NUCLEOPHILIC SUBSTITUTION AT THE $C_{(4)}$ ATOM IN SERIES OF FUNCTIONALLY 4-SUBSTITUTED HEXAHYDROPYRIMIDINE-2-THIONES. SYNTHESIS OF 4-ALKYLTHIOHEXAHYDROPYRIMIDINE-2-THIONES

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Nucleophilic substitution at the $C_{(4)}$ atom in 4-hydroxy(alkoxy)hexahydropyrimidine-2-thiones under the influence of alkanethiols in acidic, neutral, and basic media, as a result of which 4-alkylthiohexahydropyrimidine-2-thiones are formed, was studied. Hydrolysis and alcoholysis of the latter lead to the corresponding 4-hydroxy- or 4-alkoxyhexahydropyrimidine-2-thiones. The three-dimensional structures of the 4-alkylthiopyrimidines obtained were established by PMR spectroscopy, and it was shown that the stereoisomers with an axially oriented alkylthio group are thermodynamically more stable.

The specific reactivities of functionally 4-substituted hexahydropyrimidine-2-thiones [1], which are due to the mutual effect of the functional groups in their molecules, compelled us to continue the study of nucleophilic substitution reactions at the $C_{(4)}$ atom of the pyrimidine ring. In the present communication we describe the reaction of 4-hydroxyhexahydropyrimidine-2-thiones I and 4-alkoxyhexahydropyrimidine-2-thiones II with alkanethiols and the reactivities of the resulting 4-alkylthiohexahydropyrimidine-2-thiones III.

4-Ethylthiohexahydropyrimidine-2-thiones IIIa, c, e and 4-butylthiohexahydropyrimidine-2-thiones IIIb, d are formed in 88-97% yields in the reaction of Ia-c with ethanethiol or butanethiol in hydrochloric acid (over the concentration range 4-36%).

We carried out the analogous mercaptolysis of 4-alkoxypyrimidines II in the case of the reaction of butanethiol with 4-methoxyhexahydropyrimidine-2-thione (IIa) and with 6-methyl-4-methoxyhexahydropyrimidine-2-thione (IIb), as a result of which IIIb, d, respectively, were obtained in 95-97% yields.

The increased electrophilicity of the $C_{(4)}$ atom, which is characteristic for 4-hydroxy- and 4-alkoxypyrimidines I and II [1], is also retained in 4-alkylthiopyrimidines IIIa-e; we observed this in a study of reactions involving the replacement of the alkylthio group in IIIa-e by hydroxy and alkoxy groups. Thus hydroxypyrimidine Ib is formed in 93% yield when pyrimidine IIIc is heated with water in the presence of p-toluenesulfonic acid; 4-methoxypyrimidines IIa, b or 4-ethoxypyrimidine IIc are obtained in 50-89% yields when IIIa, c, d are refluxed with methanol or IIIc is refluxed with ethanol in the presence of TsOH.

The replacement of the functional groups attached to the $C_{(4)}$ atom in I-III in an acidic medium evidently proceeds through the formation of immonium cations IVa-c [2], which then add a nucleophilic molecule of mercaptan, alcohol, or water.

The mercaptolysis of hydroxypyrimidines I also proceeds in a neutral aqueous medium, although at a lower rate than in the presence of acid. Thus 4-butylthiopyrimidine IIId is formed in only 23% yield when Ib is heated in water with butanethiol for 11 h, while the analogous reaction in the presence of acid proceeds in 20 min, and the yield of IIId is 97%. Hydrolysis and alcoholysis of the alkylthiopyrimidines also occur in a neutral medium; in the latter case the reaction times and the degree of conversion of III depend on the nature of the substrate and the alcohol used, which determines the alcoholysis temperature. For example, in the case of refluxing in methanol of IIIc the degree of conversion of the latter to pyrimidine IIb after 20 h is ~50%; the analogous reaction of IIIc in refluxing ethanol is complete after 8 h (the yield of IIc is 98%). In the reaction of 4-butylthiopyrimidine

