for suspensions in Vaseline oil on a UR-10 instrument. The UV spectra were recorded on a Specord UV-vis spectrometer. The PMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker HX-90E (90 MHz) spectrometers with HMDS as internal standard. Thin-layer chromatography was performed on Silufol UV-254 plates in the 3:2 ether–acetone system, and the spots were detected with iodine vapor.

4-Hydroxyhexahydropyrimidine-2-thione (IIIa). A. To a solution of 3.62 g (31.4 mmoles) of the freshly distilled compound (IIa) [2] in 50 ml of dry ether, while stirring, at 0°C we added 50 ml of an ether solution of ammonia saturated at 0°C. Dry ammonia was passed into the obtained mixture until the crystalline product had been completely precipitated. The precipitate was washed three times with ether by decantation, filtered off, and washed on the filter with a small amount of cold acetone and with ether. We obtained 3.13 g of the technical product, which was dissolved in boiling acetone (~600 ml). The solution was decolorized with activated charcoal. After filtration the solution was evaporated to 20 ml and cooled, and the crystals were filtered off. We obtained 2.00 g (48.2%) of (IIIa).

B. A mixture of 1.107 g (7.57 mmoles) of (IVa), 0.224 g (3.99 mmoles) of potassium hydroxide, and 11 ml of water was heated on a water bath at 90°C for 3 h. The solution was cooled

†Three absorption bands are observed in this region of the spectrum for trans-(IIIb), and four bands are observed for (IIIa).

TABLE 2. The IR and PMR Spectra of Compounds (IIIa-c-VIa-c)

Compound	IR spectrum,[a] cm^{-1}	PMR Spectra[b], δ, ppm (SSCC, Hz)						
		4-H ($J_{4,5e}$; $J_{4,5a}$)	5-H_a ($J_{5a,6a}$)	5-H_e ($J_{5e,5a}$)	6-H ($J_{5e,6a}$)	6-CH_3 ($J_{CH_3,6a}$)	N—H	Other signals
IIIa	1540, 1553, 1572, 1585, 3252, 3312	4,72 (Σ=5,2)	1,45—1,83		2,93—3,30	—	8,15, 8,32	5,83 (OH, J=3)
cis-IIIb	1540, 1556, 3240, 3320	4,77 (4,5; 7,2)	1,41 (8,6)	1,94 (12,9)	3,38 (4,5)	1,14 (6,3)	7,64, 7,83	5,73 (OH, J=5,9)
trans-IIIb	1539, 1557, 1566, 3234, 3315	4,71 (2,4; 3,1)	1,29 (12,0)	1,75 (13,1)	3,48 (3,8)	1,13 (6,5)	8,16, 8,39	5,83 (OH, J=5,6)
cis-IIIc	1522, 1535, 3134, 3230[c]	4,86 (4,9; 6,5)	1,61 (8,8)	2,09 (13,2)	3,40 (4,9)	1,13 (6,7)	8,04	3,17 (N—CH_3); 6,26 (OH, J=7,1)
trans-IIIc	1523, 1536, 3215, 3317	4,81 (2,4; 3,2)	1,48 (11,9)	1,84 (13,4)	3,50 (3,6)[d]	1,12 (6,8)	8,11	3,22 (N—CH_3); 6,33 (OH, J=5,6)
IVa	1543, 1582, 3245	4,44 (2,1; 3,0)	1,71 (13,0)	1,97 (13,5)	3,16—3,42[d] (4,2)	— $J_{5e,6e}$=2,1	— $J_{5a,6e}$=6,0	3,33 (O—CH_3)
IVb	1536, 1570, 3235	4,49 (2,1; 3,1)	1,43 (12,1)	1,98 (13,1)	3,57 (3,7)	1,29 (6,4)	7,38, 8,09 $J_{NH,4e}$=4,5	3,30 (O—CH_3)
IVc	1518, 1531, 3238	4,53 (2,4; 2,6)	1,47 (12,4)	2,12 (13,5)	3,53 (3,6)	1,19 (6,2)	—	3,36 (N—CH_3); 3,38 (O—CH_3)
Va	1530, 1582, 3212	4,48 (Σ=4,4)	1,45—2,05		3,05—3,74[e]	—	—	1,12 (CH_3, J=7); 3,05—3,74[e] (—OCH_2)
Vb	1538, 1575, 3200	4,56 (2,3; 2,9)	1,47 (11,9)	2,03 (13,3)	3,66 (3,8)	1,27 (6,6)	—	1,22 (CH_3 in —OC_2H_5, J=7); 3,49 & 3,73 (H_A and H_B in — OCH_2, J_{AB}=9,3)
Vc	1522, 1535, 3224	4,62 (2,4; 2,7)	1,48 (12,2)	2,10 (13,4)	3,56 (3,7)	1,19 (6,3)	—	1,19 (CH_3 in —OC_2H_5, J=6,9); 3,35 (N—CH_3); 3,58 & 3,60 (H_A & H_B in—OCH_2)
VIa	1552, 1610, 3190	5,01 (Σ=5,4)	1,60—2,05		3,10—3,67	—	10,1	2,57 (S—CH_3); 6,76 (OH, J=4)
VIb	1571, 1604, 3200	4,97 (2,6; 2,9)	1,56 (11,1)	1,93 (13,5)	3,69 (3,6)	1,27 (6,4)	9,9	2,62 (S—CH_3); 6,68 (OH, J=4,2)
VIc	1532, 1603, 3213	4,94 (2,8; 2,7)	1,73 (12,4)	2,03 (13,7)	3,69 (3,8)	1,33 (6,6)	—	2,70 (S—CH_3); 3,20 (N—CH_3)

