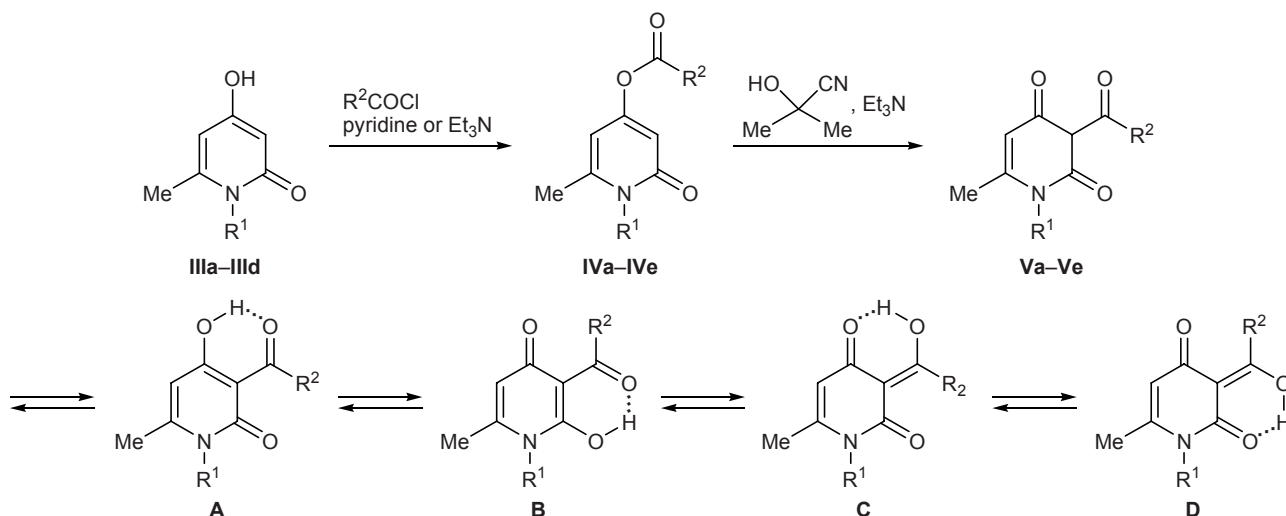


Scheme 1.



III, $R^1 = \text{Me}$ (a), Pr (b), PhCH_2 (c), 4- MeOC_6H_4 (d); IV, V, $R^1 = R^2 = \text{Me}$ (a); $R^1 = \text{Pr}$, $R^2 = \text{Et}$ (b); $R^1 = \text{PhCH}_2$, $R^2 = \text{Et}$ (c), Me (f); $R^1 = 4\text{-MeOC}_6\text{H}_4$, $R^2 = \text{Pr}$ (d); $R^1 = \text{Me}$, $R^2 = \text{Bu}$ (e).

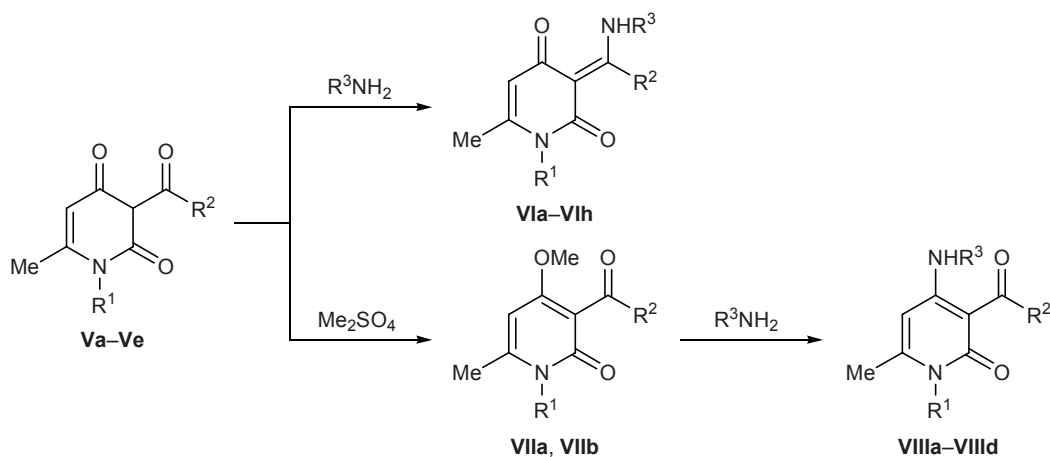
data of Schnell and Kappe [11] who failed to obtain 3-arylpyridine-2,4-diones following an analogous approach. It should be noted that we did not succeed in synthesizing β -triketones V using Lewis acids and 4-dimethylaminopyridine as catalysts.

Treatment of diketones IIIa–IIId with acetyl, propionyl, and butyryl chlorides in methylene chloride in the presence of pyridine gave enol esters IVa–IVf with high regioselectivity. Compounds IVa–IVf can be isolated as individual substances in 90–95% yield or subjected (without isolation) to O–C-migration of the acyl group with formation of 3-acyl-1,2,3,4-tetrahydropyridine-2,4-diones Va–Vf in the presence of excess triethylamine and 2-hydroxy-2-methylpropanenitrile as catalyst (Scheme 1).

The assumed structure of enol esters IV follows from the ^1H NMR spectra of compounds IVa–IVc and IVf, where the 3-H and 5-H olefinic protons (δ 5.50–6.50 ppm) displayed an allylic coupling constant 4J of 2.0–2.5 Hz. Like other cyclic β -triketones [17], 3-acylpyridine-2,4-diones Va–Vf are completely enolized: their ^1H NMR spectra contain a one-proton signal from the chelated hydroxy group in the region δ 15–16 ppm. Theoretically, unsymmetrical heterocyclic β -triketones

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Scheme 2.



