5. J. Hinze and H. H. Jaffe, J. Am. Chem. Soc., 84, 540 (1962).
6. A. V. Luzanov, A. A. Sukhorukov, and V. É. Umanskii, Teor. Éksp. Khim., 10, 456 (1974).
7. M. K. Pordeli and V. A. Chuiguk, Khim. Geterotsikl. Soedin., No. 2, 199 (1973).
8. Yu. M. Volovenko and V. A. Chuiguk, Khim. Geterotsikl. Soedin., No. 7, 984 (1974).
9. R. Johnston, Handbook of Mass Spectrometry for Organic Chemists [Russian translation], Mir, Moscow (1975).

ALKYLATION AND REDUCTIVE DETHIONATION OF 2-THIOXO- AND 1,2,3,4-TETRAHYDROPYRIMIDINE-5-CARBOXYLIC ACID DERIVATIVES

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2-Methylthio-1,4-dihydropyrimidines were obtained by methylation of 2-thioxo-4-phenyl-5-methoxycarbonyl-6-methyl-1,2,3,4-tetrahydropyrimidine or its 1-methyl derivative in a neutral medium. The alkylation of tetrahydropyrimidine-2-thiones in the anionic form leads to S- and S,N-methylation products. Iodoacetamide alkylates pyrimidine-2-thione with the formation of thiazolidino[3,2-a]pyrimidine derivatives. The reductive dethionation of derivatives of tetrahydropyrimidine-2-thiones and 2-methylthio derivatives of 1,4- and 3,4-dihydropyrimidines was accomplished.

It is known [1, 2] that exclusively S-alkyl derivatives are formed in the alkylation of 2-thioxo-1,2,3,4-tetrahydropyrimidine derivatives in a neutral medium. In the present research we studied the alkylation of methyl 2-thioxo-4-phenyl-6-methyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (I) and its 1-methyl derivative II in a neutral medium and in the presence of a strong base — sodium hydride.

The alkylation of pyrimidine-2-thiones I and II with methyl iodide in a neutral medium leads to the formation of stable salts IIIa, b, which in an aqueous alkaline medium are readily converted to the free bases — 2-methylthio-1,4-dihydropyrimidines IVa, b. It should be noted that only 1,4-dihydropyrimidine IVa was isolated in the alkylation of unsubstituted pyrimidine I; the other possible isomer — 3,4-dihydropyrimidine — is not formed under the conditions described.

It is known that an attempt to alkylate 2-thioxo-1,2,3,4-tetrahydropyrimidine in an aqueous alkaline medium leads only to hydrolysis of the C=S group to a carbonyl group [1].

We have observed the possibility of alkylation of pyrimidine-2-thione I in the presence of a base — sodium hydride; the effects of the solvent [1,2-dimethoxyethane (DME) or hexametapol (HMP)], the nature of the alkylating agent [methyl iodide or dimethyl sulfate (DMS)], and the amount of base, which is responsible for the formation of the 2-thioxo-1,2,3,4-tetrahydropyrimidine anion, were studied.

Thus S-monoalkylation product IVa is formed in the alkylation of pyrimidine-2-thione I in the anionic form (shift of the long-wave maximum in the UV spectrum from 308 nm to 362 nm when one equivalent of NaH is added to a solution of I), regardless of the solvent used and the alkylating agent. A mixture of S-monoalkyl derivative IVa and dialkylation product V, as well as a very small amount of IVb, is the result of alkylation in the presence of two equivalents of NaH. The yields of the products obtained (from the results of liquid chromatography) in different solvents and with different alkylating agents are

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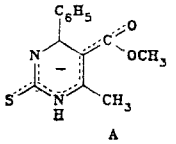
TABLE 1. Yields of the Products of Alkylation of 2-Thioxotetrahydropyrimidine I

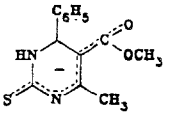
Alkylating agent	Solvent	Yield, %		
		IVa	IVb	V
DMS	HMP	63,7	3,35	30,3
CH_3I	HMP	78,4	0,96	16,8
DMS	DME	81,5	1,60	6,6
CH_3I	DME	89,0	0,24	1,2

presented in Table 1, from which it is apparent that S monoalkylation predominates, regardless of the reaction conditions, while an increase in the dipole moment of the solvent increases the percentage of the $S,N_{(3)}$-dialkylation product.

