Functional sulfur-containing compounds
14.* Study of intramolecular cyclization of 2-organylthio-, 2-organylsulfinyl-, and 2-organylsulfonylnicotinic acid esters and nitriles upon action of a base

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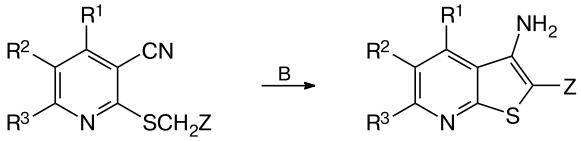
The Thorpe—Ziegler intramolecular cyclization of 2-RCH_2S-, 2-$RCH_2S(O)$-, and 2-RCH_2SO_2-substituted nicotinic acid esters and nitriles (R is alkyl, aryl, and 2-thienyl) upon the action of potassium *tert*-butoxide has been studied. The reaction results in the formation of the corresponding 2-R-substituted 3-aminothieno[2,3-*b*]pyridines, 3-aminothieno[2,3-*b*]-pyridine 1-oxides, and 3-aminothieno[2,3-*b*]pyridine 1,1-dioxides with the reaction taking place only in the case if R is aryl or 2-thienyl. Methyl esters of 2-RCH_2S-, 2-$RCH_2S(O)$-, and 2-RCH_2SO_2-substituted nicotinic acids also undergo the intramolecular cyclization of the Dieckmann type to form the corresponding 2-R-substituted 3-hydroxythieno[2,3-*b*]pyridines, thieno[2,3-*b*]pyridin-3(2*H*)-one 1-oxides, and thieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxides. Such a reaction takes place for all the R groups except when R = $AlkCH_2S$ and $AlkCH_2S(O)$.

Key words: intramolecular cyclization, the Thorpe—Ziegler reaction, potassium *tert*-butoxide, 3-cyano-4,6-dimethylpyridine-2-thione, methyl 4,6-dimethyl-2-thioxopyridine-3-carboxylate, 4,6-dimethyl-2-organylthio-3-cyanopyridines, 4,6-dimethyl-2-organylsulfinyl-3-cyanopyridines, 4,6-dimethyl-2-organylsulfonyl-3-cyanopyridines, 3-amino-2-[aryl-(2-thienyl)]thieno[2,3-*b*]pyridines, 3-amino-2-[aryl(2-thienyl)]thieno[2,3-*b*]pyridine 1-oxides, 3-amino-2-[aryl(2-thienyl)]thieno[2,3-*b*]pyridine 1,1-dioxides, 2-aryl-3-hydroxy-4,6-dimethylthieno[2,3-*b*]pyridine, 2-aryl-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1-oxides, 2-[aryl-(butyl)]-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxides.

3-Aminothieno[2,3-*b*]pyridines are of great practical interest first of all due to the wide range of their pharmacological activity. This range includes antiinflammatory,[2] antidepressant,[3] antibacterial,[4] antiviral,[5,6] and antitumor[7] activity. Therefore, a search for new methods of preparation of these compounds is an actual problem.

One of the most important methods for the synthesis of such heterocycles is the intramolecular cyclization of 3-cyano-2-(organylmethylthio)pyridines by the Thorpe—Ziegler reaction under the action of bases.



This reaction proceeds if Z is an electron-withdrawing group, for example, CN, COOR, $CONH_2$, or C(O)R (see Refs 8—15). Recently, we have shown[1] that in the case when Z is sulfinyl or sulfonyl group, the Thorpe—Ziegler reaction also takes place. In all the cases considered, the activating group Z is in the exo-cyclic position in the final products.

