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ALKYL DERIVATIVES OF 1-ARYLDIHYDRO-4(1H,3H)-PYRIMIDINONE-2-THIONES AND THEIR STRUCTURE

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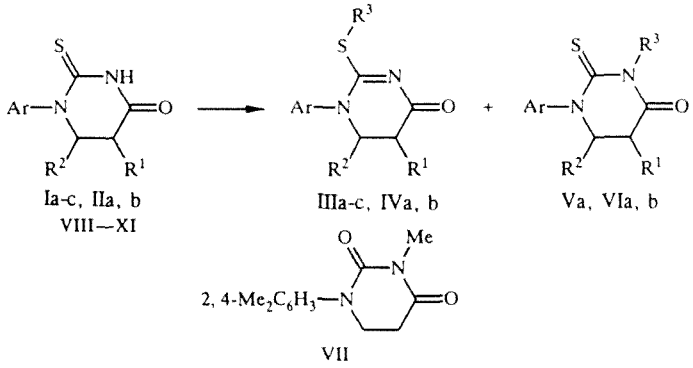
The alkylation of 1-aryldihydro-4(1H,3H)-pyrimidinone-2-thiones goes through both at the thiol group and at the amide nitrogen atom of the heterocycle. Enlargement of the alkyl radical favors an increase in the portion of the N-alkyl derivative in the mixture. The influence of the folding of the heterocycle on its barrier to rotation around the Ph–N_1 bond was shown.

We established that the alkylation of 1-aryldihydro-4(1H,3H)-pyrimidinone-2-thiones (I), (II) with iodomethane in acetone in the presence of potassium carbonate leads to the formation of the mixture of S- and N-methyl derivatives; according to the PMR spectral data, the ratio of the S- and N-methyl derivatives (IIIa) and (Va) in the reaction mixture comprises ~9:1. The application of dimethyl sulfate for the methylation of compound (Ia) leads to the formation of the mixture of three products, namely, the S-methyl derivative (IIIa), the N-methyl derivative (Va), and the dethiation product 1-(2,4-dimethylphenyl)-3-methyldihydro-2,4(1H,3H)-pyrimidinedione (VII), the ratio of which in the mixture comprises ~1:3.5:5.5.



Ia-c, IIa, b
VIII—XI

IIIa-c, IVa, b

Va, VIa, b

VII

I, III, V Ar = 2,4-$Me_2C_6H_3$; II Ar = 4-HO—C_6H_4; IV, VI, VIII—XI Ar = 4-$CH_3OC_6H_4$;
I—VI, VIII—XI a $R^1 = R^2 = H$, b R^1 = Me, $R^2 = H$, c $R^1 = H$, R^2 = Me; III—VI R^3 = Me;
VIII, X R^3 = Et; IX, XI R^3 = Pr

In the alkylation of 1-(2,4-dimethylphenyl)-5- and 1-(2,4-dimethylphenyl)-6-methyldihydro-4(1H,3H)-pyrimidinone-2-thiones (Ib,c) by iodomethane, N-methyl derivatives could not be isolated from the reaction mixture. It can be proposed that the dihydropyrimidinone-2-thiones (Ia-c) exist mainly in the thiol form under the given conditions.

The compounds (Ia-c) react analogously with iodoethane: the S-ethyl derivatives (VIIIa-c) also predominate in the reaction mixtures. The enlargement of the alkyl radical in the alkyl halide favors an increase in the portion of the N-alkyl derivative in the reaction mixture. Thus, the alkylation of the pyrimidine (Ia) with 1-bromopropane results in the formation of the S-propylthio derivative (IXa) and the N-propyl derivative (XIa) in approximately equal proportions. The enlargement of the alkyl radical introduced into the molecule of the dihydropyrimidinone-2-thione probably favors an increase in the steric hindrance between the alkyl radical and the methyl group of the aromatic nucleus, thereby increasing the portion of the N-alkyl derivatives.