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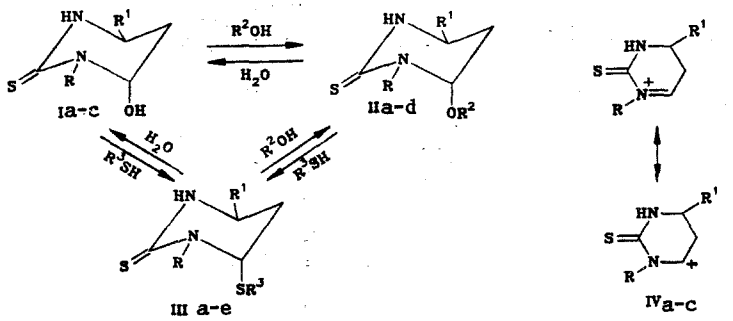
IIId with refluxing methanol for 20 h the degree of conversion of IIId to pyrimidine IIb is insignificant; this is evidently explained by the low volatility of the resulting butanethiol.



Ia, IIa, IIIa,b IVa R=R¹=H; Ib IIb,c IIIc,d IVb R=H, R¹=CH₃; Ic IId,e IIIe IVc R=R¹=CH₃; IIa,b,d R²=CH₃; c,e R²=C₂H₅; IIIa,c,e R³=C₂H₅; b,d R³=*n*-C₄H₉

The fact of the occurrence of nucleophilic substitution reactions at the $C_{(4)}$ atom in I-III in basic media, as we have previously shown in the case of the aqueous alkaline hydrolysis of 4-alkoxypyrimidines II [1], was interesting. We established that alkylthiopyrimidines IIIa-d are formed in 30-78% yields when aqueous solutions of hydroxypyrimidines Ia, b are heated with ethanethiol or sodium butanethiolate for 30 min. A further increase in the reaction time has virtually no effect on the yields of alkylthiopyrimidines. The yields of IIIa-d correlate with their polarities; thus the highest yield (78%) is observed for the least polar (and the least soluble in water) IIId, while the lowest yield (30%) is observed for the most polar (the most soluble) IIIa. According to the TLC data, in all cases of mercaptolysis of Ia, b the reaction mixture contains, in addition to the corresponding alkylthiopyrimidines IIIa-d, only unchanged starting hydroxypyrimidines Ia, b. Thus an equilibrium process, the degree of shifting of which to favor the reaction products evidently depends on the solubility of the latter in water, occurs under the indicated mercaptolysis conditions.

As we have demonstrated in the case of Ib, the reaction with sodium butanethiolate also proceeds in an aqueous dioxane (1:1) medium and in ethanol; in the latter case a mixture (1:1) of IIId and 4-ethoxypyrimidine IIc is formed.

4-Alkoxypyrimidines II also undergo mercaptolysis in basic media (under the influence of thiolate anions). Thus alkylthiopyrimidines IIIb, d are formed in 63% and 78% yields, respectively, when IIa, b are heated with sodium butanethiolate.

4-Alkylthiopyrimidines IIIa-d, in turn, undergo hydrolysis when they are refluxed in an aqueous alkali medium, as well as alcoholysis under the influence of alcohols in the presence of the corresponding alkoxide anions, with the formation of hydroxy- or alkoxypyrimidines I and II.

Methanolysis of hydroxypyrimidine Ib with the formation of IIb also proceeds on basic media (in the presence of sodium hydroxide or methoxide).

Thus we have observed that $N_{(3)}$-unsubstituted 4-hydroxy-, 4-alkoxy-, and 4-alkylthiopyrimidines in basic media are capable of interconversion under the influence of the corresponding nucleophilic reagent; poor leaving groups such as OR, OH, and SR undergo substitution in this case.

At the same time, we have established that the reactivities of pyrimidines Ic, IId, and IIIe, which have a methyl group attached to the $N_{(3)}$ atom, are substantially decreased. Thus, 4-ethylthiopyrimidine IIIe is formed in only 11% yield when Ic is heated with sodium ethanethiolate in water for 6 h, while methanolysis of Ic under the influence of a solution of sodium hydroxide in methanol does not occur. In the alkaline hydrolysis of alkoxypyrimidine IId in water in the presence of potassium hydroxide at 94°C the degree of its conversion to hydroxypyrimidine Ic after 10 h is 20%, while under similar conditions IIb is virtually completely converted to hydroxypyrimidine Ib in 1h.