VI, $R^1 = R^2 = \text{Me}$, $R^3 = \text{Ph}$ (a), $\text{CH}_2=\text{CHCH}_2$ (b); $R^1 = \text{Me}$, $R^2 = \text{Bu}$, $R^3 = \text{CH}_2=\text{CHCH}_2$ (c), 4- MeOC_6H_4 (d, h); $R^1 = \text{Pr}$, $R^2 = \text{Et}$, $R^3 = \text{PhCH}_2$ (e); $R^1 = 4\text{-MeOC}_6\text{H}_4$, $R^2 = \text{Pr}$, $R^3 = \text{PhCH}_2$ (f), 4- MeOC_6H_4 (g); $R^1 = \text{Me}$, $R^2 = \text{Bu}$, $R^3 = 4\text{-MeOC}_6\text{H}_4$ (h); VII, $R^1 = \text{Me}$, $R^2 = \text{Bu}$ (a); $R^1 = 4\text{-MeOC}_6\text{H}_4$, $R^2 = \text{Pr}$ (b); VIII, $R^1 = 4\text{-MeOC}_6\text{H}_4$, $R^2 = \text{Pr}$, $R^3 = \text{PhCH}_2$ (a), 4- MeOC_6H_4 (b); $R^1 = \text{Me}$, $R^2 = \text{Bu}$, $R^3 = 4\text{-MeOC}_6\text{H}_4$ (c), $\text{CH}_2=\text{CHCH}_2$ (d).

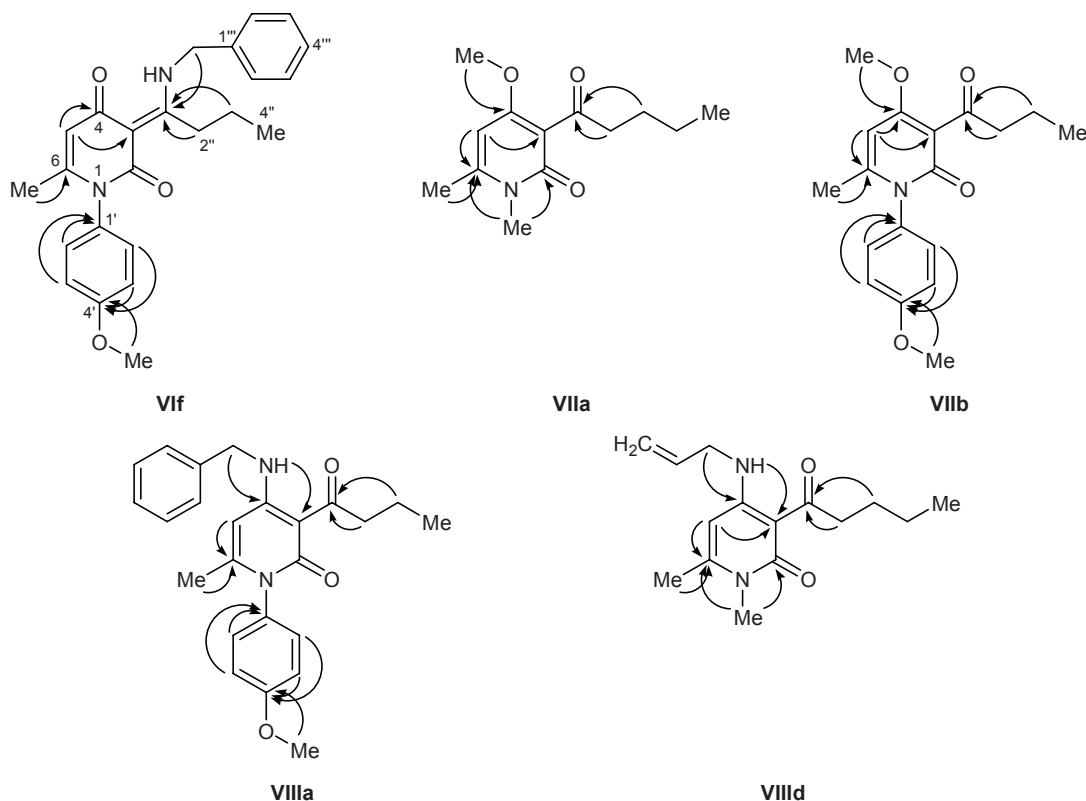
Va–Vf can give rise to four tautomeric forms **A–D**. The presence of only one enol proton signal suggests that compounds **Va–Vf** have structure **A** or **C**; the contribution of tautomers **B** and **D** is quite insignificant, or they are absent at all.

3-Acylpyridinediones **Va–Vf**, as well as other cyclic β -triketones, reacted with amines at the acyl carbonyl group, yielding enamines **Vla–Vlh** (Scheme 2). The reactions with aliphatic amines (allylamine and benzylamine) in boiling toluene required several hours, whereas the conversion of triketones **V** in the reactions with aromatic amines (aniline and *p*-methoxyaniline) was not complete even after heating for a weak, and the yields of the corresponding enamines **VI** did not exceed 50%.

With a view to extend the synthetic potential of 3-acylpyridine-2,4-diones we tried to obtain their enamino derivatives at one of the endocyclic carbonyl groups. Analogous transformations of carbocyclic β -triketones are usually accomplished via intermediate preparation of the corresponding enol methyl ethers, and these reactions involve no difficulties [17]. We previously synthesized regioisomeric enol methyl ethers at both endocyclic carbonyl groups of sulfur-containing heterocyclic β -triketones of the 3-acylthiotetronic acid

series [18] and 3-acetyltetrahydrothiopyran-2,4-dione [19]. 4-Acyl-2*H*-thiopyran-3,5-diones reacted with methylating agents to give complex mixtures of products, from which we failed to isolate the desired enol ethers [20]. By heating triketones **Vc** and **Vf** with 1.2 equiv of dimethyl sulfate and 4 equiv of anhydrous potassium carbonate in toluene we obtained the corresponding 4-methoxy derivatives **VIIa** and **VIIb** in almost quantitative yield. Compounds **VIIa** and **VIIb** reacted with allylamine, benzylamine, aniline, and *p*-methoxyaniline to produce enamino derivatives **VIIIa–VIIId** at the $C^4=O$ carbonyl group. Unlike enol ethers derived from β -triketones of the cyclohexane [17] and heterocyclic series [18, 19], 4-methoxypyridinones **VIIa** and **VIIb** turned out to be low reactive; as in the synthesis of enamino derivatives **Vla–Vlh** at the side-chain carbonyl group, the yields in the reactions of **VIIa** and **VIIb** with aromatic amines were considerably lower.