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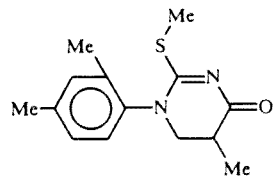
TABLE 1. Chemical Shifts of the Atoms of the S- and N-Alkyl Derivatives (III), (V), and (VIII) and the Tetrahydropyridones (XIV) and (XV)

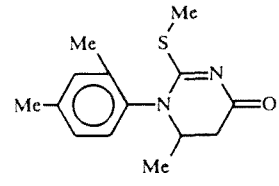
Compound	C_2	C_4	C_5	C_6	2-R	CH_3	Aromatic and other C
IIIa	173,16	171,68	30,81	48,77	13,93	20,67(4'), 16,98(2')	139,11(1'), 137,71(2'), 135,42(4'), 131,78(6'), 128,00(3' and 5')
IIIb	176,29	171,06	33,99	54,70	14,04	20,67(4'), 17,12(2')	139,06(1'), 137,57(2'), 135,55, 131,78, 127,92, 12,75 (5-CH_3)
IIIc	172,91	170,75	37,48	53,93	14,15	20,68(4'), 17,17(2')	139,34(1'), 135,96(2'), 135,78(4'), 132,11, 129,57, 127,44, 17,39 (6-CH_3)
Va	180,92	167,04	33,51	46,53	30,97	20,62(4'), 17,38(2')	142,67(1'), 137,11(2'), 134,01(4'), 131,40, 127,73, 126,52
VIIIa	172,92	170,25	37,44	53,81	25,20 and 14,45	20,65(4'), 17,20(2')	139,24(1'), 135,79(2' and 4'), 132,07, 129,46, 127,41, 17,41 (6-CH_3)
VIIIb	176,37	170,55	33,97	54,59	25,12 and 14,61	20,67(4'), 17,14(2')	139,00, 137,63, 135,42, 129,46, 131,78, 127,89, 127,60, 12,80 (5-CH_3)
XIV	162,36(2) 106,21(3)	186,50	35,47	50,12	18,76	20,58(4'), 17,12(2')	140,09(1'), 138,09(2'), 134,52(4'), 131,82, 128,01, 127,22, 167,13 (COO), 59,50 and 14,19 (OEt)
XV	162,39(2) 106,50(3)	186,71	35,76	50,35	19,00	20,55(4'), 17,01(2')	142,63(1'), 137,27(2'), 131,79(5'), 131,35, 129,48, 128,04, 167,37 (COO), 59,73 and 14,43 (OEt)

The Tables 1-3 present parameters of the ^1H and ^{13}C NMR spectra of some S-alkyl- and N-alkyl derivatives of dihydropyrimidinone-2-thiones (III), (V), and (VIII), and the dihydropyridones (XIV), (XV). It can be seen from these data that the S-alkylated compounds, as well as their precursors, exist in the form of atropoisomers. The assignment of the signals in the spectra was carried out by analogy with previously studied unalkylated derivatives [1, 2].

The temperature dependence was investigated for the compounds (IIIb,c). In contrast to earlier studies of these compounds, a significantly higher barrier to rotation around the $Ph-N_1$ bond is observed, especially when the CH_3 group is introduced at the position 6 of the pyrimidine ring. That is probably associated with a change in the folding of the ring.



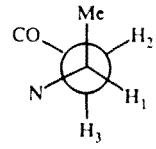
$\Delta G_c^{\neq}$ = 22,9 kcal/mole



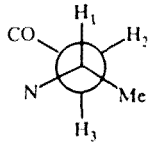
$\Delta G_c^{\neq}$ = 23,9 kcal/mole

The nonequivalence of the proton signals in the 5,6-unsubstituted derivatives allows the determination of the angle of curvature of the ring using the method of the R-factor [3]. Calculation indicates an increase in the degree of nonplanarity of the ring in the series: (IIIa)→(Va)→(XIV), (XV).

TABLE 2. SSCCs and Chemical Shifts of Protons in the Dihydropyrimidine Ring of the S-Alkyl Derivatives (IIIb,c), (VIIIb,c)



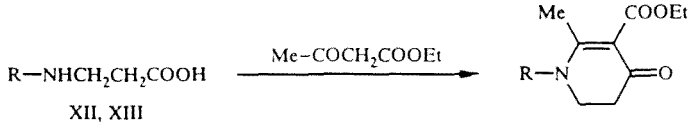
A



B

Compound		δ, ppm				J, Hz			
		1	2	3	CH_3	12	13	23	1-CH_3
IIIb	A	2,77	3,70	3,52	1,10	12,0	7,0	-13,0	6,1
	B	2,75	3,62	3,55	1,08	12,0	7,0	-13,0	6,1
IIIc	A	4,08	2,46	2,78	0,94	5,0	7,8	-14,0	6,1
	B	3,85	2,88	2,36	1,11	4,0	6,2	-14,0	6,1
VIIIb	A	2,77	3,69	3,49	1,11	10,0	6,0	-12,0	6,1
	B	2,75	3,59	3,54	1,09	12,0	6,0	-12,0	6,1
VIIIc	A	4,10	2,46	2,78	0,94	5,0	8,3	-14,1	6,1
	B	3,84	2,88	2,36	1,10	3,5	5,5	-14,1	6,0