The significant decrease in the reaction rate for $N_{(3)}$-methyl-substituted pyrimidines is difficult to explain within the framework of a classical S_N2 mechanism, since in these compounds the electrophilicity of the $C_{(4)}$ atom and the steric factors that hinder substitution evidently change little as compared with the $N_{(3)}$-unsubstituted analogs. Thus, for example, in the PMR spectra of $N_{(3)}$-substituted pyrimidines Ic, IId, e, and IIIe one observes

TABLE 1. Characteristics of 4-Alkylthiohexahydropyrimidine-2-thiones IIIa-e

Compound	mp, °C (from acetone)	UV spectrum (in methanol), λ_{max}, nm (log ε)	IR spectrum, cm^{-1}	Found, %				Empirical formula	Calculated, %				Yield, %	
				C	H	N	S		C	H	N	S	B	D
IIIa	152—153	208 (4,00), 250 (4,17)	1200, 1293, 1533, 1559, 1570, 3190	40,1	6,5	15,6	36,1	$C_6H_{12}N_2S_2$	40,9	6,9	15,9	36,4	88	30
IIIb	144,5—145	209 (4,01), 250 (4,18)	1205, 1298, 1303, 1543, 1559, 3193	47,1	8,1	13,5	—	$C_8H_{16}N_2S_2$	47,0	7,9	13,7	—	90	58
IIIc	170,5—172	208 (4,01), 251 (4,19)	1198, 1303, 1522, 1563, 3160	44,2	7,3	14,7	34,0	$C_7H_{14}N_2S_2$	44,2	7,4	14,7	33,7	96	53
IIId	164—165	209 (4,01), 251 (4,19)	1191, 1305, 1523, 1565, 3220	49,5	8,1	—	28,8	$C_9H_{18}N_2S_2$	49,5	8,3	—	29,4	97	78
IIIe	158—159	210 (4,02), 251 (4,19)	1193, 1284, 1507, 1525, 3223	46,5	7,8	13,8	—	$C_8H_{16}N_2S_2$	47,0	7,9	13,7	—	97	11

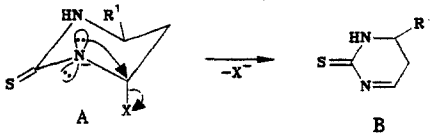
TABLE 2. PMR Spectra of 4-Alkylthiohexahydropyrimidine-2-thiones IIIa-e

Compound	Chemical shift, δ, ppm (SSCC, Hz)											
	4-H ($J_{4e,5e}$; $J_{4e,5a}$)	5-H_a ($J_{5a,6a}$)	5-H_e ($J_{5e,5a}$)	6-H_a ($J_{5e,6a}$)	6-H_e ($J_{6e,6a}$)	6-CH_3 ($J_{CH_3,6a}$)	$N_{(1)}$—H ($J_{NH,6a}$)	$N_{(3)}$—H ($J_{NH,4e}$)	SCH_2 ($J_{CH_2,CH}$)	CH_3 in SR	other signals	solvent
IIIa	4,61 (3,1; 4,4) ($J_{4e,6e}$=1,2)	2,07 (10,6) ($J_{5e,6e}$=3,7)	1,98 (13,5) ($J_{5a,6e}$=4,9)	3,43 (4,8)	3,20 (12,5)	—	—	—	2,64 (7,3)	1,26	—	CD_3OD
IIIb	4,59 (3,0; 4,4) ($J_{4e,6e}$=1,2)	2,06 (10,6) ($J_{5e,6e}$=3,8)	1,98 (13,5) ($J_{5a,6e}$=4,9)	3,43 (4,7)	3,23 (12,5)	—	8,20* (~0) ($J_{NH,6e}\approx$3)	8,55* (4,0)	2,63 (7,0)	0,92 (J=7,1)	1,34—1,64 ($-CH_2CH_2-$in$-SC_4H_9$)	CD_3OD
IIIc	4,64 (2,3; 4,3)	1,68 (11,2)	1,97 (13,7)	3,55 (4,3)	—	1,16 (6,8)	8,22 (~0)	8,66 (4,1)	2,65 (7,3)	1,21	—	d_6-DMSO
IIId	4,60 (2,0; 4,2)	1,67 (11,4)	1,96 (13,6)	3,55 (4,3)	—	1,15 (6,5)	8,21 (~0)	8,67 (4,0)	2,63 (7,0)	0,88 (J=6,6)	1,27—1,62 ($-CH_2CH_2-$in$-SC_4H_9$)	d_6-DMSO
IIIe	4,74 (2,6; 3,8)	1,83 (11,2)	2,12 (13,8)	3,62 (3,9)	—	1,16 (6,0)	8,21 (~0)	—	2,65 (7,6)	1,21	3,29 ($N-CH_3$)	d_6-DMSO