The product structure was determined using two-dimensional NMR techniques (COSY, HSQC, HMBC), and complete assignment of carbon signals in the ^{13}C NMR spectra was made. The assignment of signals from carbon atoms attached to protons involved no difficulties, for the COSY and HSQC data were fully



Principal ^{13}C – ^1H interactions in the HMBC spectra of compounds **VI f**, **VII a**, **VII b**, **VIII a**, and **VIII d**.

consistent with each other. Some problems appeared while assigning signals from protons in the 4'-methoxyphenyl substituent in compounds **Vd**, **Vif**, **VIIb**, and **VIIIa**. The COSY spectra of these compounds displayed only a weak cross-peak between the methyl protons and 3'-H. Nevertheless, taking into account more upfield positions of the ^{13}C (δ_{C} 114–115 ppm) and ^1H signals (δ 6.98–7.03 ppm), they were assigned to $\text{C}^{3'}$ and 3'-H, respectively, while the signals located at δ_{C} 129–130 ppm and δ 7.07–7.09 ppm were assigned to $\text{C}^{2'}$ and 2'-H.

Signals from quaternary carbon atoms were assigned by analysis of long-range ^1H – ^{13}C couplings in the HMBC spectra. The principal interactions are shown in figure. All compounds having an exocyclic carbonyl group displayed cross-peaks between the carbonyl carbon atoms (δ_{C} 203–208 ppm) and protons in the α - and β -positions with respect to the carbonyl group. The corresponding protons in molecule **Vif** interact with the carbon nucleus resonating at δ_{C} 179.37 ppm, and that carbon nucleus also gives a cross-peak with methylene protons in the benzyl group. These data unambiguously indicate that the enamino fragment originates from the exocyclic carbonyl group. The lactam carbonyl carbon atom (δ_{C} 162–165 ppm) showed no strong cross-peaks because of the absence of protons in the vicinity of $\text{C}^2=\text{O}$. Only the HMBC spectra of *N*-methyl derivatives **VIIa** and **VIIIb** contained cross peaks resulting from coupling between the methyl protons and the carbonyl carbon atom. The quaternary carbon atom in the 3-position of the pyridine ring is readily identified taking into account upfield position of the corresponding signal (δ_{C} 101–112 ppm) and the presence of a cross-peak due to coupling with 5-H. Enamines **VIIIa** and **VIIIb** also displayed a cross-peak between C^3 and NH proton. It should be noted that the C^3 signal in the spectra of methyl ethers **VIIa** and **VIIb** is observed in a weaker field as compared to the other examined compounds ($\Delta\delta_{\text{C}} \approx 10$ ppm).

The C^4 signal was identified by the presence of a weak cross peak with 5-H and (for 4-substituted compounds) by the coupling with protons of the methoxy group (**VIIa**, **VIIb**) and methylene protons in the secondary amine moiety (**VIIIa**, **VIIIb**). Here, variations of ^{13}C chemical shifts reflect the character of substitution and degree of conjugation in the system. The C^4 signal in the spectra of enamino derivatives appears at δ_{C} 159 ppm, methoxy compounds display the C^4 signal in a weaker field (by 5–6 ppm), while the C^4 nucleus in diketone **Vif** resonates at δ_{C} 183.73 ppm.

Interactions with protons in the methyl group and 5-H allowed us to distinguish signal from the quaternary C^6 atom in the pyridine ring. *N*-Methyl derivatives **VIIa** and **VIIIb** additionally showed a cross-peak between C^6 and NCH_3 protons. Signals from the quaternary carbon atom in the methoxyphenyl substituent in compounds **Vif**, **VIIb**, and **VIIIa** were assigned on the basis of coupling between the OCH_3 protons and carbon nucleus resonating at δ_{C} 159 ppm; the chemical shift of the latter was also taken into account.

Unlike carbo- [21] and heterocyclic β -triketones [22, 23] studied previously, we failed to obtain condensation products of triketones **IIIa** and **IIIb** with isoquinoline derivatives (diaza analogs of steroids) regardless of the reaction conditions (acid or base catalysis).

EXPERIMENTAL

The IR spectra of solid products were recorded in KBr on a UR-20 spectrometer; liquid products were examined as films (neat). The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500 instrument at 500 and 125 MHz, respectively; chloroform-*d* was used as solvent, and tetramethylsilane, as reference. The mass spectra were run on an MKh-1320 spectrometer. The melting points were determined on a Boetius hot stage. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 or Alufol UV-254 plates (Merck); spots were detected under UV light, followed by spraying with a solution of iron(III) chloride. Preparative thin-layer chromatography was performed using silica gel Kieselgel 60 HF₂₅₄ (Merck).

Enol esters IVa–IVd (general procedure). Pyridine, 10.5 ml (0.13 mol), and the corresponding carboxylic acid chloride, 0.11 mol, were added under stirring to a mixture of 0.1 mol of diketone **IIIa–IIIb** and 100 ml of methylene chloride. The mixture was stirred for 24 h at room temperature (TLC), 50 ml of cold water was added, the mixture was acidified to pH 5 by adding 2 N hydrochloric acid, the organic phase was separated, washed with water and a 5% solution of sodium carbonate, and dried over magnesium sulfate, and the solvent was removed on a rotary evaporator.

1,6-Dimethyl-2-oxo-1,2-dihydropyridin-4-yl acetate (IVa). Yield 95%, mp 136–137°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 1775, 1670, 1600, 1570. ^1H NMR spectrum, δ , ppm: 2.27 s (3H, 6- CH_3), 2.36 s (3H, CH_3CO), 3.50 s (3H, NCH_3), 5.96 d (1H, 5-H, $J = 2.5$ Hz), 6.23 d (1H, 3-H, $J = 2.5$ Hz). Found,

%; C 59.80; H 6.21; N 7.87. $[M]^+$ 181. $C_9H_{11}NO_3$. Calculated, %: C 59.66; H 6.12; N 7.73. M 181.19.