Note. a) Compounds (IIIa, Va) were recorded in tablets with potassium bromide, the remaining compounds in Vaseline oil. b) Solvent DMSO-D_6 for (IIIa-c, VIa, b), deuteromethanol for (IVa, c, Vb, c), acetone-d_6 for (IVb), mixture of DMSO-D_6 and D_2O for (Va, VIc). c) The spectrum was recorded on a Specord 71IR instrument. d) The signals overlap with the signals from the solvent and the O—CH_3 group. e) The signals overlap with each other.

to 20°C, neutralized to pH 8 with dilute hydrochloric acid, and evaporated to dryness. The crystalline precipitate was dissolved by heating in 200 ml of acetone. Activated charcoal was added, the mixture was stirred for 5-10 min, and it was then filtered through a layer of activated charcoal (0.5 cm). The solution was concentrated until crystallization began. The crystals were filtered off, and 0.546 g of (IIIa) was obtained. A further 0.087 g of the compound was obtained from the mother solutions. The total yield amounted to 63.1%.

C. A mixture of 0.982 g (6.72 mmoles) of (IVa), 0.099 g (0.786 mmoles) of oxalic acid dihydrate, and 10 ml of water was heated on a water bath at 90°C for 2.5 h. The solution was cooled to 20°C and neutralized to pH 8 with dry sodium bicarbonate. The mixture was then treated as in method B. We obtained 0.700 g (78.9%) of (IIIa).

6-Methyl-4-hydroxyhexahydropyrimidine-2-thione (IIIb). To 180 ml of dry ether, saturated with ammonia at 0°C, we added with stirring at 0°C a solution of 15.0 g (0.116 mole) of freshly distilled compound (IIb) [2] in 10 ml of ether. Ammonia was passed through the obtained mixture until the product was completely precipitated. The ether was decanted, and the precipitate was treated twice with fresh portions of dry ether. The crystals were filtered off and washed with acetone and with ether. We obtained 14.76 g (87%) of a mixture of the cis and trans isomers of (IIIb) (1:1). The individual cis and trans isomers were isolated by crystallization of the mixture from methanol, where compound cis-(IIIb) mainly separated from the solution and the pure compound trans-(IIIb) remained in solution. The pure compound cis-(IIIb) was obtained by recrystallization two or three times.

The trans isomer of (IIIb) was also obtained in the following way.

A. A solution of 15.1 g (0.103 mole) of the mixture of cis and trans isomers of (IIIb), formed as a result of the reaction of the isothiocyanatoaldehyde (IIb) with ammonia [the pure cis stereoisomer of (IIIb) can be used] in 250 ml of water, was heated at 95°C for 1.5 h. The solution was filtered and concentrated to 20 ml. The precipitate was filtered off, washed on the filter with water, and dried. We obtained 10.9 g (72.2%) of trans-(IIIb).

B. The compound was obtained by the hydrolysis of the methoxy derivative (IVb) with water with a yield of 79.4% in the presence of potassium hydroxide or with a yield of 71.3% in the presence of oxalic acid similarly to the production of compound (IIIa) by methods B and C respectively. In both cases 20-40% of methanol was added for initial homogenization of the reaction mixture.

3,6-Dimethyl-4-hydroxyhexahydropyrimidine-2-thione (IIIc). To a solution of 0.991 g (7.67 mmoles) of (IIb) in 3 ml of dry ether, while stirring at 0°C, we added dropwise 10 ml of ether saturated with methylamine at 0°C. The reaction mixture was kept for 30 min, and the precipitate was filtered off and washed with ether. We obtained 0.988 g (80.5%) of a mixture of the cis and trans isomers of (IIIc) in a ratio of 1:1. The individual stereoisomers were isolated as described for (IIIb).

4-Methoxyhexahydropyrimidine-2-thione (IVa). A. A solution of 0.10 g (0.76 mmole) of (IIIa) in 4 ml of anhydrous methanol, containing a crystal of p-toluenesulfonic acid, was boiled for 4 h. The solvent was removed, and the crystals were dissolved in 4 ml of anhydrous methanol and again boiled for 1 h (TLC). The solution was filtered and evaporated to dryness. The crystals were washed with dry ether. We obtained 0.099 g (89.5%) of compound (IVa), which we recrystallized from acetone or methanol.

Compounds (IVb, c) were obtained by a similar method.

When ethanol was used in place of methanol and the reaction time was increased to 8-10 h (TLC), the corresponding 4-ethoxy derivatives (Va-c) were obtained from (IIIa-c) with yields of up to 80%. They were purified by recrystallization from ethanol.

B. A solution of 0.192 g (1.20 mmoles) of (Va) in 5 ml of anhydrous methanol, containing two crystals of p-toluenesulfonic acid, was boiled for 3 h. The solvent was removed, and the crystals were dissolved in 5 ml of methanol and again boiled for 1 h. The solution was evaporated, and the residue was crystallized from 1 ml of methanol. We obtained 0.138 g (78.6%) of (IVa).

Compounds (IVb, c) were obtained similarly.

In the reaction of the methoxypyrimidines (IVa-c) with ethanol by the method described above (total reaction time 7-10 h) the corresponding 4-ethoxy derivatives (Va-c) were obtained with yields of up to 85%.

2-Methylthio-4-hydroxy-3,4,5,6-tetrahydropyrimidine Hydriodide (VIa). To a mixture of 75 mg (0.57 mmole) of (IIIa) and 1 ml of acetone we added 0.16 ml of methyl iodide. The mixture was left at 20°C for 24 h. The crystals were filtered off and washed with acetone, and 106 mg (68.2%) of (VIa) was obtained.

Compounds (VIb, c) were obtained by a similar method.

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