There are reactions of intramolecular cyclization where the activating group is directly included into the thiophene ring. Thus, the reaction of 2-(benzylsulfonyl)benzoic acid esters with sodium ethoxide or methoxide leads to benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide in high yield.[16,17] Treatment of 2-(benzylsulfinyl)- or 2-(benzylsulfonyl)-benzonitriles with sodium methoxide gives 3-aminobenzo[*b*]thiophene 1-oxide and 3-aminobenzo[*b*]thiophene 1,1-dioxide, respectively.[17] 4,6-Dimethoxy- and 4,6-diphenoxy-2-(benzylsulfinyl)- and 2-(sulfonyl)benzonitriles react with sodium methoxide similarly.[18] Even corresponding sulfides can undergo the intramolecular cyclization under certain conditions. The reaction of 2-(4-nitrobenzylthio)benzoic acid with sodium ethoxide leads to 2-(4-nitrophenyl)benzo[*b*]thiophen-3-ol,[19] whereas the reaction of 2-(benzylthio)benzonitrile with potassium *tert*-butoxide gives rise to 3-aminobenzo[*b*]thiophene.[17] A method for preparing benzo[*b*]thiophenes and 3-phenylbenzo[*b*]thiophenes by the reaction of benzaldehyde

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and benzophenone 2-nitro derivatives with benzyl mercaptanes in the presence of potash in dimethylformamide has been suggested.[20] In the course of this reaction, the initially formed 2-benzylthio derivatives undergo the intramolecular cyclization to form the corresponding benzo[*b*]thiophenes. However, such a reaction proceeds under very drastic conditions.

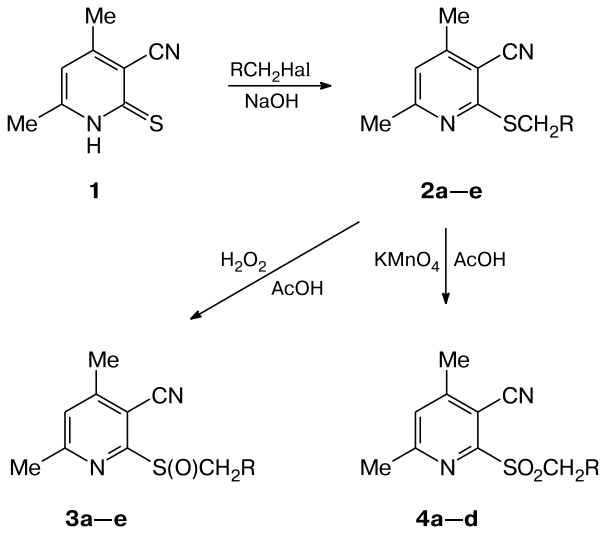
The reaction of 3-cyano-2-(2-nitrophenylmethylthio)-pyridines in the presence of potassium hydroxide in dimethylformamide is the only example of obtaining 3-amino-2-arylthieno[2,3-*b*]pyridines.[21]

It seemed reasonable to systematically study this method of construction of a thiophene ring for the synthesis of thieno[2,3-*b*]pyridines, which allows one to obtain earlier unavailable derivatives of such heterocycles.

3-Cyano-4,6-dimethylpyridine-2-thione and methyl 4,6-dimethyl-2-thioxopyridine-3-carboxylate were used as the starting pyridine-2-thiones, that allowed us to obtain two series of thieno[2,3-*b*]pyridine derivatives. Alkyl, benzyl, and 2-thienylmethyl groups were used as the organyl group.

Nicotinonitrile derivatives **2—4** were obtained by the alkylation of 3-cyano-4,6-dimethylpyridine-2-thione (**1**) with organyl halides with subsequent oxidation of sulfides **2a—e** obtained to sulfoxides **3a—e** and sulfones **4a—d** (Scheme 1).

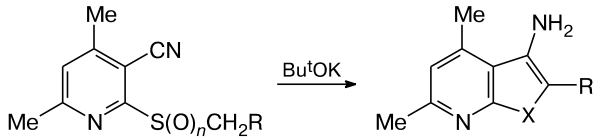
Scheme 1



2, 3: R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), 2-thienyl (**c**), H (**d**), C$_3$H$_7$ (**e**);
4: R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), H (**c**), C$_3$H$_7$ (**d**)

Treatment of sulfides **2a—c**, sulfoxides **3a—c**, and sulfones **4a,b** with potassium *tert*-butoxide in *tert*-butanol through the intramolecular cyclization finally leads to 3-amino-2-[aryl(thienyl)]thieno[2,3-*b*]pyridines **5a—c**, 3-amino-2-[aryl(thienyl)]thieno[2,3-*b*]pyridine 1-oxides **6a—c**, and 3-amino-2-arylthieno[2,3-*b*]pyridine 1,1-dioxides **7a,b**, respectively, in high yields (Scheme 2).