6-Methyl-2-oxo-1-propyl-1,2-dihydropyridin-4-yl propanoate (IVb). Yield 90%. Oily substance. IR spectrum, ν , cm^{-1} : 1780, 1670, 1600, 1570. 1H NMR spectrum, δ , ppm: 0.98 t (3H, $CH_3CH_2CH_2$, $J = 7.0$ Hz), 1.23 t (3H, CH_3CH_2CO , $J = 7.5$ Hz), 1.72 m (2H, $CH_3CH_2CH_2$), 2.38 s (3H, 6- CH_3), 2.54 q (2H, CH_3CH_2CO , $J = 7.5$ Hz), 3.96 m (2H, NCH_2), 5.94 d (1H, 5-H, $J = 2.5$ Hz), 6.20 d (1H, 3-H, $J = 2.5$ Hz). Found, %: C 64.60; H 7.83; N 6.43. $[M]^+$ 223. $C_{12}H_{17}NO_3$. Calculated, %: C 64.55; H 7.67; N 6.27. M 223.27.

1-Benzyl-6-methyl-2-oxo-1,2-dihydropyridin-4-yl propanoate (IVc). Yield 93%, mp 86–87°C. IR spectrum, ν , cm^{-1} : 1765, 1660, 1600, 1580. 1H NMR spectrum, δ , ppm: 1.25 t (3H, CH_3CH_2 , $J = 7.5$ Hz), 2.28 s (1H, 6- CH_3), 2.58 q (2H, CH_3CH_2 , $J = 7.5$ Hz), 5.34 s (2H, $CH_2C_6H_5$), 5.95 d (1H, 5-H, $J = 2.5$ Hz), 6.33 d (1H, 3-H, $J = 2.5$ Hz), 7.13–7.37 m (5H, C_6H_5). Found, %: C 70.96; H 6.51; N 5.20. $[M]^+$ 271. $C_{16}H_{17}NO_3$. Calculated, %: C 70.83; H 6.32; N 5.16. M 271.32.

1-(4-Methoxyphenyl)-6-methyl-2-oxo-1,2-dihydropyridin-4-yl butanoate (IVd). Yield 97%, mp 109–110°C. IR spectrum, ν , cm^{-1} : 1780, 1670, 1610, 1570. 1H NMR spectrum, δ , ppm: 1.04 t (3H, CH_3CH_2 , $J = 7.7$ Hz), 1.77 m (2H, CH_3CH_2), 1.97 s (3H, 6- CH_3), 2.53 t (2H, CH_2CH_2 , $J = 7.3$ Hz), 3.85 s (3H, OCH_3), 6.00 d (1H, 5-H, $J = 2.2$ Hz), 6.28 d (1H, 3-H, $J = 2.2$ Hz), 7.03 d (2H, C_6H_4 , $J = 8.8$ Hz), 7.10 d (2H, C_6H_4 , $J = 8.8$ Hz). Found, %: C 67.69; H 6.47; N 4.48. $[M]^+$ 301. $C_{17}H_{19}NO_4$. Calculated, %: C 67.76; H 6.36; N 4.65. M 301.34.

3-Acyl-6-methyl-1,2,3,4-tetrahydropyridine-2,4-diones Va–Vd (general procedure). Compound **IVa–IVd**, 0.05 mol, was dissolved in 50 ml of methylene chloride, 14 ml (0.1 mol) of triethylamine and 0.5 ml (0.005 mol) of 2-hydroxy-2-methylpropanenitrile were added, and the mixture was stirred for 48 h at 25–30°C, following the disappearance of initial compound **IVa–IVd** (TLC). The mixture was acidified to pH 5 with 10% hydrochloric acid, and the organic phase was separated, washed with water, dried over magnesium sulfate, and passed through a thin layer of silica gel. The solvent was removed under reduced pressure on a rotary evaporator, and the oily residue was recrystallized from ethyl acetate–petroleum ether.

3-Acetyl-1,6-dimethyl-1,2,3,4-tetrahydropyridine-2,4-dione (Va). Yield 83%, mp 130–131°C. IR

spectrum, cm^{-1} : 1655 (C=O, lactam), 1615 ($CH_3C=O$), 1580 (C=C, enol). 1H NMR spectrum, δ , ppm: 2.36 s (3H, 6- CH_3), 2.74 s (3H, $COCH_3$), 3.45 s (3H, CH_3N), 5.86 s (1H, 5-H), 15.52 s (1H, OH). Found, %: C 59.59; H 6.07; N 7.84. $[M]^+$ 181. $C_9H_{11}NO_3$. Calculated, %: C 59.66; H 6.12; N 7.73. M 181.19.

6-Methyl-1-propyl-3-propionyl-1,2,3,4-pyridine-2,4-dione (Vb). Yield 85%, mp 58–59°C. IR spectrum, ν , cm^{-1} : 1665 (C=O, lactam), 1620 (EtC=O), 1570 (C=C, enol). 1H NMR spectrum, δ , ppm: 0.99 t (3H, $CH_3CH_2CH_2$, $J = 7.4$ Hz), 1.16 t (3H, CH_3CH_2CO , $J = 7.4$ Hz), 1.69 m (2H, $CH_3CH_2CH_2$), 2.37 s (3H, 6- CH_3), 3.18 q (2H, CH_3CH_2CO , $J = 7.0$ Hz), 3.87 m (2H, NCH_2), 5.81 s (1H, 5-H), 15.60 s (1H, OH). Found, %: C 64.47; H 7.50; N 6.37. $[M]^+$ 223. $C_{12}H_{17}NO_3$. Calculated, %: C 64.55; H 7.67; N 6.27. M 223.27.

