

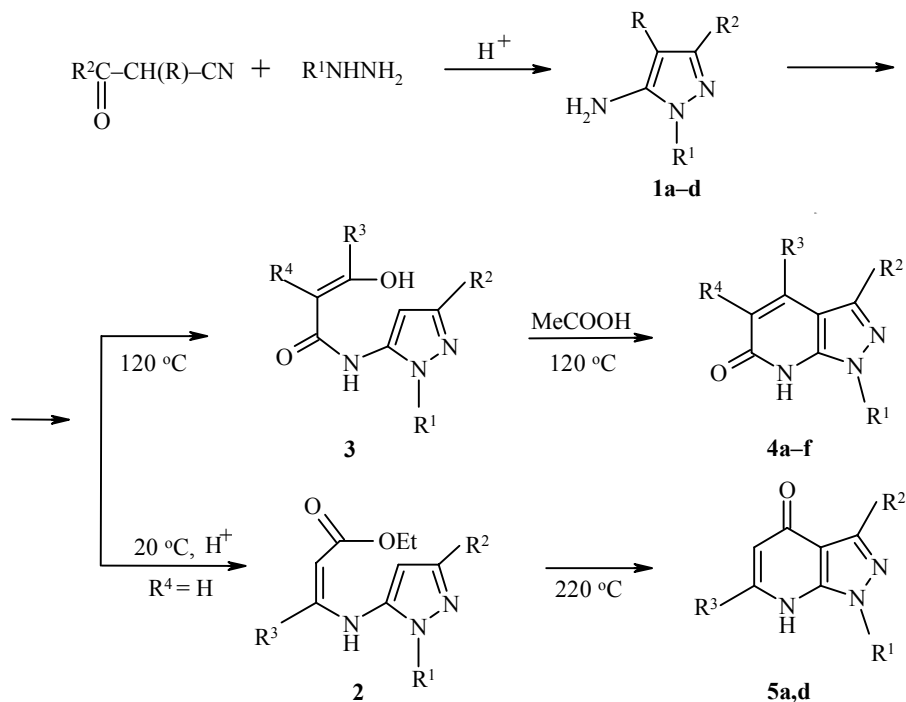
CONDENSATION OF 1-SUBSTITUTED 5-AMINOPYRAZOLES WITH β -DICARBONYL COMPOUNDS

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Condensation of *N*-substituted 5-aminopyrazoles with β -diketones occurs with the formation of pyrazolo[4,5-*b*]pyridines. Depending on the conditions, their reaction with β -keto acids can give either 6-oxo- or 4-oxopyrazolo[4,5-*b*]pyridines.

Keywords: 5-aminopyrazoles, β -diketones, β -keto esters, pyrazolopyridines.

In the case of acetoacetic ester and 5-amino-3-methyl-1-phenylpyrazole (**1a**), an acetoacetic ester condensation reaction with aminopyrazoles leads to type **3** amides or type **2** crotonates. Thermal condensation or condensation in the presence of acids then gives the pyrazolopyridones **4a** and **5a** respectively [1, 2].

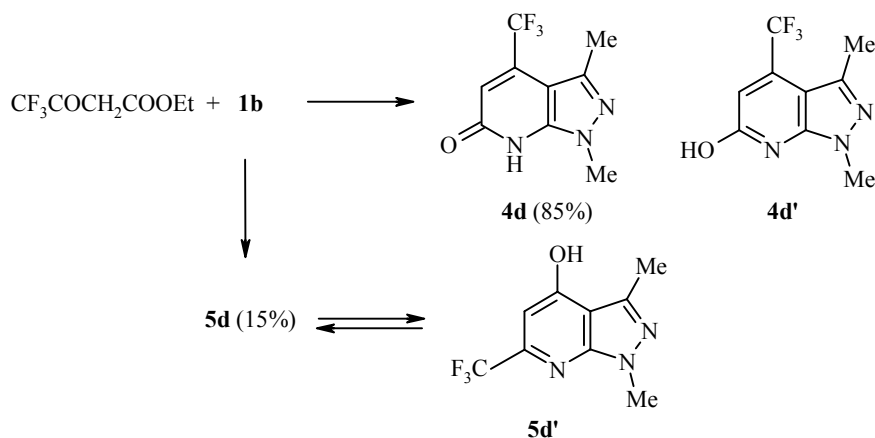


1 a-d R = H, **e, f** R = Me, **a, c, f** R¹ = Ph, **b, d, e** R¹ = Me, **a, b** R² = Me, **c, d** R² = Ph, **e, f** R² = Et; **4 a, b, e, f** R¹ = Ph, **c, d** R¹ = Me, **a-f** R² = Me, **a, c, e, f** R³ = Me, **b, d** R³ = CF₃, **a-d** R⁴ = H, **e** R⁴ = Et, **f** R⁴ = Me; **5 a** R¹ = Ph, R² = R³ = Me; **d** R¹ = R² = Me, R³ = CF₃

