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NOVEL METHOD FOR SYNTHESIS OF 4-HYDROXYHEXAHYDROPYRIMIDINE-2-THIONES

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4-Hydroxyhexahydropyrimidine-2-thiones were obtained by reaction of N-(azidomethyl)- or N-(p-tolylsulfonylmethyl)thioureas with anions of 1,3-dicarbonyl compounds. The corresponding 1,2,3,6-tetrahydropyrimidine-2-thiones were synthesized by dehydration of the pyrimidines obtained.

Interest in the chemistry of 4-hydroxyhexahydropyrimidine-2-thiones is due to their diverse reactivity, linked with the presence of several interconnected functional groups, and also with the possibility of their transition to acyclic isomeric forms (ring-chain isomerism) [1, 2]. The indicated compounds are widely used in the synthesis of derivatives of pyrimidine [3-8], pyridine [9], 1,3-thiazine [10], and condensed heterocyclic systems [11, 12].

Familiar methods for obtaining 4-hydroxyhexahydropyrimidine-2-thiones from acyclic precursors are based on: a) reaction of β-isothiocyanatoaldehydes or β-isothiocyanatoketones with ammonia or primary amines [1, 13, 14]; b) reactions of β-aminoaldehydes or β-aminoketones with isothiocyanates [15, 16]; c) reaction of α,β-unsaturated carbonyl compounds with thioureas [3, 17]. However, these methods are insufficiently universal and their use is limited to synthesis of alkyl-substituted 4-hydroxyhexahydropyrimidine-2-thiones.

Earlier [5, 7, 18] we observed that azide or arylsulfonyl groups in the α position relative to the nitrogen atom of heterocyclic amides and thioamides exhibit high nucleofugacity in reactions of these compounds with various nucleophilic reagents. In the development of these investigations, and also with the goal of developing a new general method for synthesis of 4-hydroxyhexahydropyrimidine-2-thiones, including those containing functional groups at the $C_{(5)}$ carbon atom, it seemed very advisable to synthesize α-azido- or α-arylsulfonyl-substituted acyclic thioureas and to study the reaction of these compounds with enolate anions, which creates the prerequisites for heterocyclization of the initially formed products of nucleophilic substitution.

As the starting compound, we used the readily available hydroxymethylthiourea (I), obtained by reaction of thiourea with formaldehyde in water in the presence of $Ba(OH)_2$. We showed that compound I easily reacts with hydrazoic acid (generated *in situ* by reaction of sodium azide with hydrochloric acid) in water a 20°C with formation of N-(azidomethyl)thiourea (II). The yield of compound II depends on the reaction time and is 59.2% after 2 h and 74.9% after 20 h. We established that hydroxymethylthiourea I also reacts with p-toluenesulfinic acid in water at 20°C, as a result of which N-(p-tolylsulfonylmethyl)thiourea (III) is formed in 94.3% yield. We should note that the latter reaction occurs regioselectively with participation of the sulfur atom of the sulfinic acid. We could not detect formation of the second possible product of this reaction (N-(p-tolylsulfinylhydroxymethyl)thiourea). The reactions described above are general and may be used for obtaining other α-azido- α-arylsulfonyl-substituted thioureas and ureas, which will be the subject of our next papers.

We have shown that the azide or p-tolylsulfonyl group of thioureas II and III, as expected, is easily substituted upon reaction of these compounds with nucleophilic reagents, as which in this work we used sodium enolates of acetoacetic ester, acetylacetone, benzoylacetone, and benzoylacetic ester (IVa-d), obtained from the corresponding C−H acids by reaction with sodium hydride. Thus as a result of reaction of compounds II and III with polyfunctional C-nucleophiles IVa-d, the products of intramolecular heterocyclization of the intermediate 3-oxopropylthioureas (Va-d) are formed, namely the 5-substituted 4-hydroxyhexahydropyrimidine-2-thiones (VIa-d).