The substitution of the nitrogen atom at the position 3 by a carbon atom also increases the nonplanarity of the ring; this should lead to the disturbance of the p—π-conjugation of the N_1 nitrogen atom with the endocyclic double bond. That, in turn, may raise the degree of conjugation of this nitrogen atom with the phenyl ring, and exert influence (besides steric interactions, having destabilizing influence) on the barrier to rotation around the Ph—N_1 bond.



XII, XIII

XIV, XV

XII, XIV R = 2, 4-$Me_2C_6H_3$; XIII, XV R = 2, 5-$Me_2C_6H_3$

We synthesized the 1-aryl-2-methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydro-4(1H)-pyridones (XIV), (XV) by reaction of the N-(2,4- and 2,5-dimethylphenyl)-β-alanines (XII), (XIII) with ethyl acetoacetate.

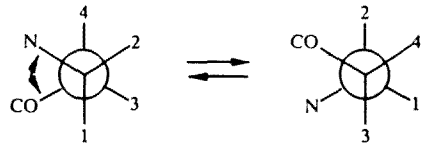
EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on the Bruker WM-360 and Hitachi R-22 (90 MHz) spectrometers. The internal standard was TMS. The IR spectra were taken on the UR-20 instrument using tablets of KBr. The monitoring of the course of reaction and purity of the compounds obtained was accomplished using TLC on plates of Silufol UV-254, with development in UV light or with iodine.

1-(2,4-Dimethylphenyl)-2-methylthio-1,4,5,6-tetrahydropyrimidinon-4-one (IIIa) and 1-(2,4-Dimethylphenyl)-3-methyldihydro-4-(1H,3H)-pyrimidinone-2-thione (Va). The mixture of 2.3 g (0.01 mole) of the pyrimidinone-2-thione (Ia), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 3.7 ml (0.06 mole) of iodomethane is boiled for 8 h. The mixture is cooled and filtered, and the crystals are washed with 50 ml of acetone. The liquid fractions are distilled off *in vacuo*, and the residue is treated with 50 ml of ethyl ether. The crystals of (IIIa), which were isolated at 4°C, are filtered and washed with ether. The yield was 1.9 g (76.6%). The mp was 106-108°C (from hexane). The IR spectrum was characterized at 1680 (C=O).

In order to isolate the N-methyl derivative (Va), the solution is concentrated *in vacuo*, and the residue is chromatographed on a column with silica gel L 40/100, performing the elution with the 9:1 mixture of ethyl ether—hexane. The fraction with the R_f 0.62 is collected. The yield was 0.2 g (8.1%). The mp was 132-133°C.

TABLE 3. SSCCs and Chemical Shifts of Protons in the Dihydropyrimidine and Hydropyridine Rings of (IIIa), (Va), (XIV), (XV), and the Angle of Deviation from the Plane



Compound	δ, ppm				J, Hz						φ
	1	2	3	4	12	13	14	23	24	34	(deg)
IIIa	3,79	3,67	2,59	2,66	-12,8	5,9	9,8	5,9	5,9	-15,6	55,7
Va	3,83	3,73	2,96	2,92	-12,7	5,9	7,9	6,1	6,1	-16,1	53,2
XIV	3,76	3,66	2,43	2,56	-12,9	5,0	11,1	6,0	6,0	-15,4	58,7
XV	3,78	3,68	2,45	2,57	-12,9	5,8	11,0	6,4	6,0	-15,5	57,7