3,4-Dihydropyrimidine V is the principal reaction product in the alkylation of 2-methyl thio-1,4-dihydropyrimidine IVa in the presence of NaH, and its isomer IVb is formed in very small amounts (~9%).

On the basis of the data obtained it might be assumed that pyrimidinethione I forms anions A and B in the presence of strong bases in solutions:


A

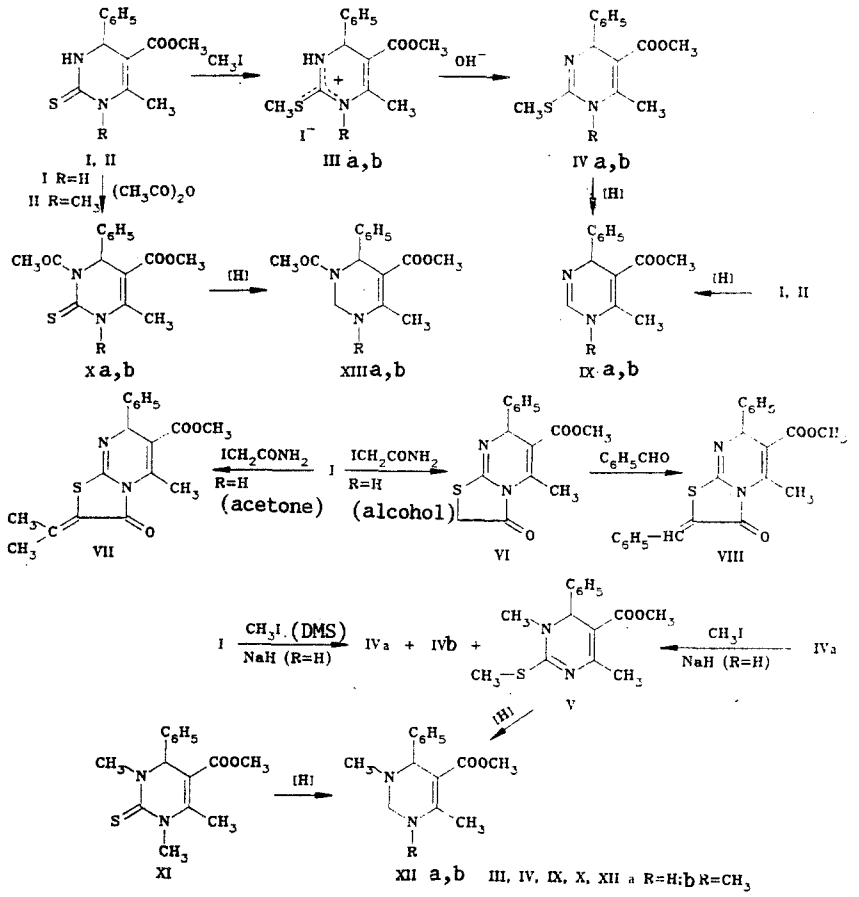

B

The structure of anion A is confirmed by the absence in its ^1H NMR spectrum of a vicinal $^3J_{3,4}$ spin-spin coupling constant (SSCC) and by the presence of a strong-field 2 ppm shift of the 1-H signal as compared with the corresponding signal of pyrimidine I. The concentration of anion B is so low that it could not be recorded in the ^1H NMR spectrum. It is apparent that the alkylation of pyrimidine-2-thiones proceeds as a function of the concentrations of the anions and the distribution of the nucleophilicity in the corresponding anions.