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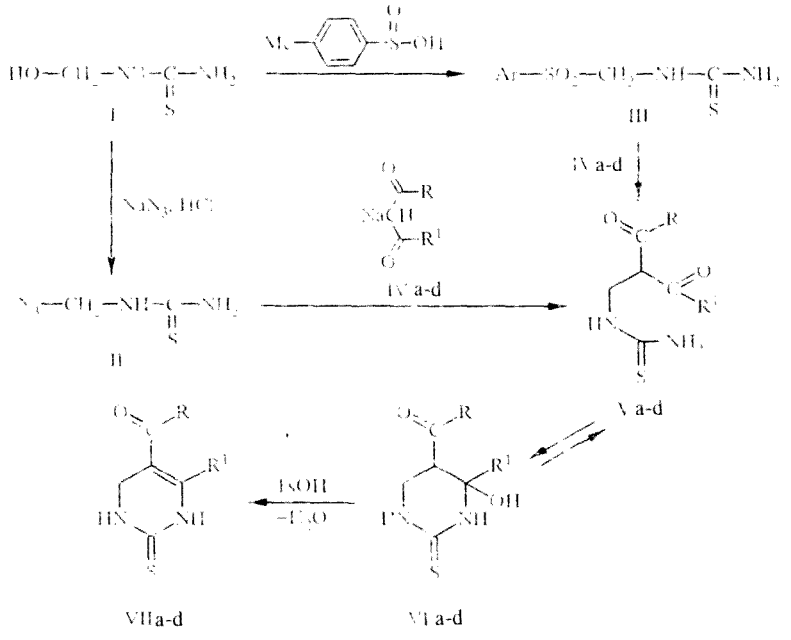

Ar = p-tolyl; IV-VII a R = OEt, R^1 = Me; b R = R^1 = Me; c R = Ph, R^1 = Me; d R = OEt, R^1 = Ph

We should note that in all cases, the yields of the products of nucleophilic substitution are somewhat higher when using azidomethylthioureas II than when using p-tolylsulfonylmethylthioureas III. We also note that heterocyclization of compounds Va, c occurs, as expected, with participation of the acetyl group, while cyclization of the compound Vd occurs with participation of the benzoyl carbonyl groups.

Thus mild reaction conditions, the ready availability of all the starting compounds and the possibility of wide variation in their structures, and the rather high yields make the proposed method for obtaining 5-substituted 4-hydroxy-hexahydropyrimidine-2-thiones very promising.

The synthesized 4-hydroxyhexahydropyrimidine-2-thiones VIa-d are easily dehydrated upon boiling solutions of these compounds in ethanol in the presence of TsOH for 0.5-1 h, as a result of which the corresponding 1,2,3,6-tetrahydropyrimidine-2-thiones (VIIa-d) are formed. The described synthesis route for compounds of type VII is, in our opinion, a useful alternative to obtaining these compounds by the Biginelli reaction [19, 20], which as we known successfully occurs only when using aromatic aldehydes.

The structure of compounds II, III, VI-VIIa-d was established by IR, UV, and PMR spectroscopy.

In the IR spectra of thioureas II and III in the range 3048-3392 cm^{-1}, we observe broad bands for stretching vibrations of the NH groups, while in the 1548-1608 cm^{-1} region there are two strong absorption bands connected with vibrations of the thioureide moiety of the molecules [21]. Furthermore, in the spectrum of compound II we observe an intense band for the stretching vibrations of the azide group at 2082 cm^{-1}, while in the spectrum of compound III there are two strong bands for the stretching vibrations of the SO_2 group at 1271 and 1133 cm^{-1}.

The IR spectra of the 4-hydroxyhexahydropyrimidine-2-thiones VIa-d are characterized by the presence of absorption bands for stretching vibrations of the OH and NH groups in the 3166-3467 cm^{-1} region, intense absorption bands for "thioamides-II" in the range 1514-1588 cm^{-1}, and also bands for stretching vibrations of the carbonyl group of the substituent at the $C_{(5)}$ atom (1680-1738 cm^{-1}). We should also note the presence in the IR spectra of the pyrimidines VIa-d of a strong absorption band in the 1194-1220 cm^{-1} region, characteristic for cyclic thioureas not substituted at the nitrogen atom [6].