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We have broadened the scope of use of this condensation of 5-aminopyrazoles and have synthesized the 1-substituted 5-aminopyrazoles **1b-d** from diacetonitrile and benzoylacetone. By using β -imino- α -methylbutyronitrile (dipropionitrile) in this reaction we have also prepared two novel 5-aminopyrazoles which are substituted in position 4 (**1e,f**). With the aim of producing pyrazolopyridines (which are of interest as physiologically active compounds) we have also studied other β -diketones (methylacetylacetone and hexafluoroacetylacetone) and β -keto esters (trifluoroacetoacetic, methyl- and ethylacetoacetic esters) in the reaction. There also remains open the question of the condensation route in the case of the keto esters and hence their type **4** and **5** structures. In addition, the position of the hydroxy and methyl groups in the pyridine nucleus for the cyclization was not resolved by the authors in the work [3, 4]. Our observation [2] that only one of the pyrazolopyridones forms a picrate is indirect proof of the positioning of the keto group in the pyridine nucleus and the structure of the condensation product (amide or crotonate, see the Scheme). Since the most basic nitrogen atom in the pyrazolopyridine structure is that in the pyridine ring it is logical to propose that compound **4a** has more weakly basic properties than compound **5a** (2-hydroxypyridine is a weaker base than 4-hydroxypyridine by a factor of 1500 [5]).

It is known [1, 2] that 4-oxopyrazolo[4,5-*b*]pyridine **5a**, forming the picrate, is exclusively obtained from the crotonate **2** when it is slowly introduced into refluxing dioxane whereas all of the other variants of the cyclization reaction give the product 6-oxopyrazolo[4,5-*b*]pyridine **4a**. Hence the use of the cyclization reaction conditions of heating both components at 150°C without solvent should give the 6-oxopyrazolo[4,5-*b*]pyridines. In all cases except one the actual compounds **4** were obtained (see Experimental) without isomeric contamination and in high yields. Unfortunately, the 6-oxopyrazolopyridines obtained do not form crystals suitable for X-ray analysis and hence an absolute structural proof could not be achieved.

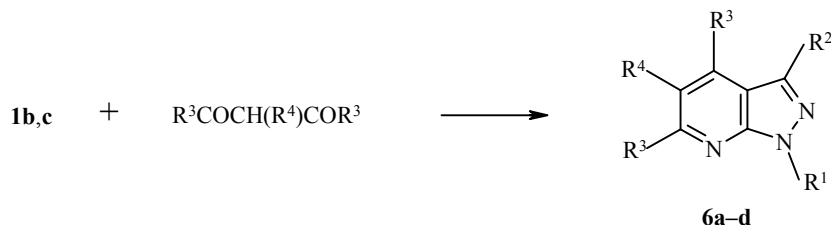


However, in the case of the condensation of 5-amino-1,3-dimethylpyrazole (**1b**) with trifluoroacetoacetic ester a mixture of pyrazolopyridines was obtained. The ^1H NMR spectrum showed both signals for the pyrazolopyridone **4d** and the presence of doubled signals for a second component (15%) which was initially assigned the lactim form **4d'**.