In the ^1H NMR spectrum of the monoalkylation product – salt IIIa – the chemical shifts of the 1-NH and 3-NH protons are averaged and are found at weak field (10.31 ppm), on the basis of which the structure of the salt can be conceived of in the form of a cation with the charge delocalized among the $N_{(3)}$, S, $N_{(1)}$, and $C_{(2)}$ atoms. The signal of the 4-H proton in the spectrum of IVb is located at weaker field as compared with the signal of the corresponding isomer V ($\Delta\delta$ 0.57 ppm), while the positions of the signals of the $N-CH_3$ group of these compounds differ by 0.22 ppm. According to the ^{15}N NMR spectral data, the $N_{(3)}$ atom in IVb has sp^2 hybridization, whereas in isomer V it has sp^3-hybrid character. The assignment of the signals in the ^{15}N NMR spectrum was made on the basis of a study of the corresponding spectrum of starting pyrimidine I, in which the signal of the $N_{(1)}$ atom in the form of a multiplet has δ –235.69 ppm ($J_{^{15}NH}$ = 96.4 Hz), while the signal of the $N_{(3)}$ atom in the form of a doublet has δ –253.74 ppm ($J_{^{15}NH}$ = 96.1 Hz).

A thiazolidine ring with the participation of the nitrogen atom of the pyrimidine ring is formed in the alkylation of unsubstituted pyrimidinethione I with iodoacetamide. The chemical shift of the 4-H signal in the ^1H NMR spectrum of the cyclization product to weak field (6.02 ppm) makes it possible to assume that the $N_{(3)}$ atom has sp^2 hybridization, and consequently, the formation of thiazolidine ring VI with the participation of the $N_{(1)}$ atom occurs. If the alkylation is carried out in solution in acetone, condensation product VII is isolated. 8-Benzylidene derivative VIII of the thiazolidinopyrimidine is also readily formed in the reaction of VI with benzaldehyde.

The reductive dethionation of pyrimidines I, II, and IVa, b with Raney nickel results in the formation of 1,4-dihydropyrimidines IXa, b. According to the ^1H and ^{13}C NMR spectral data, IXa exists in the 1,4-dihydro form. However, proton exchange between the nitrogen atoms was observed in the ^{15}N NMR spectra; this constitutes evidence for the existence of a tautomeric equilibrium between the 1,4- and 3,4-dihydro forms.



1,2,3,4-Tetrahydropyrimidines XII and XIII were obtained by the reductive dethionation of 3-mono- and 1,3-disubstituted pyrimidinethiones Xa, b and XI, as well as 2-methyl derivative V (Table 2). Thus in the reduction of pyrimidine V the reaction does not terminate with splitting out of the SCH_3 group and the formation of the corresponding 3,4-dihydropyrimidine; a 3,4-dihydropyrimidine also was not obtained from unsubstituted pyrimidinethione Xa.

The 3-acetyl derivatives Xa, b used in this reaction were obtained by acetylation of I and II, while 1,3-dimethyl derivative XI was obtained by direct synthesis using 1,3-dimethylthiourea.

An analysis of the SSCC in the ^1H NMR spectra of tetrahydropyrimidines XII and XIII showed that in chloroform these compounds have a half chair conformation with an axial orientation of the 4-phenyl substituent. The geminal SSCC was measured for the protons of the 2-CH_2 group (Table 3); SSCC through four bonds, as well as a constant of spin-spin coupling with the proton of the 1-NH group, was noted for the equatorially oriented 2-H_e atom. The signal of the axial 2-H_a proton is broadened, and for it we were therefore able to measure only the geminal SSCC.

Two rotamers associated with retarded rotation of the acetyl group about the $N_{(3)}$–CO bond were observed in the ^1H NMR spectra of acetyl derivatives XIIIa, b at room temperature. We investigated the temperature dependences of the ^1H NMR spectra and, using Eyring's equation [3], were able to evaluate the energy barrier of the process. For 1-unsubstituted XIIIa the coalescence point is reached at 323°K, whereas it is reached at 334°K for XIIIb; these values correspond to energies of activation $\Delta\sigma$ of 16.6 and 17.0 kcal/mole, respectively.

The strongest effect of anisotropy of the carbonyl group was noted for cis rotamers XIIIa, b, for which the resonance signals of the 2-H_e proton are shifted to weak field (5.45 and 5.27 ppm), while the signals of the 2-H_a proton are located at strong field (3.70 and 3.72 ppm). In the trans rotamer the corresponding resonance signals of the 2-H_e proton are found at 4.62 and 4.35 ppm, while those of the 2-H_a proton are found at 4.26 and 4.22 ppm. The anisotropic effect of the carbonyl group is expressed more weakly in the latter case.