1-Benzyl-6-methyl-3-propionyl-1,2,3,4-tetrahydropyridine-2,4-dione (Vc). Yield 80%, mp 75–76°C. IR spectrum, ν , cm^{-1} : 1670 (C=O, lactam), 1625 (EtC=O), 1570 (C=C, enol). 1H NMR spectrum, δ , ppm: 1.60 t (3H, CH_3CH_2 , $J = 7.0$ Hz), 2.28 s (3H, 6- CH_3), 3.21 q (2H, CH_3CH_2), 5.27 s (2H, $CH_2C_6H_5$), 5.86 s (1H, 5-H), 7.13 d (2H, H_{arom}), 7.26 m (1H, H_{arom}), 7.33 m (2H, H_{arom}), 15.74 s (1H, OH). Found, %: C 70.89; H 6.33; N 5.22. $[M]^+$ 271. $C_{16}H_{17}NO_3$. Calculated, %: C 70.83; H 6.32; N 5.16. M 271.32.

3-Butyryl-1-(4-methoxyphenyl)-6-methyl-1,2,3,4-tetrahydropyridine-2,4-dione (Vd). Yield 82%, mp 105–106°C. IR spectrum, ν , cm^{-1} : 1670 (C=O, lactam); 1620 (PrC=O); 1610, 1570 (C=C, enol). 1H NMR spectrum, δ , ppm: 0.94 t (3H, CH_3CH_2 , $J = 7.4$ Hz), 1.66 m (2H, CH_3CH_2), 1.99 s (3H, CH_3CH_2), 2.28 s (3H, $CH_3C=CH$), 3.11 t (2H, CH_2CH_2 , $J = 7.4$ Hz), 3.85 s (3H, OCH_3), 5.93 s (1H, 5-H), 7.03 m (2H, H_{arom}), 7.08 m (2H, H_{arom}), 15.97 s (1H, OH). ^{13}C NMR spectrum, δ_c , ppm: 13.82 ($C^{4''}$), 17.36 ($C^{3''}$), 22.33 (6-Me), 44.71 ($C^{2''}$), 55.54 (MeO), 100.90 (C^5), 105.43 (C^3), 115.12 ($C^{3'}$), 129.08 ($C^{2'}$), 130.60 ($C^{1'}$), 154.08 (C^6), 159.72 ($C^{4'}$), 163.50 (C^2), 176.30 (C^4), 208.30 ($C^{1''}$). Found, %: C 67.89; H 6.32; N 4.72. $[M]^+$ 301. $C_{17}H_{19}NO_4$. Calculated, %: C 67.76; H 6.36; N 4.65. M 301.34.

3-Acyl-6-methyl-1,2,3,4-tetrahydropyridine-2,4-diones Ve and Vf (general procedure). Triethylamine, 18.2 ml (0.13 mol), was added under stirring to a mixture of 0.1 mol of diketone **IIIa** or **IIIc** in 100 ml of methylene chloride, and a solution of 0.11 mol of pentanoyl or acetyl chloride in methylene chloride (1:1 by volume) was added dropwise over a period of 4 h under stirring. The mixture was then stirred for 0.5 h at

room temperature, and 28 ml (0.20 mol) of triethylamine and 0.5 ml (0.005 mol) of 2-hydroxy-2-methylpropanenitrile were added. As in the reactions with enol esters **IV**, the C–O isomerization was complete in 48 h (TLC). The mixture was treated as described above.

1,6-Dimethyl-3-pentanoyl-1,2,3,4-tetrahydropyridine-2,4-dione (Ve). Yield 73%. Oily substance. IR spectrum, ν , cm^{-1} : 1660 (C=O, lactam), 1620 (BuC=O), 1565 (C=C, enol). ^1H NMR spectrum, δ , ppm: 0.95 t (3H, $\text{CH}_3\text{CH}_2\text{CH}_2$, $J = 7.3$ Hz), 1.41 m (2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.65 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.35 s (3H, 6- CH_3), 3.17 t (2H, $\text{CH}_2\text{CH}_2\text{CO}$, $J = 7.7$ Hz), 3.45 s (3H, NCH_3), 5.84 s (1H, 5-H), 15.67 s (1H, OH). Found, %: C 64.69; H 7.65; N 6.40. $[M]^+$ 223. $\text{C}_{12}\text{H}_{17}\text{NO}_3$. Calculated, %: C 64.55; H 7.67; N 6.27. M 223.27.

3-Acetyl-1-benzyl-6-methyl-1,2,3,4-tetrahydropyridine-2,4-dione (Vf). Yield 75%. Oily substance. IR spectrum, ν , cm^{-1} : 1660 (C=O, lactam), 1620 (MeC=O), 1575 (C=C, enol). ^1H NMR spectrum, δ , ppm: 2.28 s (3H, 6- CH_3), 2.74 s (3H, CH_3CO), 5.27 s (2H, $\text{CH}_2\text{C}_6\text{H}_5$), 5.86 s (1H, 5-H), 7.13 d (2H, H_{arom}), 7.27 m (1H, H_{arom}), 7.33 m (2H, H_{arom}), 15.65 s (1H, OH). Found, %: C 70.13; H 5.78; N 5.42. $[M]^+$ 257. $\text{C}_{15}\text{H}_{15}\text{NO}_3$. Calculated, %: C 70.02; H 5.88; N 5.44. M 257.19.

Enamines VIa–VIh (general procedure). Triketone **Va**, **Vb**, **Vd**, or **Ve**, 5 mmol, was dissolved in 50 ml of toluene, 6.5 mmol of the corresponding amine was added, and the mixture was heated under reflux for 4–6 (aliphatic amines) or 60 h (aromatic amines), the progress of the reaction being monitored by TLC. The mixture was washed with 5% hydrochloric acid and water, the aqueous phases were combined and extracted with chloroform (3×10 ml), the chloroform extracts were combined with the toluene layer, dried over anhydrous magnesium sulfate, and passed through a thin layer of silica gel, and the solvent was evaporated under reduced pressure.

1,6-Dimethyl-3-[1-(phenylamino)ethylidene]-1,2,3,4-tetrahydropyridine-2,4-dione (VIa). Yield 52%, mp 116–118°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3060, 1660, 1620, 1560. ^1H NMR spectrum, δ , ppm: 2.25 s (3H, 6- CH_3), 2.71 s (3H, CH_3CN), 3.42 s (3H, CH_3N), 5.79 s (1H, 5-H), 7.10–7.40 m (5H, C_6H_5), 17.1 s (1H, NH). Found, %: C 70.39; H 6.21; N 11.02. $[M]^+$ 256. $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$. Calculated, %: C 70.29; H 6.29; N 10.93. M 256.30.