However, a change in the solvent from DMSO-d_6 to C_6D_6 when recording the spectrum did not change the ratio of these peaks (85 and 15%) and it is clear that the compound is actually the second isomer **5d**. A detailed study of the spectrum of the mixture in C_6D_6 showed that the signal for the CH_3 group in position three of the pyrazole nucleus at 2.43 ppm in the main product (85%) is split to an indistinct quadruplet ($J = 1.65$ Hz) and this can only be explained by a through space interaction with the CF_3 group. This is additional proof that the condensation occurs to form the 6-oxopyrazolopyridine **4d** as the main product since such a splitting is not possible in the isomer **5d**. It should also be noted that the methyl groups in the pyrazole nucleus undergo a marked shift to higher field when the spectra are recorded in C_6D_6 (1- CH_3 from 3.84 to 2.99 and 3- CH_3 from

2.42 to 1.60 ppm). This is because the equilibrium between the hydroxy and keto forms **5d'** and **5d** is shifted in non-polar solvent towards the hydroxy form **5d'**. As the same time, the position of the signals for compound **4** is little affected by solvent. This evidently supports the keto form and also indirectly confirms our deductions regarding the direction of cyclization.

The condensation of all of the β -diketones (with the exclusion of dibenzoylmethane) with the 5-aminopyrazoles occurs without complication upon heating equimolar amounts of both components at 150-160°C with distillation of water. All of the pyrazolo[4,5-*b*]pyridines **6** are obtained in high yields (60-95%).



6 a-c $R^1 = \text{Ph}$, **d** $R^1 = \text{Me}$, **a-d** $R^2 = \text{Me}$, **a, b, d** $R^3 = \text{Me}$, **c** $R^3 = \text{CF}_3$, **a, c, d** $R^4 = \text{H}$, **b** $R^4 = \text{Me}$

EXPERIMENTAL

IR spectra were taken on a Perkin-Elmer instrument (for KBr tablets), UV spectra on a Specord M-40 spectrometer, and ^1H NMR spectra on a Bruker AM-300 instrument (300 MHz) using DMSO- d_6 . TLC was carried out on Silufol plates and revealed using iodine or an alcoholic solution of FeCl_3 with subsequent heating.

5-Amino-3-methyl-1-phenylpyrazole (1a) was prepared according to method [6].

β -Imino- α -methylbutyronitrile. Finely divided sodium (27.6 g, 1.2 mol) was added to a three necked two liter flask fitted with a reflux condenser and a Hershberg stirrer. A solution of dry propionitrile (110 g, 2 mol) in absolute ether (150 ml) and absolute alcohol (1 ml) was added dropwise with vigorous stirring (care, evolution of hydrogen, all of the work was carried out in a fume cupboard). After the end of the addition, the reaction mixture was refluxed for 24 h with stirring and the precipitated sodium salt was filtered off and washed with absolute ether (200 ml). The salt was then added carefully to water (150 ml). The separated oil was extracted with ether and dried with sodium sulfate. Distillation then gave the β -imino- α -methylbutyronitrile (36.7 g, 33.4%) with bp 109-111°C (4 mm Hg) which solidified to a crystalline mass with mp 46-47°C (mp 46-48°C [7]). R_f 0.74 (methanol-acetone, 1:1). UV spectrum, λ_{max} , nm (log ϵ): 256 (4.38). IR spectrum, ν , cm^{-1} : 1580, 2280, 3300. Found, %: C 65.3; H 9.1; N 25.3. $\text{C}_6\text{H}_{10}\text{N}_2$. Calculated, %: C 65.5; H 9.1; N 25.5.

5-Amino-1,3-dimethylpyrazole (1b). A mixture of water (20 ml), isopropanol (30 ml), methylhydrazine sulfate (47.5 g, 0.33 mol), and β -aminocrotonitrile (24.6 g, 0.3 mol) was heated on a steam bath for 30 min. Concentrated hydrochloric acid (70 ml) was then added to the mixture which was refluxed using the condenser for 8 h. The reaction mixture was then neutralized with sodium hydroxide solution (40%) and evaporated to dryness on a rotary evaporator. The dry residue was extracted with isopropanol in a Soxhlet apparatus for 18 h. Evaporation under vacuum gave the aminopyrazole (19.3 g, 58%) with bp 121-123°C (9 mm Hg) which crystallized upon standing to a white crystalline mass with mp 52-54°C and R_f 0.57 (methanol-acetone, 1:1). UV spectrum, λ_{max} , nm (log ϵ): 233 (3.81). IR spectrum, ν , cm^{-1} : 1550, 1630, 3200. Found, %: C 53.7; H 8.3; N 37.8. $\text{C}_5\text{H}_9\text{N}_3$. Calculated, %: C 54.1; H 8.1; N 37.8.