TABLE 2. Characteristics of I-XIII

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Yield, %
I	$C_{13}H_{14}N_2O_2S$	221...223	3310, 3190, 1690, 1650, 1590, 1445	310 (4,25)	88
II	$C_{14}H_{16}N_2O_2S$	114...116	3180, 1695, 1640, 1532, 1495	305 (4,01)	71
IIIa	$C_{14}H_{17}IN_2O_2S$	170...172	3100, 1695, 1615, 1610, 1590	240 (3,62), 303 (3,17)	98
IIIb	$C_{15}H_{19}IN_2O_2S$	156...158	3460, 1665, 1564	248 (3,24), 300 (3,03)	89
IVa	$C_{14}H_{16}N_2O_2S$	164...166	3310, 1650	238 (4,00), 309 (4,21)	58*1
IVb	$C_{15}H_{18}N_2O_2S$	120...122	1698, 1635, 1580	232 (4,40), 306 (4,18)	69
V	$C_{15}H_{18}N_2O_2S$	108...110	1670, 1598, 1500	250 (3,40), 337 (4,07)	86
VI	$C_{15}H_{14}N_2O_2S$	106...107	1738, 1710, 1620, 1555		83
VII	$C_{18}H_{18}N_2O_2S$	132...133	1715, 1705, 1672, 1610, 1540		89
VIII	$C_{22}H_{18}N_2O_2S$	163...166	1740, 1710, 1620, 1608, 1550		90
IXa	$C_{13}H_{14}N_2O_2$	197...198	3150, 1700, 1675, 1630, 1600	228(sh) (4,12), 312 (3,96)	63*2, 69*3
IXb	$C_{14}H_{16}N_2O_2$	110...112	1685, 1672, 1590, 1570	222 (sh) (3,94), 324 (3,72)	71*4, 69*5
Xa	$C_{15}H_{16}N_2O_3S$	143...145	3250, 1690, 1675, 1655, 1515	250 (3,40), 327 (4,07)	86
Xb	$C_{16}H_{18}N_2O_3S$	128...129	1708, 1690, 1635	250 (3,73), 327 (4,07)	95
XI	$C_{15}H_{18}N_2O_2S$	134...135	1705, 1695, 1615	305 (3,80)	60
XIIa	$C_{14}H_{18}N_2O_2$	123...125	3350, 1680, 1665, 1640, 1595, 1525	282 (4,32)	44
XIIb	$C_{15}H_{20}N_2O_2$	98...100	1670, 1545	294 (4,48)	50
XIIIa	$C_{15}H_{18}N_2O_3$	161...163	3320, 1690, 1640, 1575, 1532	280 (4,40)	45
XIIIb	$C_{16}H_{20}N_2O_3$	113...114	1688, 1655, 1590, 1575, 1500	290 (4,21)	40

*1By Method A. *2From I. *3From IIIa. *4From II. *5From IIIb.

EXPERIMENTAL

The IR spectra of suspensions in mineral oil were recorded with a PE-580B spectrometer. The UV spectra of solutions in ethanol ($c = 5 \cdot 10^{-5}$ mole/liter) were recorded with a Specord UV-vis spectrophotometer. The ^1H NMR spectra of solutions in $CDCl_3$ were recorded with a Bruker WH-90 spectrometer with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra were obtained with a WH-360 spectrometer at 22.63 MHz with cyclohexane as the internal standard. The ^{15}N NMR spectra were recorded with a WH-360 spectrometer at 36.5 MHz with nitromethane as the external standard. The course of the reaction was monitored by TLC on Silufol UV-254 plates in a chloroform–hexane–acetone system (9:7:1). Liquid chromatography was carried out with a 4.6 by 100 mm column packed with Silasorb C-18 with acetonitrile 0.2 M CH_3COONH_4 (6:4) as the eluent; the speed of the mobile phase was 1.5 ml/min, and UV detection was realized at 254 nm. The results of elementary analysis of the synthesized compounds for C, H, and N were in agreement with the calculated values.