As indicated above, for 4-hydroxyhexahydropyrimidine-2-thiones, in particular for compounds VIa-d, the phenomenon of ring-chain isomerism is possible. Based on analysis of the IR spectra of compounds VIa-d, we concluded that in the crystalline state these compounds exist predominantly in the cyclic form. Thus, for example, in the spectrum of compound VIc in the 1600-1759 cm^{-1} region we observe only one absorption band at 1680 cm^{-1}, assigned to stretching vibrations of the C=O bond of the benzoyl group of the cyclic form.

Upon going from the hexahydropyrimidine-2-thiones VIa-d to 1,2,3,6-tetrahydropyrimidine-2-thiones VIIa-d, as a result of formation of the C=C bond a polyconjugated system arises which leads to significant change in the nature of the IR spectra, especially in the 1500-1750 cm^{-1} region. Thus in the IR spectra of compounds VIIa-d the bands for stretching vibrations of the C=O group are observed in the shorter wavelength region of the spectrum compared with the corresponding compounds VIa-d. Furthermore in the indicated region of the spectrum an absorption band appears for the stretching vibrations of the C=C bond.

In the UV spectra of 4-hydroxyhexahydropyrimidine-2-thiones VIa, b, there are two intense (lg ε 3.97-4.24) absorption bands with maxima at 206-207 and 247 nm, characteristic for the unconjugated thioureide chromophore [22]. A similar type of absorption is observed in the electronic spectra of compounds VIc, d, but in this case both absorption bands have enhanced intensity (lg ε 4.36-4.42) due to their overlap with the absorption bands of the aromatic ring.

A characteristic feature of the UV spectra of 1,2,3,6-tetrahydropyrimidine-2-thiones VIIa-d compared with the spectra of 4-hydroxyhexahydropyrimidine-2-thiones (VIa-d) is a significant bathochromic shift (by 59-87 nm) of the long-wavelength absorption band assigned to a $\pi - \pi^*$ transition in the thioureidine chromophore [23]. Furthermore, in the spectra of compounds VIIa-d, in the 280-290 nm region there is a new band of medium intensity which appears as a shoulder on the short-wavelength side of the 306-336 nm band. This new band can probably be assigned to a $\pi - \pi^*$ transition in the C=C bond [23].

In the PMR spectra of the hydroxypyrimidines VIa, c recorded before their purification, only one set of proton signals is present, which suggests formation of these compounds as individual diastereomers. Based on the spin–spin coupling constants of the 5-H proton with the 6-H_a and 6-H_e protons (12.3-12.7 and 4.3-5.0 Hz respectively), we concluded that the substituent at the $C_{(5)}$ carbon atom in molecules of the compounds VIa, c, but bearing in mind that the most stable conformation of the 4-hydroxyhexahydropyrimidine-2-thiones is the conformation with an axial orientation of the hydroxyl group (the appearance of the anomeric effect [14]), we can hypothesize that the hydroxyl group will also be axially oriented in molecules of the indicated compounds.

In the PMR spectrum of the hydroxypyrimidine VIb in DMSO-D_6, we observe two sets of proton signals for both possible diastereomers in the ratio 76:24. Analysis of the multiplets of the 5-H, 6-H_a, and 6-H_e protons shows that the major isomer has an equatorial orientation of the acetyl group ($J_{5a,6a}$ = 12.8, $J_{5a,6e}$ = 4.8 Hz), while the minor isomer has an axial orientation for this group ($J_{5e,6a} \approx J_{5e,6e} \approx$ 5.6 Hz).