5-Amino-1,3-diphenylpyrazole (1c). Initially phenylhydrazine (2.1 g, 0.02 mol) and then benzoylacetonitrile (2.9 g, 0.02 mol) were introduced into a hot mixture of water (8 ml) and concentrated HCl (2 ml) and the product was stirred for 15 min. A further 8 ml of concentrated HCl was added to the mixture which was then heated to reflux for 2 h with use of a condenser. It was then neutralized using aqueous ammonia

until the appearance of an odour. The crystals obtained were dried and recrystallized from benzene–hexane (1:2) to give the aminopyrazole (3.1 g, 66%) with mp 124°C (mp 124–125°C [7]) and R_f 0.67 (benzene–acetone, 5:1). UV spectrum, λ_{\max} , nm (log ϵ): 261 (4.40); 281 (4.24). IR spectrum, ν , cm^{-1} : 1490, 1560, 1620, 3200. ^1H NMR spectrum, δ , ppm: 5.85 (s, 4-H); 7.4–8.2 (m, H_{arom}).

5-Amino-1-methyl-3-phenylpyrazole (1d). A mixture of benzoylacetonitrile (5.2 g, 0.0346 mol), methylhydrazine sulfate (5.0 g, 0.036 mol), and water (10 ml) was refluxed for 30 min with use of a condenser. Concentrated HCl (20 ml) was added and the product was heated for a further 3 h and neutralized with aqueous ammonia to the appearance of an odour. The crystals produced were dried and recrystallized from a mixture of benzene–hexane (1:2) to give the aminopyrazole (3.6 g, 60%) with mp 129°C and R_f 0.24 (benzene–acetone, 5:1). UV spectrum, λ_{\max} , nm (log ϵ): 251 (4.35); 333 (2.76). IR spectrum, ν , cm^{-1} : 1510, 1560, 1620, 3200. Found, %: C 68.9; H 6.4; N 24.6. $\text{C}_{10}\text{H}_{11}\text{N}_3$. Calculated, %: C 69.4; H 6.4; N 24.3.

5-Amino-3-ethyl-4-methyl-1-phenylpyrazole (1f) was prepared similarly to compound **1c** from phenylhydrazine (0.03 mol) and β -imino- α -methylbutyronitrile (see above) (0.03 mol) in 81% yield. Recrystallization from a mixture of benzene–hexane, 2:1 gave mp 62°C (mp 63°C [7]) and R_f 0.54 (benzene–acetone, 5:1). UV spectrum, λ_{\max} , nm (log ϵ): 251 (4.22). IR spectrum, ν , cm^{-1} : 1600, 1630, 3200, 3300.

5-Amino-3-ethyl-1,4-dimethylpyrazole (1e). A mixture of compound **1a** (3.92 g, 0.04 mol), water (15 ml), and methylhydrazine sulfate (6 g, 0.042 mol) was refluxed for 30 min. Concentrated HCl (25 ml) was added and the product was refluxed for a further 3 h. The reaction product was basified with excess sodium hydroxide. The crystals produced were recrystallized from a mixture of benzene–hexane (1:2) to give the aminopyrazole **1e** (4.1 g, 74%) with mp 111°C. UV spectrum, λ_{\max} , nm (log ϵ): 231 (3.77). IR spectrum, ν , cm^{-1} : 1630, 3200, 3300. Found, %: C 59.8; H 9.4; N 30.1. $\text{C}_7\text{H}_{11}\text{N}_3$. Calculated, %: C 60.4; H 9.4; N 30.2.

3,4,6-Trimethyl-1-phenylpyrazolo[4,5-*b*]pyridine (6a). A mixture of the pyrazole **1a** (1.75 g, 0.01 mol), acetylacetone (1.1 g, 0.011 mol), and acetic acid (6 ml) was heated for 8 h, water (5 ml) was added to the hot solution, and the product was cooled. The precipitated crystals were filtered off, dried, and recrystallized from a mixture of benzene–hexane (1:1) to give the pyrazolopyridine **6a** (1.75 g, 74%) with mp 127–128°C (mp 128°C [2]). ^1H NMR spectrum, δ , ppm: 2.60 (3H, s, 3- CH_3); 2.62 (3H, s, 4- CH_3); 2.64 (3H, s, 6- CH_3); 6.78 (s, 5-H); 7.23 (t, *p*- H_{arom}); 7.48 (dd, *m*- H_{arom}); 8.31 (d, *o*- H_{arom}).