*In d_6-DMSO.

only a slight weak-field shift (0.04-0.10 ppm) of the chemical shifts of the 4-H proton as compared with the chemical shifts of the corresponding proton in $N_{(3)}$-unsubstituted pyrimidines Ib, IIb, c, and IIIc (see Table 2 and [1]). The S_N2 mechanism also does not explain the stereochemistry of the investigated substitution reactions in basic media, as a result of which retention of the configuration at the $C_{(4)}$ atom is observed.

On the basis of the information set forth above and taking into account the high acidities of thioureas [3] we assumed that the replacement of the functional groups attached to the $C_{(4)}$ atom in I-III, which do not have a substituent attached to the $N_{(3)}$ atom, in basic media proceeds via a cleavage—addition mechanism with the assistance of the $N_{(3)}$—H group. The reversible detachment of a proton from the $N_{(3)}$ atom under the influence of bases results in the formation of an anion (A) in which one of the unshared pairs of the $N_{(3)}$ atom has an antiperiplanar orientation with respect to the axial substituent attached to the $C_{(4)}$ atom and, acting like a strong internal nucleophile [4], ejects this substituent in the form of an anion; the latter is stabilized by interaction with the proton-donor solvent (water, alcohol). The resulting compressed cyclic imine (B) then adds a nucleophilic molecule with the formation of the thermodynamically more stable substituted hexahydropyrimidines with an axial orientation of the substituent attached to the $C_{(4)}$ atom.



The structures of the synthesized IIIa-e were established on the basis of the set of data from IR, UV, and PMR spectroscopy (Tables 1 and 2).

Two intense absorption bands with maxima at 208-210 (log ε 4.00-4.02) and 250-251 nm (log ε 4.17-4.19) are observed in the UV spectra of alkylthiopyrimidines IIIa-e; we assigned the low-frequency absorption band to a π—π^* transition of the thioureide chromophore [5].

The IR spectra of IIIa-e at 1507-1570 cm^{-1} contain strong thioamide-II absorption bands due to the vibrations of the atoms of the thioureide fragment of the molecules [6]. In addition, a broad band of stretching vibrations of NH groups is observed in the IR spectra of IIIa-e at 3160-3244 cm^{-1} (Table 1).

An analysis of the spin-spin coupling constants (SSCC) of the pyrimidine ring in the PMR spectra of IIIa, b (Table 2), which have one chiral center, shows that in solutions the molecules of these compounds exist in a conformation with an axial orientation of the alkylthio group. This conclusion follows from the low spin-spin constants of coupling of the 4-H proton with the 5a-H and 5e-H protons, which are equal to 4.4 and 3.0 Hz. An additional confirmation of this conclusion is the development of a long-range spin-spin coupling of the 4-H proton with the 6-H_e proton ($J_{4e,6e}$ = 1.2 Hz); this is possible only for the conformer with an equatorial orientation of the 4-H proton [7].

On the basis of the PMR spectroscopic data we established that IIIc-e, which have two chiral centers in their molecules, are produced exclusively in the form of the trans diastereomer with an equatorial orientation of the 6-CH_3 group and an axial orientation of the alkylthio group, i.e., the mercaptolysis of Ib, c and IIb in acidic, neutral, and basic media proceeds stereospecifically. This conclusion follows from the presence in the spectra of only one set of signals of protons, as well as from an analysis of the SSCC of the 4-H, 5-H, and 6-H protons (Table 2).