We should not that the preferred cyclic structure for compounds VIa-c in the crystalline state (see above) is also retained for solutions of these compounds in DMSO-D_6, which has been established by PMR spectroscopy (the absence of spectral indications of the acyclic isomeric forms of Va-c). At the same time, when compound VId (having a cyclic structure in the crystalline state) is dissolved, slow opening of the pyrimidine ring occurs with formation of a mixture of 4-hydroxyhexahydropyrimidine-2-thione VId and its acyclic isomer Vd. The content of the latter under equilibrium conditions in solutions in DMSO-D_6 or in $CdCl_3$ is 50-60%. Thus 2 h after dissolution of compound VId in DMSO-D_6, in the spectrum we observe proton signals from the cyclic form of VId (91%) (a mixture of the two diastereomers in the ratio 80:20), an also characteristic proton signals from the OCH_2CH_3 group, the CH group, the NH and NH_2 groups of the acyclic form of Vd (98%). Upon prolonged holding of the indicated solution, in the PMR spectrum there are proton signals from the cyclic form of VId (41%), which is a mixture of the two diastereomers in the ratio 72:28, and proton signals from the acyclic form of Vd (59%).

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR-435 in the form of vaseline oil mulls. The electronic spectra in the 200-400 nm regions were obtained on a Beckman DU-6 spectrophotometer for solutions in methanol with concentration $5 \cdot 10^{-5}$ moles/liter. The PMR spectra were recorded on a Bruker MSL-200 (200 MHz) spectrometer for solutions in $CDCl_3$ or DMSO-D_6, internal standard HMDS. The course of the reactions and the purity of the products were monitored by TLC on Kieselgel 60 F_{254} plates (Merck) in the system chloroform–methanol, 9:1, detection in iodine vapor.

The elemental analysis data for C, H, N, and S for compounds II, III, VI-VIIIa-d correspond to the calculated values.

N-(Azidomethyl)thiourea (II, $C_2H_5N_5S$). A solution of 6.10 ml (7.20 g, 71.11 mmoles) concentrated hydrochloric acid in 7 ml water, cooled down to −15°C, was added to a mixture of 4.441 g (41.84 mmoles) hydroxymethylthiourea I [24], 4.622 g (71.11 mmoles) sodium azide and 7 ml water cooled down to the same temperature. With stirring of the reaction mixture in a closed vessel at room temperature, the residue rapidly dissolved; and after 30 min, the reaction product began

to separate from the solution obtained in the form of a heavy oil. The mixture was held for 20 h and cooled down to 0°C. The oil was converted to a white solid material which was filtered off, washed with ice water and hexane, and then dried. Compound II (4.107 g, 74.9%) was obtained in sufficiently pure form and then used without additional purification. The analytical samples was obtained by recrystallization from a hexane–ethylacetate mixture, 3:2, mp 96-97°C. IR spectrum: 3357, 3263, 3164, 3048, (NH), 2082 (N_3), 1608, 1568 (thioamide-II), 1343, 1273, 1221 cm^{-1}.

N-(p-Tolylsulfonylmethyl)thiourea (III, $C_9H_{12}N_2O_2S_2$). A mixture of 1.356 g (12.77 mmoles) hydroxymethylthiourea I, 2.399 g (15.36 mmoles) p-toluenesulfinic acid, and 15 ml water were stirred a room temperature for 24 h and then cooled down to 0°C; the residue was filtered off, washed with ice water and hexane, and dried. Compound III (2.943 g, 94.3%) was obtained in sufficiently pure form and was then used without additional purification. The analytical samples as obtained by recrystallization from acetone, mp 156.5-157°C. IR spectrum: 3392, 3291, 3180 (NH), 3077, 3041 (CH_{Ar}), 1608, 1548 (thioamide-II), 1271, 1133 (SO_2), 745, 712 cm^{-1} (CH_{Ar}).