3,4,5,6-Tetramethyl-1-phenylpyrazolo[4,5-*b*]pyridine (6b) was prepared similarly to the pyrazolopyridine **6a** from the pyrazole **1a** (0.1 mol) and methylacetylacetone (0.011 mol) in 98% yield with mp 133–134°C and R_f 0.42 (benzene). UV spectrum, λ_{\max} , nm (log ϵ): 260(4.54); 317 (3.92). IR spectrum, ν , cm^{-1} : 1595. ^1H NMR spectrum, δ , ppm: 2.28 (3H, s, 3- CH_3); 2.62 (3H, s, 5- CH_3); 2.68 (3H, s, 6- CH_3); 7.29 (t, *p*- H_{arom}); 7.44 (dd, *m*- H_{arom}); 8.32 (d, *o*- H_{arom}). Found, %: C 76.5; H 6.9; N 16.7. $\text{C}_{16}\text{H}_{17}\text{N}_3$. Calculated, %: C 76.5; H 6.8; N 16.7.

3-Methyl-1-phenyl-4,6-di(trifluoromethyl)pyrazolo[4,5-*b*]pyridine (6c) was prepared similarly to compound **6a** from the aminopyrazole **1a** (0.01 mol) and hexafluoroacetylacetone (0.011 mol) in 94% yield with mp 78–79°C and R_f 0.91 (ethyl acetate–hexane, 1:2.5). Visualization in UV light. UV spectrum, λ_{\max} , nm (log ϵ): 221 (4.02); 255 (4.48); 282 (3.88). IR spectrum ν , cm^{-1} : 1600. ^1H NMR spectrum, δ , ppm: 2.75 (3H, s, 3- CH_3); 7.85 (s, 5-H); 7.38 (t, *p*- H_{arom}); 7.62 (dd, *m*- H_{arom}); 8.31 (d, *o*- H_{arom}). Found, %: C 51.8; H 2.7; N 12.1. $\text{C}_{14}\text{H}_9\text{F}_6\text{N}_3$. Calculated, %: C 76.5; H 6.8; N 16.7.

1,3,4,6-Tetramethylpyrazolo[4,5-*b*]pyridinium hydrochloride (6d) was prepared similarly to compound **6a** from the pyrazole **1b** (0.02 mol) and acetylacetone (0.022 mol). After heating the reaction mixture it was distilled in vacuo to give the non crystallizing pyrazolopyridine **6d** (2.39 g) with bp 161–162°C (9 mm Hg). The product was dissolved in absolute ether (30 ml) and the hydrochloride **6d** was precipitated by passage of a stream of dry HCl to give 2.6 g (61%) with mp 242–243°C (in a sealed capillary). UV spectrum, λ_{\max} , nm (log ϵ): 222 (4.46); 268 (3.65); 275 (3.68); 305 (3.82). IR spectrum, ν , cm^{-1} : 1610, 1630. ^1H NMR spectrum, δ , ppm: 4.15 (3H, s, 1- CH_3); 2.59 (3H, s, 3- CH_3); 2.69 (3H, s, 4- CH_3); 2.69 (3H, s, 6- CH_3); 6.82 (s, 5-H). Found, %: C 56.3; H 6.8; N 19.9. $\text{C}_{10}\text{H}_{13}\text{N}_3\cdot\text{HCl}$. Calculated, %: C 56.7; H 6.2; N 19.9.

3,4-Dimethyl-6-oxo-1-phenylpyrazolo[4,5-*b*]pyridine (4a) was prepared similarly to the pyrazolopyridine **6a** from compound **1a** (0.01 mol) and acetoacetic ester (0.011 mol). Recrystallization from 60% ethanol gave a 65% yield with mp 189-190°C (mp 188-190°C [2]) and R_f 0.10 (ethyl acetate–hexane, 1:2.5). The same compound could be prepared in 35% yield by mixing both components without solvent and by heating for 3 h with distillation of water and alcohol [2]. UV spectrum, λ_{\max} , nm (log ϵ): 221 (4.10); 259 (4.57); 292 (4.16). IR spectrum, ν , cm^{-1} : 1660 (s), 2960. ^1H NMR spectrum, δ , ppm: 2.58 (3H, s, 3- CH_3); 2.58 (3H, s, 4- CH_3); 6.31 (s, 5-H); 7.20 (t, *p*- H_{arom}); 7.48 (dd, *m*- H_{arom}); 8.22 (d, *o*- H_{arom}).