We propose a method that gives additional evidence for the orientation of the groups attached to the $C_{(4)}$ and $C_{(6)}$ atoms in the molecules of substituted hexahydropyrimidine-2-thiones that is based on an analysis of the SSCC of the $N_{(3)}$—H and 4-H and $N_{(1)}$—H and 6-H protons in the PMR spectra of solutions of I-III in dry d_6-DMSO. The values of these SSCC are close to zero in the case of an axial orientation of the 4-H and 6-H protons and are 3.5-5.0 Hz in the case of an equatorial orientation of these protons. This regularity is explained by the magnitudes of the dihedral angles in the corresponding systems of bonds of the compressed chair conformation of the hexahydropyrimidine-2-thione molecules [8]. In fact, in the PMR spectra of IIIc, d the constant of spin-spin coupling of the $N_{(3)}$—H proton with the 4-H proton is 4.0-4.1 Hz, while the constant of spin-spin coupling of the $N_{(1)}$—H proton with the 6-H proton is zero; this confirms the equatorial orientation of the 4-H proton and the axial orientation of the 6-H proton. In the PMR spectrum of IIIe, which has only one

labile proton attached to the $N_{(1)}$ atom, one observes a singlet signal of this proton; this constitutes evidence for an equatorial orientation of the 6-CH_3 group. We observed similar principles in series of hydroxy- and alkoxypyrimidines I and II. To find the $J_{NH,CH}$ SSCC it is sufficient to examine the region of resonance of the NH protons (8-9 ppm), which lies at very weak field and is not overlapped with the regions of resonance of the other protons; this is an advantage of the proposed method.

Thus the most stable conformers in series of 4-alkylthiohexahydropyrimidine-2-thiones, just as in series of 4-hydroxy- and 4-alkoxyhexahydropyrimidine-2-thiones [1], are the conformers with an axial orientation of the substituent attached to the $C_{(4)}$ atom; we explain this by the manifestation of an anomeric effect in the $N_{(3)}$—$C_{(4)}$—SR system.

A study of the PMR spectra of IIIb in various solvents shows that the nature and polarity of the solvent evidently have little effect on the degree of manifestation of the anomeric effect: we did not detect the spectral features of a conformer with an equatorial orientation of the butylthio group in $CDCl_3$, d_6-acetone, d_4-methanol, and d_6-DMSO.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord 75-IR spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with Bruker WM-250 (250 MHz) and Bruker HX-90E (90 MHz) spectrometers with hexamethyldisiloxane as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates in a chloroform—methanol system (19:1); the spots of the compounds were detected with iodine vapors. The synthesis of the starting 4-hydroxy-(alkoxy)hexahydropyrimidine-2-thiones was described in [1]. Compounds IIIa-e were purified by recrystallization from acetone or acetonitrile.

4-n-Butylthio-6-methylhexahydropyrimidine-2-thione (IIId). A) A 1.28-ml [1.067 g (11.83 mmole)] sample of butanethiol was added to a solution of 0.877 g (6.00 mmole) of Ib in 2.2 ml of concentrated HCl, and the resulting mixture was stirred at 95°C for 15 min. The solution was cooled to 20°C and neutralized with a saturated aqueous solution of sodium carbonate, and the resulting precipitate was removed by filtration, washed with water, and dried to give 1.218 g (93%) of IIId.

B) A mixture of 0.777 g (5.31 mmole) of Ib, 0.691 g (7.66 mmole) of butanethiol, and 3 ml of 3.6% hydrochloric acid was stirred at 93°C. After 2 min, a voluminous white precipitate formed from the solution. The reaction mixture was stirred at this temperature for another 20 min, after which it was cooled, and the precipitate was removed by filtration and washed with cold water to give 1.126 g (97%) of IIId.

Similar methods were used to obtain IIIb, as well as IIIa, c, e; however, in the latter case the reaction was carried out at 28-32°C for 2.5-3 h.

C) Compound IIId was obtained by method B by the reaction of 0.839 g (5.24 mmole) of methoxypyrimidine IIb with 0.659 g (7.31 mmole) of butanethiol in 3 ml of 3.6% hydrochloric acid. The yield was 1.106 g (96.7%).