4-Hydroxy-4-methyl-5-ethoxycarbonylhexahydropyrimidine-2-thione (VIa, $C_8H_{14}N_2O_3S$). A solution of 0.3560 g (2.736 mmoles) acetoacetic ester in 5 ml acetonitrile was added dropwise over the course of 5 ml acetonitrile was added dropwise over the course of 5 min to a mixture of 0.0654 g (2.725 mmoles) sodium hydride in 5 ml dry acetonitrile wit stirring and cooling down to 0°C. Azidomethylthiourea II (0.2966 g, 2.261 mmoles) was added to the suspension of sodium acetoacetic ester formed. This was stirred at room temperature for 2.5 h; the solvent was driven off under vacuum and 4 ml water was added to the residue. This was cooled down to 0°C; the precipitate was filtered off, washed with ice water, and dried. Obtained: 0.3901 g (79.0%) compound VIa, mp 236-237°C (decomp.; acetone). IR spectrum: 3308, 3288 shoulder, 3227 (NH, OH), 1738, 1727 (C=O), 1588, 1574, 1529 (thioamide-II), 1196 cm^{-1}. UV spectrum, λ_{max} (log ε): 206 (3.97), 248 nm (4.19). PMR spectrum (DMSO-D_6): 8.46 (1H, br.s, $N_{(3)}$–H), 8.27 (1H, br.d, $J_{NH,6e}$ = 4.0, $J_{NH,6a}$ = 0 Hz, $N_{(1)}$–H), 5.99 (1H, s, OH), 4.12 (1H, d.q, J_{AB} = 10.9 Hz, H_A in OCH_2), 4.03 (1H, d.q, H_B in OCH_2), 3.43 (1H, d.d., $J_{6e,6a}$ = 12.8 Hz, 6-Ha), 3.13 (1H, d.d.d, 6-H_e), 2.61 (1H, d.d, $J_{5a,6a}$ = 12.7, $J_{5a,6e}$ = 5.0 Hz, 5-H_a), 1.51 (3H, s, 4-CH_3), 1.17 ppm (3H, t, J = 7.1 Hz, CH_3 in OEt).

Compound VIa was also synthesized using a similar technique in 67.6% by reaction of N-(p-tolylsulfonylmethyl)thiourea III with sodium acetoacetic ester.

5-Acetyl-4-hydroxy-4-methylhexahydropyrimidine-2-thione (VIb, $C_7H_{12}N_2O_2S$). Obtained as for compound VIa from thiourea II or III and acetylacetone in 62.7 and 48.6% yields respectively. The compound was formed as a mixture of the two diastereomers in the ratio 76:24, mp 221.5-222°C (decomp.; ethanol). IR spectrum: 3308, 3236 (NH, OH), 1709 (C=O), 1584, 1571, 1527 (thioamide-II), 1220, 1180, 1142 cm^{-1}. UV spectrum, λ_{max} (log ε: 207 (4.04), 247 nm (4.24). PMR spectrum of the major diastereomer (DMSO-D_6): 8.44 (1H, br.s, $N_{(3)}$–H), 8.28 (1H, br.d, $J_{NH,6e}$ = 4.7, $J_{NH,6a}$ = 0 Hz, $N_{(1)}$–H), 5.96 (1H, s, OH), 3.49 (1H, d.d, $J_{6e,6a}$ = 12.5 Hz, 6-H_a), 3.18 (1H, d.d.d, 6-H_e), 2.58 (1H, d.d., $J_{5a,6a}$ = 12.8, $J_{5a,6e}$ = 4.8 Hz, 5-H_a), 2.13 (3H, s, CH_3C=O), 1.43 ppm (3H, s, 4-CH_3). PMR spectrum of minor diastereomer (DMSO-D_6): 6.14 (1H, s, OH), 2.91 (1H, t, $J_{5e,6e}$ + $J_{5e,6a}$ = 11.3 Hz, 5-H_e), 2.17 (3H, s, CH_3C=O), 1.23 ppm (3H, s, 4-CH_3).