TABLE 4. Data of the Elemental Analysis

Compound	Found, %				Empirical formula	Calculated, %			
	C	H	N	S		C	H	N	S
IIIa	63,0	6,8		12,7	$C_{13}H_{16}N_2OS$	62,9	6,5		12,9
Va	63,0	6,5		12,8	$C_{13}H_{16}N_2OS$	62,9	6,5		12,9
IIIb	64,4	7,0		12,0	$C_{14}H_{18}N_2OS$	64,1	6,9		12,2
IIIc	64,1	7,1		12,0	$C_{14}H_{18}N_2OS$	64,1	6,9		12,2
IVa	57,0	5,5	11,0		$C_{12}H_{14}N_2O_2S$	57,6	5,6	11,2	
VIa	57,3	5,7	11,3		$C_{12}H_{14}N_2O_2S$	57,6	5,6	11,2	
IVb	59,4	5,8	10,4		$C_{13}H_{16}N_2O_2S$	59,1	6,1	10,6	
VIb	59,3	6,0	10,5		$C_{13}H_{16}N_2O_2S$	59,1	6,1	10,6	
VII	67,6	7,1	12,3		$C_{13}H_{16}N_2O_2$	67,3	6,9	12,1	
VIIIa	64,3	7,1		12,1	$C_{14}H_{18}N_2OS$	64,1	6,9		12,2
Xa	64,4	7,1		12,4	$C_{14}H_{18}N_2OS$	64,1	6,9		12,2
VIIIb	65,2	7,4		11,4	$C_{15}H_{20}N_2OS$	65,2	7,3		11,6
VIIIc	65,4	7,4		11,3	$C_{15}H_{20}N_2OS$	65,2	7,3		11,6
IXa	65,0	7,1		11,7	$C_{15}H_{20}N_2OS$	65,2	7,3		11,6
XIa	65,1	7,2		11,4	$C_{15}H_{20}N_2OS$	65,2	7,3		11,6
XIV	70,9	7,7	4,9		$C_{17}H_{21}NO_3$	71,1	7,4	4,9	
XV	70,9	7,5	5,1		$C_{17}H_{21}NO_3$	71,1	7,4	4,9	

1-(2,4-Dimethylphenyl)-2-methylthio-5-methyl-1,4,5,6-tetrahydropyrimidin-4-one (IIIb). The mixture of 2.5 g (0.01 mole) of compound (Ib), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 3.7 ml (0.06 mole) of iodomethane is boiled for 5 h. The mixture is filtered, and the liquid crystals are distilled off *in vacuo*. The residue is chromatographed on a column with silica gel L 40/100, performing the elution with the 9:1 mixture of ethyl ether—hexane. The fraction with the R_f 0.27 is collected. The yield was 0.5 g (19.1%). The mp was 124-125°C. The IR spectrum was characterized at 1676 (C=O).

1-(2,4-Dimethylphenyl)-2-methylthio-6-methyl-1,4,5,6-tetrahydropyrimidin-4-one (IIIc). The mixture of 2.5 g (0.01 mole) of compound (Ic), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 3.7 ml (0,06 mole) iodomethane is boiled for 9 h. The isolation is performed analogously to that of (IIIb), with the collection of the fraction with the R_f 0.24. The yield was 0.94 g (35.9%). The mp was 126-128°C. The IR spectrum was characterized at 1676 (C=O).

1-(4-Methoxyphenyl)-2-methylthio-1,4,5,6-tetrahydropyrimidin-4-one (IVa) and 1-(4-Methoxyphenyl)-3-methyl-dihydro-4(1H,3H)-pyrimidinone-2-thione (VIa). The mixture of 6.7 g (0.03 mole) of the dihydropyrimidinone-2-thione (IIa), 16.6 g (0.12 mole) of potassium carbonate, 12 ml (0.2 mole) of iodomethane, and 70 ml of acetone is boiled for 8 h. The mixture is cooled and filtered, and the crystals are washed with 50 ml of acetone. The liquid fractions are distilled off *in vacuo*, and the residue is treated with 10 ml of ethanol. The isolated crystals of (IVa) are filtered and washed with 5 ml of

ethanol. The yield was 1.78 g (23%). The mp was 193-195°C (from ethanol). The PMR spectrum (CF_3COOH) was as follows: 2.30 ppm (3H, s, SCH_3), 2.85 ppm (2H, t, 5-CH_2), 3.48 ppm (3H, s, OCH_3), 3.85 ppm (2H, t, 6-CH_2), and 6.6-7.1 ppm (4H, m, H_{arom}).