2-Thioxo-4-phenyl-5-methoxycarbonyl-6-methyl-1,2,3,4-tetrahydropyrimidine (I). A mixture of 10.5 g (0.1 mole) of benzaldehyde, 11.5 g (0.1 mole) of methyl acetoacetate, and 7.6 g (0.1 mole) of thiourea in 100 ml of absolute ethanol with three drops of concentrated HCl was refluxed for 3 h, after which it was cooled, and the white precipitate of I was removed by filtration and crystallized from ethanol. Compounds II and XI were similarly obtained using N-methylthiourea and 1,3-dimethylthiourea, respectively. In the latter case the reaction was carried out in glacial acetic acid with the addition of five drops of concentrated HCl.

Alkylation of Pyrimidines I and II. A) 2-Methylthio-4-phenyl-5-methoxycarbonyl-6-methyl-1,2,3,4-tetrahydropyrimidinium Iodide (IIIa). A mixture of 1.32 g (5 mmole) of pyrimidine I and 0.64 g (10 mmole) of methyl iodide in 30 ml of acetone was allowed to stand for 1 day. The solution gradually darkened, and a precipitate formed. Workup gave 1.85 g of reaction product IIIa. Salt IIIb was similarly obtained from pyrimidine II and methyl iodide. 2-Methylthio-4-phenyl-5-methoxycarbonyl-6-methyl-1,4-dihydropyrimidine (IVa). A 2.6-g (5 mmole) sample of salt IIIa was dissolved in 50 ml of acetone with heating. Ammonium hydroxide was added to the resulting yellow solution until it was neutral, during which it

TABLE 3. ^{1}H NMR Spectra of Pyrimidines I-V, X, and XI and the Products (IX, XII, and XIII) of Their Reductive Dethionation (δ, ppm)

Compound	1-R	Substituen in the 2 position	3-R'	4-H, 1H	4-C_6H_5, 5H, s	5-$COOCH_3$, 3H, s	6-CH_3, 3H, s	SSCC, Hz
I	7,20 (brs, 1H)	—	7,62 (1H, d)	5,33 (d)	7,22	3,60	2,33	^3J=4,0
II	3,60 (3H, s)	—	7,60 (1H, d)	5,33 (d)	7,18	3,69	2,44	^3J=4,0
IIIa	10,31 (2H, br. s)	2,64 (3H, s)	10,31 (2H, br. s)	5,92 (br. s)	7,33	3,62	2,78	
IIIb	3,47 (3H, s)	3,09 (3H, s)	11,26 (1H, br. s)	6,29 (br. s)	7,38	3,71	2,44	
IVa	5,87 (1H. br s)	2,27 (3H, s)	—	5,58 (br. s)	7,13	3,60	2,44	
IVb	3,18 (3H, s)	2,38 (3H, s)	—	5,57 (s)	7,17	3,64	2,49	
V	—	2,33 (3H, s)	2,96 (3H, s)	5,20 (s)	7,27	3,60	2,49	
IXa	7,20 (1H, s)	7,02 (1H, s)	—	5,56 (s)	7,16	3,58	2,32	
IXb	3,11 (3H, s)	6,96 (1H, s)	—	5,62 (s)	7,24	3,58	2,48	
Xa	8,31 (1H, s)	—	2,76 (3H, s)	6,67 (s)	7,27	3,73	2,40	
Xb	3,44 (3H, s)	—	2,67 (3H, s)	6,71 (s)	7,20	3,72	2,56	
XI	3,47 (3H, s)	—	3,76 (3H, s)	5,55 (s)	7,20	3,56	2,47	
XIIa	4,42 (1H, d)	3,86 ... 3,57 (2H m)	2,57 (3H, s)	4,64 (s)	7,27	3,52	2,40	$^3J_{1,2}$=4,2; J_{gem} = 12.4
XIIb	2,89 (3H, s)	3,86 ... 3,38 (2H, m)	2,57 (3H, s)	4,64 (s)	7,20	3,45	2,49	$^4J_{2,4}$=2,0 $^4J_{2,4}$=2,2; J_{gem} = 12.1
XIIIa (trans)	4,40 (3H, s)	4,27 and 4,57 ($1H_a$ and $1H_e$; 2H, m)	2,15 (3H, s)	6,69 (s)	7,21	3,50	2,37	J_{gem} = 11,8
XIIIa (cis)	4,40 (3H, d)	3,70 and 5,45 ($1H_e$ and $1H_a$. 2H, m)	2,35 (3H, s)	5,91 (s)	7,21	3,60	2,40	$^3J_{1,2}$=5,2; J_{gem} = 11.6
XIIIb (trans)	3,10 (3H, s)	4,37 and 4,22 ($1H_e$ and $1H_a$, 2H, m)	2,17 (3H, s)	6,69 (s)	7,26	3,49	2,51	$^4J_{2,4}$=2,0 J_{gem} = 12.5
XIIIb (cis)	3,09 (3H, s)	5,27 and 3,72 ($1H_e$ and $1H_a$, 2H, m)	2,40 (3H, s)	5,97 br s	7,26	3,56	2,51	$^4J_{2e,4}$=1,5; J_{gem} = 12.0