Compound IIIb was similarly obtained in 95.1% yield from methoxypyrimidine IIa.

D) A 0.551-g (3.77 mmole) sample of hydroxypyrimidine Ib was added to a solution of sodium butanethiolate, obtained by the reaction of 0.508 g (5.63 mmole) of butanethiol with 0.234 g (5.85 mmole) of sodium hydroxide in 1.6 ml of water, and the resulting mixture was heated with stirring at 93-95°C. After 5 min, a precipitate formed from the solution. The reaction mixture was stirred at this temperature for 20 min, after which it was cooled, and the precipitate was removed by filtration and washed with cold water to give 0.643 g (78.1%) of IIId.

Compounds IIIa-c were similarly obtained.

Compound IIId was also obtained in 72% yield by method D at a pyrimidine Ib—butanethiol—sodium hydroxide ratio of 1:1.5:0.5.

E) A 0.693-g (7.68 mmole) sample of butanethiol was added to a solution of 0.315 g (7.88 mmole) of sodium hydroxide in 2.5 ml of water, and 0.823 g (5.13 mmole) of methoxypyrimidine IIb was added after homogenization of the resulting mixture. The mixture was then stirred for 4 h at 90-92°C and cooled to 0°C, and the precipitate was removed by filtration and washed with cold water to give 0.877 g (78.2%) of IIId.

Compound IIIb was similarly obtained in 63% yield from methoxypyrimidine IIa.

Reaction of 4-Hydroxy-3,6-dimethylhexahydropyrimidine-2-thione (Ic) with Sodium Ethanethiolate. A 0.727-g (4.54 mmole) sample of Ic was added to a solution of sodium ethanethiolate obtained from 0.422 g (6.80 mmole) of ethanethiol and 0.277 g (6.93 mmole) of sodium hydroxide in 2.5 ml of water, and the mixture was stirred at 90-92°C for 6 h. It was then cooled and extracted with 8 ml of chloroform, and the solution was applied to a column (1.4 by 5 cm) packed with silica gel L 40/100 μ (Czechoslovakian SSR) and eluted with chloroform. Removal of the solvent in vacuo and treatment of the residue with hexane gave 0.103 g (11.1%) of IIIe.

Hydrolysis of 4-Alkylthiohexanhydropyrimidine-2-thiones IIIa-c. A) A mixture of 0.062 g (0.33 mmole) of IIIc and 5 ml of water was refluxed for 4.5 h (with monitoring by TLC), after which the solvent was removed by distillation, and the residue was washed with acetone and ether to give 0.044 g (92.4%) of Ib.

The hydrolysis of IIIa was carried out by a similar method to give pyrimidine Ia (54.2% yield).

B) A mixture of 0.120 g (0.63 mmole) of IIIc, 1 mg of TsOH, and 5 ml of water was refluxed for 3 h (with monitoring by TLC), after which it was evaporated to dryness, and the solid residue was washed with cold water and acetone to give 0.086 g (93.3%) of Ib.

The hydrolysis of IIIa, b in an alkaline medium with the addition of sodium hydroxide in an amount that was 2-2.5% of the mass of IIIa, b was carried out similarly.

Alcoholysis of 4-Alkylthiohexahydropyrimidine-2-thiones IIIa, c, d. A) A solution of 0.121 g (0.64 mmole) of IIIc in 5 ml of anhydrous ethanol containing a small crystal of TsOH was refluxed for 4 h, after which the solvent was removed, and the resulting crystals were washed with dry ether to give 0.099 g (89.4%) of ethoxypyrimidine IIc.

B) A solution of 0.074 g (0.39 mmole) of IIIc in 3 ml of anhydrous ethanol was refluxed for 8 h, after which it was evaporated to a volume of 1 ml. The concentrate was cooled to 0°C, and the resulting crystals were removed by filtration and washed with cold ether to give 0.039 g of IIc. An additional 0.027 g of the compound was isolated from the mother liquor. The overall yield was 0.066 g (97.5%).