5-Benzoyl-4-hydroxy-4-methylhexahydropyrimidine-2-thione (VIc, $C_{12}H_{14}N_2O_2S$). Obtained as for compound VIa from thiourea III and benzylacetone in 91.2% yield, mp 225-226°C (decomp.; ethanol). IR spectrum: 3318, 3212 (NH, OH), 1680 (C=O), 1600 (C=C) 1578, 1565, 1524 (thioamide-II, 700 (CH_{Ar}), 1225, 1212 cm^{-1}. UV spectrum, λ_{max} (lg ε): 207 (4.36), 249 nm (4.36). PMR spectrum (DMSO-D_6): 8.53 (1H, br.s, $N_{(3)}$–H), 8.34 (1H, br.d, $J_{NH,6e}$ = 4.0, $J_{NH,6a}$ = 0 Hz, $N_{(1)}$–H), 7.46–8.02 (5H, m, C_6H_5), 5.78 (1H, s, OH), 3.91 (1H, d.d, $J_{5a,6a}$ = 12.3, $J_{5a,6e}$ = 4.3 Hz, 5-H_a), 3.66 (1H, d.d, $J_{6e,6a}$ = 12.6 Hz, 6-H_a), 3.10 (1H, d.d.d, 6-H_e), 1.21 ppm (3H, s, CH_3).

4-Hydroxy-4-phenyl-5-ethoxycarbonylhexahydropyrimidine-2-thione (VId, $C_{13}H_{16}N_2O_3S$). Synthesized as for compound VIa from thiourea II or III and benzoylacetic ester in 81.3 and 80.8% yields respectively. In order to isolate the product, the reaction mixture was evaporated to dryness and the residue was treated with a 3:1 water–ether mixture. This was cooled down to 0°C; the precipitate was filtered off, washed with cold water and hexane, and dried. Compound VId was purified by dissolving in ethanol followed by filtration and precipitation of the product with water, mp 102-103.5°C. IR spectrum: 3467, 3356, 3316, 3266, 3166 (NH, OH), 1733, 1721 (C=O), 1613, 1491 (C=C), 1573, 1555, 1514 (thioamide-II), 760, 696 (CH_{Ar}), 1194, 1115 cm^{-1}. UV spectrum, λ_{max} (lg ε): 209 (4.42), 248 nm (4.36). PMR spectrum of the cyclic isomer of VId (major isomer)(DMSO-D_6): 8.55 (1H, br.d, $J_{NH,6e}$ = 3.8, $J_{NH,6a}$ = 0 Hz, $N_{(1)}$–H), 8..26 (1H, br.s, $N_{(3)}$–H), 7.28-7.46 (5H, m, C_6H_5), 6.71 (1H, s, OH), 3.78 (1H, d.q, J_{AB} = 10.7 Hz, H_A = OCH_2), 3.69 (1H, d.q, H_B in OCH_2), 3.61 (1H, d.d, $J_{6e,6a}$ = 12.8 Hz, 6-H_a), 3.21 (1H, m, 6-H_e), 2.94 (1H, d.d, $J_{5a,6a}$ = 12.4, $J_{5a,6e}$ = 4.9 Hz, 5-H_a), 0.76 ppm (3H, t, J = 7.0 Hz, CH_3). PMR spectrum of the cyclic isomer of VId (minor isomer) (DMSO-D_6): 8.44 (1H, br.s, $N_{(1)}$–H), 8.31 (1H, br.s, $N_{(3)}$–H), 6.81 (1H, s, OH), 0.85 ppm (3H, t, J = 7.0 Hz, CH_3). PMR spectrum of the acyclic isomer of Vd

(DMSO-D_6): 7.77 (1H, br.t, NH), 7.51-8.13 (5H, m, C_6H_5), 7.17 (2H, br.s, NH_2), 5.06 (1H, br.t, Ch), 4.08 (2H, q, OCH_2), 3.85-3.96 (2H, unresolved m, NCH_2), 1.10 ppm (3H, t, J = 7.1 Hz CH_3).