became colorless. The mixture was evaporated, and the precipitate was crystallized from methanol. Dihydropyrimidine IVb was similarly obtained. ^{15}N NMR spectrum of IVb (d_6-DMSO): −259.24 [$N_{(1)}$], −150.15 ppm [$N_{(3)}$].

B) A 0.16-g (6 mmole) sample of NaH was added to a solution of 1.32 g (5 mmole) of 2-thioxopyrimidine I in 30 ml of hexametapol or 1,2-dimethoxyethane; after 30 min, 0.6 ml (5 mmole) of DMS or 0.45 ml (5 mmole) of CH_3I was added. After 2 h, the mixture was poured into 600 ml of 10% aqueous NaCl solution. After 1 day, the precipitated IVa was crystallized from methanol.

C) The reaction of 5 mmole of I with 12 mmole of NaH and 10 mmole of DMS or CH_3I was carried out as in method B to give a mixture of reaction products IVa, IVb, and 2-methylthio-4-phenyl-5-methoxycarbonyl-3,6-dimethyl-3,4-dihydropyrimidine (V). This mixture was dissolved in 50 ml of $CHCl_3$ and chromatographed in four stages on a plate with silica gel (plate size 250 by 250 mm, thickness of the loose layer of silica gel L 40/100 2-3 mm) using chloroform–acetone (5:1) as the eluent. Two bands that absorb UV light were collected. From the first band, beginning with the front, we used acetone to elute 3,4-dihydropyrimidine V, which, after evaporation of the solvent, was crystallized from alcohol. Compound IVa was similarly isolated from the second band and crystallized from methanol. The yields of IVa are presented in Table 4. Compound IVb could not be isolated preparatively under these conditions. The yields of 3,4-dihydropyrimidine V were as follows: 23% (DMS in HMP), 10% (CH_3I in HMP), 14% (DMS in DME), and 4% (CH_3I in DME). ^{15}N NMR spectrum (α_6-DMSO): −167.53 [$N_{(1)}$], −279.20 ppm [$N_{(3)}$].

TABLE 4. Yields of IVa as a Function of the Alkylation Conditions

Method	Solvent	Alkylating agent	Yield, %
B	HMP	DMS	50
B	HMP	CH_3I	80
B	DME	DMS	82
B	DME	CH_3I	56
C	HMP	DMS	50
C	HMP	CH_3I	63
C	DME	DMS	78
C	DME	CH_3I	54

2-Methylthio-4-phenyl-5-methoxycarbonyl-3,6-dimethyl-3,4-dihydropyrimidine (V). A 0.16-g (6 mmole) sample of NaH was added to a solution of 1.38 g (5 mmole) of 1,4-dihydropyrimidine IVa in 30 ml of HMP, and, after 1 h, 0.6 ml (5 mmole) of DMS or 0.45 ml of CH_3I was added. The mixture was allowed to stand for 2 h, after which it was poured into 600 ml of 10% aqueous NaCl solution. The resulting precipitate was removed by filtration to give 1 g (66%) of V. The filtrate was extracted with chloroform (three 100-ml portions), and the chloroform extract was dried and evaporated. The residue was chromatographed on a plate with silica gel as described above. Dihydropyrimidine V was eluted from the first band with acetone, while IVb was eluted from the second band. The overall yield of V was 90% (DMS) and 87% (CH_3I). The yield of product IVb was 6-9%.