3,6-Dimethyl-4-oxo-1-phenylpyrazolo[4,5-*b*]pyridine (5a). The crotonate from pyrazole **1a** and acetoacetic ester was prepared as described in method [1]. The crotonate (2.85 g, 0.01 mol) was added portionwise to gently refluxing diphenyl ether (30 ml) and it was heated under gentle reflux for 20 min. After cooling and dilution with hexane (100 ml) the precipitate was separated, refluxed in hexane (20 ml) for 10 min, again separated and then dried and recrystallized from 60% alcohol to give the pyrazolopyridine (2.05 g, 86%) with mp 214°C. Picrate 184°C (methanol) (mp 184°C [2]). R_f 0.3 (ethyl acetate–hexane, 1:1). UV spectrum, λ_{\max} , nm (log ϵ): 250 (4.60); 300 (3.80). IR spectrum, ν , cm^{-1} : 1630 (med.), 2960. ^1H NMR spectrum, δ , ppm: 2.62 (3H, s, 3- CH_3); 3.11 (3H, s, 6- CH_3); 6.42 (s, 5-H); 7.18 (t, *p*- H_{arom}); 7.43 (dd, *m*- H_{arom}); 8.32 (d, *o*- H_{arom}); 11.08 (s, NH).

3-Methyl-6-oxo-4-trifluoromethyl-1-phenylpyrazolo[4,5-*b*]pyridine (4b) was prepared similarly to the 6-oxo derivative **4a** in 93% yield by heating the 5-aminopyrazole **1a** (0.01 mol) and trifluoroacetoacetic ester (0.011 mol) in acetic acid and recrystallization from 70% alcohol to give mp 175-176°C and R_f 0.53 (ethyl acetate–hexane, 1:5). UV spectrum, λ_{\max} , nm (log ϵ): 258 (4.55); 294 (4.12). IR spectrum, ν , cm^{-1} : 1615, 1660 (s). ^1H NMR spectrum, δ , ppm: 2.57 (3H, s, 3- CH_3); 6.85 (s, 5-H); 11.9 (s, NH); 7.27 (t, *p*- H_{arom}); 7.48 (dd, *m*- H_{arom}); 8.15 (d, *o*- H_{arom}). Found, %: C 57.4; H 3.5; N 14.3. $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}_3\text{O}$. Calculated, %: C 57.4; H 3.4; N 14.3.

1,3,4-Trimethyl-6-oxopyrazolo[4,5-*b*]pyridine (4c) was prepared similarly to compound **4a** from the pyrazole **1b** and acetoacetic ester in 67% yield and was recrystallized from 70% alcohol to give mp 261-263°C and R_f 0.65 (methanol). UV spectrum, λ_{\max} , nm (log ϵ): 233 (3.82); 300 (4.08); 320 (3.86). IR spectrum, ν , cm^{-1} : 1605, 1640. ^1H NMR spectrum, δ , ppm: 3.72 (3H, s, 1- CH_3); 2.44 (3H, s, 3- CH_3); 2.44 (s, 4- CH_3); 6.06 (s, 5-H); 11.35 (s, NH). Found, %: C 59.5; H 6.2; N 23.2. $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$. Calculated, %: C 61.0; H 6.2; N 23.7.

1,3-Dimethyl-6-oxo-4-trifluoromethylpyrazolo[4,5-*b*]pyridine (4d) was prepared similarly to the derivative **4a** in 57% yield and recrystallized from 50% alcohol to give mp 210-211°C and R_f 0.39 (ethyl acetate–hexane, 1.5:2.5). UV spectrum, λ_{\max} , nm (log ϵ): 247 (3.34); 306 (4.11). IR spectrum, ν , cm^{-1} : 1650. ^1H NMR spectrum, δ , ppm: 3.87 (3H, s, 1- CH_3); 2.39 (3H, s, 3- CH_3); 6.72 (s, 5-H); 12.18 (br s, NH). The 1,3-dimethyl-4-oxo-6-trifluoromethylpyrazolo[4,5-*b*]pyridine **5d** was also formed in 15% yield. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.84 (3H, s, 1- CH_3); 2.42 (3H, s, 3- CH_3); 6.43 (s, 5-H); 12.18 (br. s, NH). ^1H NMR spectrum (C_6D_6), δ , ppm (J , Hz): **4d** 3.63 (3H, s, 1- CH_3); 2.43 (3H, $J = 1.65$, 3- CH_3); 6.54 (s, 5-H); 13.2 (br. s, NH); **5d** (15%) 2.99 (3H, s, 1- CH_3); 1.60 (3H, s, 3- CH_3); 6.65 (s, 5-H); 13.2 (br. s, NH). Found, %: C 46.8; H 3.5; N 18.3. $\text{C}_9\text{H}_8\text{F}_3\text{N}_3\text{O}$. Calculated, %: C 46.8; H 3.5; N 18.2.