4-Methyl-5-ethoxycarbonyl-1,2,3,6-tetrahydropyrimidine-2-thione (VIIa, $C_8H_{12}N_2O_2S$). A mixture of 0.513 g (2.35 mmoles) hydroxyhexahydropyrimidine VIa, 0.010 g $TsOH \cdot H_2O$ and 10 ml absolute ethanol was boiled with stirring for 30 min. Soon after heating began, the precipitate was dissolved and the reaction product began to separate the solution formed. The reaction mixture was cooled down to −15°C; the residue was filtered off, washed with cold ethanol, and dried. Obtained: 0.399 g compound VIIa. We obtained an additional 0.007 g of product by treatment of the mother liquor. The overall yield of compound VIIa was 0.406 g (86.3%), mp 236-237°C (decomp. methanol. IR spectrum 3194, 3152 (NH), 1716 (C=O), 1662 (C=C), 1615, 1595, 1505 (thioamide-II), 1274, 1205, 1104 cm^{n1}. UV spectrum, λ_{max} (lg ε): 206 (4.11), ~280 shoulder, 306 nm (4.18). PMR spectrum (DMSO-D_6): 9.78 (1H, br.s $N_{(3)}$−H, 8.79 (1H, br. s, $N_{(1)}$−H), 4.08 (2H, q, OCH_2), 3.89 (2H, s, 6-H), 2.18 (3H, s, 4-CH_3), 1.19 ppm (3H, t, J = 6.9 Hz, CH_3 in OEt).

5-Acetyl-4-methyl-1,2,3,6-tetrahydropyrimidine-2-thione (VIIb, $C_7H_{10}N_2OS$). Obtained as for compound VIIa from hydroxyhexahydropyrimidine VIb in 83.7% yield, mp 230-230.5°C (decomp. ethanol). IR spectrum: 3274, 3180, 3128 (NH), 1647 shoulder, 1613, 1592 (C=C, C=O, "thioamide-II"), 1189 cm^{-1}. UV spectrum, λ_{max} (lg ε): 207 (3.99), ~290 shoulder, 325 nm (4.19). PMR spectrum (DMSO-D_6): 9.88 (1H, br.s, $N_{(3)}$−H), 8.90 (1H, br.s, $N_{(1)}$−H), 3.96 (2H, s, 6-H), 2.17 ppm (6H, s, 4-CH_3 and CH_3C=O).

5-Benzoyl-4-methyl-1,2,3,6-tetrahydropyrimidine-2-thione (VIIc, $C_{12}H_{12}N_2OS$). Obtained as for VIIa from hydroxyhexahydropyrimidine VIc in 60.3% yield, mp 227.5-228°C (decomp.; ethanol). IR spectrum: 3282, 3172, 3108 (NH), 1651, 1606, 1590 (C=C, C=O, "thioamide-II"), 730, 700 (CH_{Ar}), 1200 cm^{-1}. UV spectrum, λ_{max} (lg ε): 207, (4.37), 253 (4.05), ~288 shoulder, 336 nm (4.22). PMR spectrum (DMSO-D_6): 10.00 (1H, br.s, $N_{(3)}$−H), 8.97 (1H, br.s, $N_{(1)}$−H), 7.40-7.60 (5H, m, C_6H_5), 3.91 (2H, s, 6-H), 1.72 ppm (3H, s, 4-CH_3).

4-Phenyl-5-ethoxycarbonyl-1,2,3,6-tetrahydropyrimidine-2-thione (VIId, $C_{13}H_{14}N_2O_2S$). Obtained as for compound VIIa from the hydroxyhexahydropyrimidine VId in 77.7% yield, mp 196-197°C (ethanol), IR spectrum: 3303, 3174 (NH), 1665 (C=C, C=O), 1581 (thioamide-II), 758, 693 (CH_{Ar}), 1292, 1187, 1138 cm^{-1}. UV spectrum, λ_{max} (lg ε): 208 (4.43), 244 shoulder, ~284 shoulder, 310 nm (4.19). PMR spectrum ($CDCl_3$): 7.75 (1H, br.s, $N_{(3)}$−H), 7.49 (1H, br.s, $N_{(1)}$−H), 7.26-7.44 (5H, m, C_6H_5), 4.26 (2H, d $J_{NH,6\text{-}H}$ = 1.8 Hz, 6-H), 3.93 (2H, q, OCH_2), 0.92 ppm (3H, 5, J = 7.1 Hz, CH_3 in OEt).

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