C) A solution of 0.200 g (1.05 mmole) of IIIc and 0.004 g (0.10 mmole) of sodium hydroxide in 5 ml of anhydrous alcohol was refluxed for 7.5 h, after which it was neutralized with dilute hydrochloric acid, filtered, and worked up as in method B to give 0.153 g (83.6%) of IIc.

Similar methods were used to carry out the methanolysis of IIIa, c, d in acidic (in the presence of TsOH) or basic (in the presence of sodium hydroxide or methoxide) media with the formation of the corresponding methoxypyrimidines IIa, b in 50-93% yields.

Methanolysis of 4-Hydroxy-6-methylhexahydropyrimidine-2-thione (Ib) in a Basic Medium. A 0.200-g (1.37 mmole) sample of Ib was added to a solution of sodium methoxide, obtained by dissolving 0.006 g (0.26 mmole) of sodium in 5 ml of anhydrous methanol, and the mixture was refluxed for 16 h (with monitoring by TLC). The solution was concentrated to a volume of 2 ml, and the concentrate was cooled to 0°C. The precipitated crystals were removed by filtration and washed with methanol to give 0.156 g (71.2%) of methoxypyrimidine IIb.

The methanolysis of Ib was also carried out with the use of of sodium hydroxide as the base in a molar ratio with Ib of 1:1. After refluxing in methanol for 9 h, the yield of IIb was 85.8%.

The constants and spectral characteristics of Ia, b and IIa-c correspond to those presented in [1].

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sym-TRIAZINE DERIVATIVES.

7.* STRUCTURE AND PROPERTIES OF TRIAZINYL DERIVATIVES OF CH ACIDS

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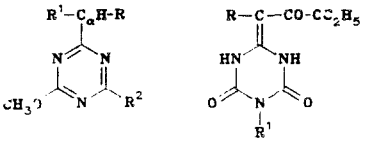
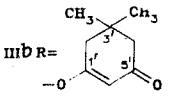
The structures, tautomerism, and acid-base properties of some sym-triazinyl-substituted CH acids were studied.

The tautomerism and acid-base properties of the previously obtained [2-4] sym-triazinyl derivatives of CH acids were studied. 2-(3',3'-Dimethyl-5'-oxo-6'-cyclohexen-1'-yloxy)-4,6-dimethoxy-sym-triazine (IIIb) was synthesized to accurately determine the structures of some of them.



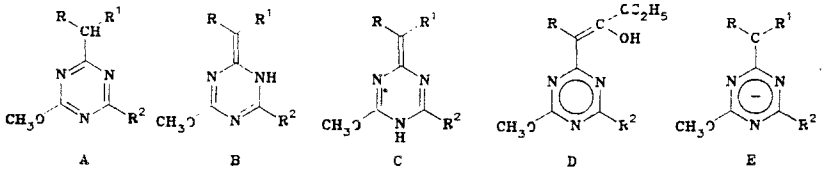
I a-d II a-d III a-c

Ia-c, IIa,c R=$COOC_2H_5$, Id, IIb,d R=CN; Ia,b R^1=$COOC_2H_5$, c,d R^1=CN, IIa,b R^1=CH_3, c,d R^1=H; Ia,c,d R^2=OCH_3, b R^2=NH_2; IIIa R=$H_3C_{(3')}$—$C_{(2')}$(=O)=$HC_{(1')}$—$COOC_2H_5$; c R=Cl



IIIb R=

A single set of signals‡ in the ^1H spectra of 2-(dicarbethoxymethyl)-4,6-dimethoxy-sym-triazine (Ia) (Table 1) in both $CDCl_3$ and d_6-DMSO over the concentration range 10^{-1} to $3\cdot10^{-4}$ M; a singlet signal of the CH proton of a malonic residue is observed along with the signals of protons of OCH_3 and $COOC_2H_5$ groups. The presence of a CH group was confirmed by the ^{13}C NMR spectra (Table 2) (recorded without proton decoupling), in which the signal of the corresponding carbon atom is a doublet with spin-spin coupling constant $^1J_{CH}$ = 134 Hz. The virtual



A B C D E

*See [1] for Communication 6.
†Deceased.
‡The absence of an alternative set of signals can be ascertained with an accuracy of up to 10^{-4} M.

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