In order to isolate the N-methyl derivative (VIa), the filtrate remaining after the separation of (IVa) is concentrated *in vacuo*, and the residue is chromatographed on a column with silica gel L 40/100. Elution is performed with the 4:1 mixture of ether—hexane. The fraction with the R_f 0.44 is collected. Compound (VIa) is obtained with the yield of 0.43 g (5.8%). The mp was 129-131°C. The PMR spectrum ($CDCl_3$) was as follows: 2.85 ppm (2H, t, 5-CH_2), 3.54 ppm (3H, s, OCH_3), 3.77 ppm (3H, s, N-CH_3), 3.9-4.6 ppm (2H, m, 6-CH_2), and 6.7-7.4 ppm (4H, m, H_{arom}).

1-(4-Methoxyphenyl)-2-methylthio-5-methyl-1,4,5,6-tetrahydropyrimidin-4-one (IVb) and 1-(4-Methoxyphenyl)-3,5-dimethyldihydro-4(1H,3H)-pyrimidinone-2-thione (VIb). The mixture of 2.4 g (0.01 mole) of the 5-methyldi-hydro-pyrimidinone-2-thione (IIb), 5.5 g (0.04 mole) of potassium carbonate, 6 ml (0.1 mole) of iodomethane, and 30 ml of acetone is boiled for 8 h. The mixture is cooled and filtered, and the crystals are washed with 30 ml of acetone. The liquid fractions are distilled off *in vacuo*. The residue is treated with 5 ml of ethanol, and the separated crystals of (IVb) are filtered and washed with 5 ml of ethanol and ether. The yield was 0.11 g (4.2%). The mp was 122-123°C (from ethanol). The PMR spectrum (CF_3COOH) was as follows: 0.96 ppm (3H, d, J = 7 Hz, CH_3), 2.27 ppm (3H, s, SCH_3), 2.7-3.4 ppm (1H, m, CH), 3.50 ppm (2H, s, OCH_3), 3.5-4.1 ppm (2H, m, CH_2), and 6.6-7.2 ppm (4H, m, H_{arom}).

Compound (VIb) is isolated analogously to (VIa), with the collection of the fraction with the R_f 0.31 using the 4:1 mixture of ether—hexane as the eluent. The yield was 0.74 g (28%). The mp was 91-92°C.

1-(2,4-Dimethyl)-3-methyldihydro-2,4(1H,3H)-pyrimidinedione (VII) and Compounds (IIIa) and (Va). The mixture of 2.3 g (0.01 mole) of compound (Ia), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 2.8 ml (0.03 mole) of dimethyl sulfate is boiled for 4.5 h. The mixture is filtered, and the liquid fractions are distilled off *in vacuo*. The residue is chromatographed on a column with silica gel L 40/100, performing the elution with the 9:1 mixture of ether—hexane. Compound (Va) is isolated with the R_f 0.62 and the yield of 0.21 g (8.1%). The mp was 131-133°C. Compound (IIIa) had the R_f 0.09 and the yield of 0.74 g (29.8%). According to the PMR spectral data, the ratio of (IIIa):(Va):(VII) comprises 1:3.5:5.5.

1-(2,4-Dimethylphenyl)-2-ethylthio-1,4,5,6-tetrahydropyrimidin-4-one (VIIIa) and 1-(2,4-Dimethylphenyl)-3-ethyldihydro-4(1H,3H)-pyrimidinone-2-thione (Xa). The mixture of 2.3 g (0.01 mole) of compound (Ia), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 4.4 ml (0.06 mole) of iodoethane is boiled for 5 h. The mixture is filtered, and the liquid fractions are distilled off *in vacuo*. The residue is chromatographed on a column with silica gel L 40/100, performing the elution with the 9:1 mixture of ether—hexane. Compound (VIIIa) is isolated with the R_f 0.12 and the mp 90-91°C. The yield was 1.15 g (43.9%). The PMR spectrum ($CDCl_3$) was as follows: 1.12 ppm (3H, t, CH_3), 2.15 ppm (3H, s, 2-CH_3), 2.24 ppm (3H, s, 4-CH_3), 2.65 ppm (2H, t, 5-CH_2), 2.94 ppm (2H, q, SCH_2), 3.5-3.8 ppm (2H, m, 6-CH_2), and 6.9-7.2 ppm (3H, m, H_{arom}). Compound (Xa) had the R_f 0.73. The yield was 0.08 g (3.1%). The mp was 95-97°C. The PMR spectrum ($CDCl_3$) was as follows: 1.16 ppm (3H, t, CH_3), 2.11 ppm (3H, s, 2-CH_3), 2.24 ppm (3H, s, 4-CH_3), 2.7-3.0 ppm (2H, m, 5-CH_2), 3.5-3.9 ppm (2H, m, 6-CH_2), 4.32 ppm (2H, q, N-CH_2), and 6.9-7.2 ppm (3H, m, H_{arom}).