3-[1-(2-Allylamino)ethylidene]-1,6-dimethyl-1,2,3,4-tetrahydropyridine-2,4-dione (VIb). Yield

85%, mp 69–69.5°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3070, 1660, 1620, 1600, 1560. ^1H NMR spectrum, δ , ppm: 2.22 s (3H, 6- CH_3), 2.70 s (2H, CH_3CN), 3.35 s (3H, CH_3N), 4.13 t (2H, NHCH_2 , $J = 5.5$ Hz), 5.29 m (2H, $\text{CH}_2=\text{CH}$), 5.70 s (1H, 5-H), 5.90 m (1H, $\text{CH}_2=\text{CH}$), 15.3 s (1H, NH). Found, %: C 65.61; H 7.42; N 12.66. $[M]^+$ 220. $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_2$. Calculated, %: C 65.43; H 7.32; N 12.72. M 220.27.

3-[1-(2-Allylamino)pentylidene]-1,6-dimethyl-1,2,3,4-tetrahydropyridine-2,4-dione (VIc). Yield 87%, mp 38–40°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3070, 1655, 1620, 1590, 1560. ^1H NMR spectrum, δ , ppm: 0.97 t (3H, CH_3CH_2 , $J = 7.4$ Hz), 1.51 m (2H, CH_2CH_3), 2.22 s (3H, 6- CH_3), 3.13 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.35 s (3H, CH_3N), 4.13 t (2H, NHCH_2 , $J = 5.5$ Hz), 5.30 m (2H, $\text{CH}_2=\text{CH}$), 5.67 s (1H, 5-H), 5.90 m (1H, $\text{CH}_2=\text{CH}$), 15.3 s (1H, NH). Found, %: C 68.77; H 8.55; N 10.46. $[M]^+$ 262. $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2$. Calculated, %: C 68.67; H 8.45; N 10.68. M 262.35.

3-{1-[(4-Methoxyphenyl)amino]propylidene}-6-methyl-1-propyl-1,2,3,4-tetrahydropyridine-2,4-dione (VIId). Yield 44%, mp 89–90°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3080, 1670, 1620, 1590, 1560. ^1H NMR spectrum, δ , ppm: 1.00 t (3H, $\text{CH}_3\text{CH}_2\text{CH}_2$, $J = 7.5$ Hz), 1.22 t (3H, $\text{NHCCH}_2\text{CH}_3$, $J = 7.5$ Hz), 1.68 m (2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 2.30 s (3H, 6- CH_3), 3.10 q (2H, $\text{NHCCH}_2\text{CH}_3$, $J = 7.5$ Hz), 3.80 m (2H, NCH_2), 3.84 s (3H, OCH_3), 5.73 s (1H, 5-H), 6.94 d (2H, C_6H_4 , $J = 9.0$ Hz), 7.12 d (2H, C_6H_4 , $J = 9.0$ Hz), 16.85 s (1H, NH). Found, %: C 69.77; H 7.61; N 8.37. $[M]^+$ 328. $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_3$. Calculated, %: C 69.49; H 7.37; N 8.53. M 328.41.

3-[1-(Benzylamino)propylidene]-6-methyl-1-propyl-1,2,3,4-tetrahydropyridine-2,4-dione (VIe). Yield 82%. Oily substance. IR spectrum, ν , cm^{-1} : 3080, 1670, 1620, 1590, 1560. ^1H , δ , ppm: 0.95 t (3H, $\text{CH}_3\text{CH}_2\text{CH}_2$, $J = 7.5$ Hz), 1.23 t (3H, $\text{NHCCH}_2\text{CH}_3$, $J = 7.5$ Hz), 1.68 m (2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 2.23 s (3H, 6- CH_3), 3.24 q (2H, $\text{NHCCH}_2\text{CH}_3$, $J = 7.5$ Hz), 3.82 m (2H, NCH_2), 4.78 d (2H, NHCH_2Ph , $J = 5.5$ Hz), 5.68 s (1H, 5-H), 7.20–7.42 m (5H, C_6H_5), 15.65 s (1H, NH). Found, %: C 73.10; H 7.65; N 9.01. $[M]^+$ 312. $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$. Calculated, %: C 73.05; H 7.74; N 8.97. M 312.41.

3-[1-(Benzylamino)butylidene]-6-methyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydropyridine-2,4-dione (VIIf). Yield 85%, mp 154–155°C (from ethyl acetate). IR spectrum, ν , cm^{-1} : 3080, 1670, 1630, 1590, 1560. ^1H NMR spectrum, δ , ppm: 1.00 t (3H, $\text{CH}_3\text{CH}_2\text{CH}_2$, $J = 7.4$ Hz), 1.64 m (4H, $\text{CH}_3\text{CH}_2\text{CH}_2$),

1.82 s (3H, 6-CH₃), 3.13 t (1.6H, $J = 8.0$ Hz) and 3.31 br.s (0.4H, NHCH₂CH₂), 3.83 s (3H, OCH₃), 4.64 br.s (0.4H) and 4.71 d (1.6H, $J = 5.5$ Hz) (NHCH₂Ph), 5.74 s (1H, 5-H), 6.97 m (2H, H_{arom}), 7.08 m (2H, H_{arom}), 7.33–7.38 m (5H, H_{arom}), 15.59 s (1H, NH). Found, %: C 73.98; H 6.65; N 7.03. $[M]^+$ 390. C₂₄H₂₆N₂O₃. Calculated, %: C 73.82; H 6.71; N 7.17. *M* 390.48.