3-Phenyl-4-methoxycarbonyl-5-methyl-7-oxo-8-dimethylene-3H-thiazolidino[3,2-a]pyrimidine (VII). A 1.38-g (10 mmole) sample of iodoacetamide was added to a solution of 1.32 g (5 mmole) of 2-thioxopyrimidine I in 50 ml of acetone, and the mixture was allowed to stand for 1 day at room temperature. Ammonium hydroxide was then added until the mixture was neutral, the solvent was evaporated, and the resulting yellow precipitate of VII was crystallized from methanol. ^1H NMR spectrum: 1.96 and 2.35 (3H, two s, CH_3—C—CH_3), 2.48 (3H, s, 5-CH_3), 3.63 (3H, s, $COOCH_3$), 6.04 (1H, s, 3-H), and 7.27 ppm (5H, s, Ph). ^{13}C NMR spectrum (d_6-DMSO): 21.08 (5-CH_3), 22.54 and 22.67 (CH_3—C—CH_3), 51.37 (OCH_3), 107.79 [$C_{(4)}$], 116.45 (C=), 127.28 (C_m-C_6H_5), 128.55 (C_p-C_6H_5), 128.85 (C_o-C_6H_5), 140.96 [$C_{(5)}$], 151.33 [$C_{(8)}$], 152.03 [$C_{(3)}$ and C_i], 155.65 [$C_{(1)}$], 162.133 (7-CO), and 165.69 ppm (4-CO).

Compound VI was similarly obtained when ethanol was used as the solvent. ^1H NMR spectrum: 2.47 (3H, s, 5-CH_3, J_{gem} = 13.5 Hz), 3.60 (3H, s, $COOCH_3$), 3.76 (2H, q, CH_2), 6.02 (1H, s, 3-H), and 7.33 ppm (5H, s, C_6H_5).

3-Phenyl-4-methoxycarbonyl-5-methyl-7-oxo-8-benzylidene-3H-thiazolidino[3,2-a]pyrimidine (VIII). A 0.6-ml sample of benzaldehyde was added to a solution of 1.52 g of VI in 50 ml of acetone, and the yellow precipitate of VIII was removed by filtration after 10 min. ^1H NMR spectrum: 2.53 (3H, s, 5-CH_3), 3.67 (3H, s, $COOCH_3$), 6.22 (1H, s, 3-H), 7.27-7.47 (10H, m, aromatic protons), and 7.76 ppm (1H, s, 8-H).

2-Thioxo-3-acetyl-4-phenyl-5-methoxycarbonyl-6-methyl-1,2,3,4-tetrahydropyrimidine (Xa). A solution of 1.32 g (5 mmole) of 2-thioxopyrimidine I in 30 ml of acetic anhydride was refluxed for 1 h, after which the mixture was evaporated to dryness, and the residue was crystallized from ethanol. Compound Xb was similarly obtained.

Reductive Dethionation of Pyrimidine-2-thiones I, II, IVa, V, Xa, b, and XI. A 1-g sample of Raney nickel was added to a solution of 0.01 mole of pyrimidine in 20 ml of acetone, and the mixture was refluxed for 1 h. The catalyst was removed by filtration and washed with acetone, and the filtrate was evaporated in vacuo. The residual oil was crystallized from hexane. This procedure was used to obtain 1,4-dihydropyrimidines IXa, b and 1,2,3,4-tetrahydropyrimidines XIIa, b and XIIIa, b.

LITERATURE CITED

1. G. I. Ovechkina, L. A. Ignatova, M. A. Ratomskaya, and B. V. Unkovskii, Khim. Geterotsikl. Soedin., No. 9, 1258 (1971).
2. W. Wendellin, Z. Scharmanz, A. Fuchsgruber, and A. Harler, Monatsh. Chem., 111, 1399 (1980).
3. H. Günther, Introduction to a Course in NMR Spectroscopy [Russian translation], Mir, Moscow (1984), p. 261.