1-(2,4-Dimethylphenyl)-2-ethylthio-5-methyl-1,4,5,6-tetrahydropyrimidin-4-one (VIIIb). The mixture of 2.5 g (0.01 mole) of compound (Ib), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 4.8 ml (0.06 mole) of iodoethane is boiled for 12 h. The isolation is performed analogously to (IIIb), with the collection of the fraction with the R_f 0.29. The yield was 1.35 g (48.9%). The mp was 124-125°C. The IR spectrum was characterized at 1678 (C=O).

1-(2,4-Dimethylphenyl)-2-ethylthio-6-methyl-1,4,5,6-tetrahydropyrimidin-4-one (VIIIc). The mixture of 2.5 g (0.01 mole) of compound (Ic), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 4.8 ml (0.06 mole) of iodoethane is boiled for 16 h. The isolation is performed analogously to that of (IIIb), with the collection of the fraction with the R_f 0.20. The yield was 0.33 g (12.0%). The mp was 94-95°C. The IR spectrum was characterized at 1680 (C=O).

1-(2,4-Dimethylphenyl)-2-propylthio-1,4,5,6-tetrahydropyrimidin-4-one (IXa) and 1-(2,4-Dimethylphenyl)-3-propyldihydro-4(1H,3H)-pyrimidinone-2-thione (XIa). The mixture of 2.3 g (0.01 mole) of compound (Ia), 4.1 g (0.03 mole) of potassium carbonate, 1 g of calcium oxide, 50 ml of acetone, and 7.3 ml (0.08 mole) of propyl bromide is boiled for 16 h. The isolation is performed analogously to that of (VIIIa), with the collection of the fraction with the R_f 0.23 [compound (IXa)]. The yield was 1.07 g (38%). The PMR spectrum ($CDCl_3$) was as follows: 0.84 ppm (3H, t, $CH_2\underline{CH_3}$), 1.3-1.7 ppm (2H, t, $\underline{CH_2}CH_3$), 2.19 ppm (3H, s, 2-CH_3), 2.30 ppm (3H, s, 4-CH_3), 2.69 ppm (2H, t, 5-CH_2), 2.99 ppm (2H, t, SCH_2),

3.5-3.9 ppm (2H, m, 6-CH_2), and 6.9-7.3 ppm (3H, m, H_{arom}). Compound (XIa) is isolated analogously; it had the R_f 0.81. The yield was 1.18 g (42.8%). The PMR spectrum ($CDCl_3$) was as follows: 0.84 ppm (3H, t, $CH_2\underline{CH_3}$), 1.4-1.8 ppm (2H, t, $\underline{CH_2}CH_3$), 2.13 ppm (3H, s, 2-CH_3), 2.27 ppm (3H, s, 4-CH_3), 2.6-3.0 ppm (2H, m, 5-CH_2), 3.5-3.9 ppm (2H, m, 6-CH_2), 4.1-4.4 ppm (2H, m, N-CH_2), and 6.9-7.2 ppm (3H, m, H_{arom}).

1-(2,4-Dimethylphenyl)-2-methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydro-4(1H)-pyridone (XIV). The mixture of 4.9 g (0.025 mole) of the β-alanine (XII), 6.5 ml (0.05 mole) of acetoacetic ester, and 50 ml of toluene is boiled for 9 h, with the separation of water using a Dean—Stark attachment. The solvent is distilled off *in vacuo*, and the mixture obtained is chromatographed on a column with silica gel L 40/100. Elution is performed with the 9:1 mixture of ethyl ether—hexane. The fraction with the R_f 0.22 is collected. The yield was 2.7 g (38.6%). The mp was 122-123°C. The IR spectrum was characterized at 1684 and 1640 (C=O).

1-(2,5-Dimethylphenyl)-2-methyl-3-ethoxycarbonyl-1,4,5,6-tetrahydro-4(1H)-pyridone (XV). This compound is obtained from 4.9 g (0.025 mole) of the β-alanine (XIII) and 6.5 ml (0.05 mole) of acetoacetic ester by analogy with (XIV). The R_f was 0.27. The yield was 1.7 g (24%). The mp was 99-100°C. The IR spectrum was characterized at 1688 and 1638 (C=O).

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