1-(4-Methoxyphenyl)-6-methyl-3-[1-(4-tolyl-amino)butylidene]-1,2,3,4-tetrahydropyridine-2,4-dione (VIg). Yield 44%, mp 150–152°C (from diethyl ether). IR spectrum, ν , cm⁻¹: 3060, 1660, 1625, 1560, 1520. ¹H NMR spectrum, δ , ppm: 0.80 t (2.4H, $J = 7.4$ Hz) and 0.89–0.98 m (0.6H) (CH₃CH₂CH₂), 1.60 m (2H, CH₃CH₂CH₂), 1.86 s (3H, 6-CH₃), 2.39 s (CH₃C₆H₄), 2.98 t (1.6H, $J = 7.7$ Hz) and 3.14 m (0.4H) (CH₂CH₂CH₃), 3.84 s (3H, CH₃O), 5.81 s (1H, 5-H), 6.97–7.25 m (8H, H_{arom}), 14.7 s (0.2H) and 16.85 s (0.8H) (NH). ¹³C NMR spectrum, δ_c , ppm: 14.60 (C^{4''}), 20.86 (C^{3''}), 21.81 (6-Me), 31.95 (C^{2''}), 47.20 (CH₂Ph), 55.44 (MeO), 101.92 (C³), 107.50 (C⁵), 114.76 (C^{3'}), 127.16 (C^{2'''}), 127.96 (C^{4'''}), 129.03 (C^{3'''}), 129.76 (C^{2'}), 131.87 (C^{1'}), 136.04 (C^{1'''}), 149.12 (C⁶), 159.17 (C^{4'}), 165.03 (C²), 183.73 (C⁴), 179.37 (C^{1''}). Found, %: C 74.01; H 6.61; N 7.30. $[M]^+$ 390. C₂₄H₂₆N₂O₃. Calculated, %: C 73.82; H 6.71; N 7.17. *M* 390.48.

1,6-Dimethyl-3-[1-(4-methoxyphenylamino)-pentyldiene]-1,2,3,4-tetrahydropyridine-2,4-dione (VIh). Yield 48%, mp 120–121°C (from methanol). IR spectrum, ν , cm⁻¹: 3050, 1650, 1625, 1570, 1555. ¹H NMR spectrum, δ , ppm: 0.79 t (3H, CH₃CH₂CH₂, $J = 7.1$ Hz), 1.29 m (2H, CH₃CH₂CH₂), 1.56 m (2H, CH₃CH₂CH₂), 2.26 s (3H, 6-CH₃), 3.05 m (2H, NH-CCH₂CH₂), 3.80 s (3H, NCH₃), 3.84 s (3H, CH₃O), 5.74 s (1H, 5-H), 6.93 m (2H, H_{arom}), 7.08 m (2H, H_{arom}), 16.85 s (1H, NH). Found, %: C 69.33; H 7.17; N 8.47. $[M]^+$ 328. C₁₉H₂₄N₂O₃. Calculated, %: C 69.49; H 7.37; N 8.53. *M* 328.41.

Enol ethers VIIa and VIIb (general procedure). Triketone **Vd** or **Ve**, 0.05 mol, was dissolved in 50 ml of toluene, 2.8 g (0.02 mol) of finely powdered anhydrous potassium carbonate and 0.57 ml (0.06 mol) of dimethyl sulfate were added, and the mixture was heated for 6–8 h under reflux with stirring. The mixture was cooled and filtered from potassium carbonate, the precipitate was washed on a filter with toluene, the filtrate was passed through a thin layer of silica gel, the solvent was removed under reduced pressure, and the residue was recrystallized from a mixture of diethyl ether and petroleum ether.

4-Methoxy-1,6-dimethyl-3-pentanoyl-1,2-dihydropyridin-2-one (VIIa). Yield 98%, mp 52–53°C. IR spectrum, ν , cm⁻¹: 1700, 1655, 1590, 1560. ¹H NMR spectrum, δ , ppm: 0.90 t (3H, CH₃CH₂CH₂, $J = 7.4$ Hz), 1.35 m (2H, CH₃CH₂CH₂), 1.64 m (2H, CH₂-CH₂CH₂), 2.39 s (3H, 6-CH₃), 2.83 t (2H, CH₂CH₂CO, $J = 7.7$ Hz), 3.48 s (3H, NCH₃), 3.82 s (3H, OCH₃), 5.95 s (1H, 5-H). ¹³C NMR spectrum, δ_c , ppm: 13.97 (C^{5''}), 21.74 (6-Me), 22.41 (C^{4''}), 26.11 (C^{3''}), 30.82 (C^{1'}), 43.54 (C^{2''}), 56.02 (MeO), 94.84 (C⁵), 112.64 (C³), 127.16 (C^{2'''}), 149.25 (C⁶), 162.03 (C²), 164.08 (C⁴), 203.18 (C^{1''}). Found, %: C 65.64; H 7.95; N 6.02. $[M]^+$ 237. C₁₃H₁₉NO₃. Calculated, %: C 65.80; H 8.07; N 5.90. *M* 237.30.

3-Butanoyl-4-methoxy-1-(4-methoxyphenyl)-6-methyl-1,2-dihydropyridin-2-one (VIIb). Yield 97%, mp 142–143°C. IR spectrum, ν , cm⁻¹: 1710, 1650, 1610, 1585. ¹H NMR spectrum, δ , ppm: 0.92 t (3H, CH₃CH₂CH₂, $J = 7.4$ Hz), 1.67 m (2H, CH₃CH₂CH₂), 2.03 s (3H, 6-CH₃), 2.85 t (2H, CH₂CH₂CO, $J = 7.4$ Hz), 3.84 s (3H, NCH₃), 3.88 s (3H, OCH₃), 6.02 s (1H, 5-H), 7.08 m (2H, H_{arom}), 7.14 m (2H, H_{arom}). ¹³C NMR spectrum, δ_c , ppm: 13.93 (C^{4''}), 17.58 (C^{3''}), 22.50 (6-Me), 45.75 (C^{2''}), 55.67 (4'-MeO), 56.36 (4-MeO), 94.95 (C⁵), 113.05 (C³), 115.18 (C^{3'}), 129.06 (C^{2'}), 130.70 (C^{1'}), 150.09 (C⁶), 159.81 (C^{4'}), 162.84 (C²), 165.30 (C⁴), 202.96 (C^{1''}). Found, %: C 65.64; H 7.95; N 6.02. $[M]^+$ 315. C₁₈H₂₁NO₄. Calculated, %: C 68.55; H 6.71; N 4.44. *M* 315.37.