5-Ethyl-3,4-dimethyl-6-oxo-1-phenylpyrazolo[4,5-*b*]pyridine (4e). The pyrazole **1a** (1.75 g, 0.01 mol), propionic acid (10 ml), ethylacetoacetic ester (1.9 g, 0.011 mol), and SOCl_2 (1 drop) were added to a flask for distillation. The mixture was heated for 12 h with distillation of water and alcohol such that the temperature of the reaction mixture was not lower than 140°C with the addition of the propionic acid as necessary. The reaction mixture was then diluted with water (5 ml) and left overnight in the fridge. The precipitated crystals were filtered off and recrystallized from 80% alcohol to give the pyrazolopyridine **4e** (1.21 g, 45%) with mp 182-183°C, R_f 0.62 (benzene–acetone, 5:1). UV spectrum, λ_{\max} , nm (log ϵ): 260 (4.54); 297 (4.15). IR spectrum, ν , cm^{-1} : 1625. ^1H NMR spectrum, δ , ppm: 2.56 (3H, s, 3- CH_3); 2.62 (3H, s, 4- CH_3); 1.11 (1H, t, 5- CH_3); 2.68 (2H, q, 5- CH_2); 7.19 (t, *p*- H_{arom}); 7.45 (dd, *m*- H_{arom}); 8.21 (d, *o*- H_{arom}). Found, %: C 71.4; H 6.3; N 15.7. $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$. Calculated, %: C 71.9; H 6.4; N 15.7.

3,4,5-Trimethyl-6-oxo-1-phenylpyrazolo[4,5-*b*]pyridine (4f) was prepared similarly to the pyridine **4a** in 47% yield. Recrystallization from 60% alcohol gave mp 234-235°C and R_f 0.59 (benzene–acetone, 5:1). UV spectrum, λ_{\max} , nm (log ϵ): 258 (4.27); 261 (4.28); 263 (4.28); 266 (4.27); 300 (4.00). IR spectrum, ν , cm^{-1} : 1635. ^1H NMR spectrum, δ , ppm: 2.19 (3H, s, 3- CH_3); 2.54 (3H, s, 4- CH_3); 2.62 (3H, s, 5- CH_3); 7.20 (t, *p*- H_{arom}); 7.42 (dd, *m*- H_{arom}); 8.24 (d, *o*- H_{arom}); 10.95 (br. s, NH). Found, %: C 71.5; H 5.9; N 16.8. $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$. Calculated, %: C 71.1; H 5.9; N 16.6.

REFERENCES

1. S. V. Tabak, I. I. Grandberg, and A. N. Kost, *Zh. Obshch. Khim.*, **34**, 2756 (1964).
2. S. V. Tabak, I. I. Grandberg, and A. N. Kost, *Khim. Geterotsykl. Soedin.*, 116 (1965).
3. S. Checchi, M. Ridi, and P. Papini, *Gazz. Chim. Ital.*, **85**, 1160 (1955).
4. M. Ridi, P. Papini, and S. Checchi, *Gazz. Chim. Ital.*, **91**, 973 (1961).
5. L. S. Efros (editor), *Physical Methods in the Chemistry of Heterocyclic Compounds* [in Russian], Khimiya, Leningrad (1966), p. 92.
6. N. L. Nam, I. I. Grandberg, and V. I. Sorokin, *Izv. Timiryazev Agricultural Academy*, 172 (2000).
7. I. I. Grandberg, Din-Vei-Py, and A. N. Kost, *Zh. Obshch. Khim.*, **21**, 2311 (1961).
8. I. I. Grandberg and N. F. Krokhina, *Khim.-Farm. Zh.*, No. 1, 16 (1968).