Enamines VIIa–VIIId (general procedure). A mixture of 0.01 mol of 4-methoxypyridine **VIIa** or **VIIb** and 0.013 mmol of the corresponding amine in 50 ml of toluene was heated for 18–24 h under reflux (TLC). The mixture was then treated as described above for enamino derivatives **VI**.

4-Benzylamino-3-butanoyl-1-(4-methoxyphenyl)-6-methyl-1,2-dihydropyridin-2-one (VIIa). Yield 85%, mp 145–146°C (from methanol). IR spectrum, ν , cm⁻¹: 3070, 1660, 1630, 1560, 1520. ¹H NMR spectrum, δ , ppm: 0.92 t (3H, CH₃CH₂CH₂, $J = 7.4$ Hz), 1.63 m (2H, CH₃CH₂CH₂), 1.87 s (3H, 6-CH₃), 3.10 t (2H, CH₂CH₂CO, $J = 7.4$ Hz), 3.83 s (3H, OCH₃), 4.52 d (2H, NHCH₂, $J = 5.8$ Hz), 5.73 s (1H, 5-H), 6.99 m (2H, H_{arom}), 7.07 m (2H, H_{arom}), 7.26–7.40 m (5H, H_{arom}), 11.53 t (1H, NH, $J = 5.45$ Hz). ¹³C NMR spectrum, δ_c , ppm: 14.12 (C^{4''}), 18.15 (C^{3''}), 22.58 (6-Me), 46.31 (C^{2''}), 46.64 (CH₂Ph), 55.56 (4'-MeO), 94.48 (C⁵), 101.73 (C³), 114.95 (C^{3'}), 127.05 (C^{2'''}, C^{6'''}), 127.66 (C^{4'''}), 128.98 (C^{3'''}, C^{5'''}), 129.46 (C^{2'}), 131.48 (C^{1'}), 150.80 (C⁶), 137.41 (C^{1'''}), 159.45 (C^{4'}), 164.52 (C²), 159.82 (C⁴), 204.82 (C^{1''}).

Found, %: C 73.78; H 6.60; N 7.25. $[M]^+$ 390. $C_{24}H_{26}N_2O_3$. Calculated, %: C 73.82; H 6.71; N 7.17. M 390.48.

3-Butanoyl-1-(4-methoxyphenyl)-6-methyl-4-(4-tolylamino)-1,2-dihydropyridin-2-one (VIIIb). Yield 43%, mp 153–154°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3070, 1665, 1630, 1560, 1520. 1H NMR spectrum, δ , ppm: 0.95 t (3H, $CH_3CH_2CH_2$, $J = 7.4$ Hz), 1.67 m (2H, CH_3CH_2), 1.83 s (3H, $CH_3C_6H_4$), 2.38 s (3H, 6- CH_3), 3.15 t (2H, CH_2CH_2CO , $J = 7.7$ Hz), 3.84 s (3H, NCH_3), 5.87 s (1H, 5-H), 7.01 m (2H, H_{arom}), 7.09 m (2H, H_{arom}), 7.14 m (2H, H_{arom}), 7.21 m (2H, H_{arom}), 12.63 s (1H, NH). Found, %: C 73.98; H 6.65; N 7.03. $[M]^+$ 390. $C_{24}H_{26}N_2O_3$. Calculated, %: C 73.82; H 6.71; N 7.17. M 390.48.

4-(4-Methoxyphenylamino)-1,6-dimethyl-3-pentanoyl-1,2-dihydropyridin-2-one (VIIIc). Yield 45%, mp 98–99°C (from hexane). IR spectrum, ν , cm^{-1} : 3050, 1650, 1620, 1565, 1520. 1H NMR spectrum, δ , ppm: 0.96 t (3H, $CH_3CH_2CH_2$, $J = 7.4$ Hz), 1.42 m (2H, $CH_3CH_2CH_2$), 1.67 m (2H, $CH_3CH_2CH_2$), 2.19 s (3H, 6- CH_3), 3.20 t (2H, CH_2CH_2CO , $J = 7.4$ Hz), 3.41 s (3H, NCH_3), 3.83 s (3H, OCH_3), 5.69 s (1H, 5-H), 6.91 m (2H, H_{arom}), 7.10 m (2H, H_{arom}), 12.26 s (1H, NH). Found, %: C 69.48; H 7.27; N 8.35. $[M]^+$ 328. $C_{19}H_{24}N_2O_3$. Calculated, %: C 69.49; H 7.37; N 8.53. M 328.41.

4-Allylamino-1,6-dimethyl-3-pentanoyl-1,2-dihydropyridin-2-one (VIIId). Yield 65%, mp 59–60°C (from diethyl ether). IR spectrum, ν , cm^{-1} : 3090, 1660, 1620, 1570, 1520. 1H NMR spectrum, δ , ppm: 0.94 t (3H, $CH_3CH_2CH_2$, $J = 7.4$ Hz), 1.39 m (2H, $CH_3CH_2CH_2$), 1.63 m (2H, $CH_3CH_2CH_2$), 2.29 s (3H, 6- CH_3), 3.14 t (2H, CH_2CH_2CO , $J = 7.69$ Hz), 3.41 s (3H, NCH_3), 3.88 m (2H, $NHCH_2$), 5.23 m (2H, $CH_2=CH$), 5.62 s (1H, 5-H), 5.88 m (1H, $CH_2=CH$), 10.90 s (1H, NH). ^{13}C NMR spectrum, δ_C , ppm: 14.30 (C^5), 22.03 (6-Me), 22.83 (C^4), 27.33 (C^3), 30.52 (C^1), 44.10 (C^2), 44.85 ($C^{1'}$), 94.56 (C^5), 101.74 (C^3), 133.33 ($C^{2'}$), 116.89 ($C^{3'}$), 150.15 (C^6), 164.06 (C^2), 159.01 (C^4), 205.01 ($C^{1'}$). Found, %: C 68.77; H 8.55; N 10.46. $[M]^+$ 262. $C_{15}H_{22}N_2O_2$. Calculated, %: C 68.67; H 8.45; N 10.68. M 262.35.

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