Scheme 2



2a—c, 3a—c, 4a,b **5a—c, 6a—c, 7a,b**

X = S (**2a—c**, **5a—c**), S=O (**3a—c**, **6a—c**), SO$_2$ (**4a,b**, **7a,b**)

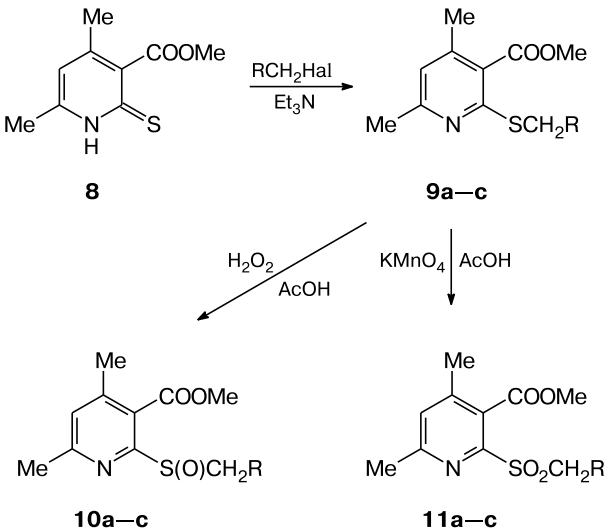
R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), 2-thienyl (**c**)

Sulfides **2d,e**, sulfoxides **3d,e**, and sulfones **4c,d**, where RCH_2 = CH_3 or C_4H_9, do not give the corresponding thienopyridines even under reflux for three hours. In this case, their partial decomposition is observed.

The fact that such a feature is observed irrespective of the oxidation state of the sulfur atom, apparently, can be explained by stabilization of the carbanion formed during the reaction by the benzyl system.

Methyl nicotinate derivatives **9—11** were obtained from methyl 4,6-dimethyl-2-thioxopyridine-3-carboxylate **8** similarly to this scheme (Scheme 3).

Scheme 3

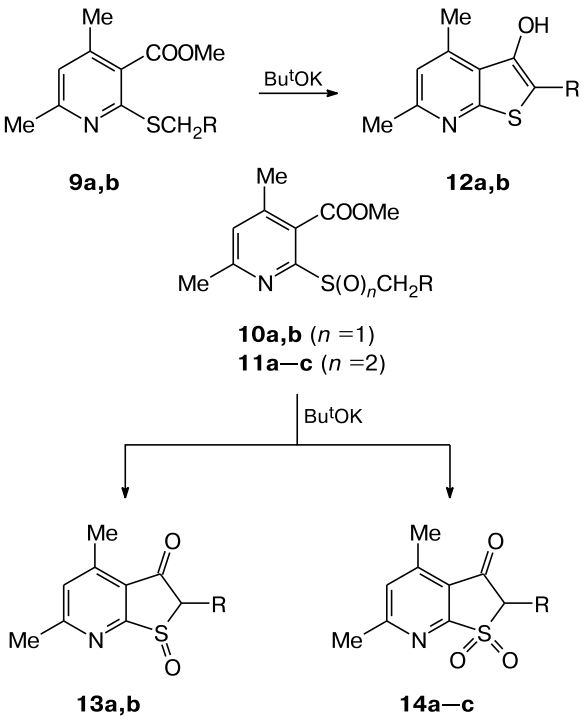


R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**), C$_3$H$_7$ (**c**)

In the course of the reaction of compounds **9—11** with potassium *tert*-butoxide, the same picture is observed, which was found for nitriles **2—4**. Thus, benzyl-substituted sulfides **9a,b**, sulfoxides **10a,b**, and sulfones **11a,b**, where R is aryl, afford the corresponding thieno[2,3-*b*]-

pyridine derivatives **12—14**. However, the structure of the final products depends on the oxidation state of the sulfur atom. If during the cyclization of sulfides **9a,b**, 2-aryl-3-hydroxy-4,6-dimethylthieno[2,3-*b*]pyridines **12a,b** are formed, then the intramolecular cyclization of sulfoxides **10a,b** and sulfones **11a,b** gives 2-aryl-4,6-dimethylthieno-[2,3-*b*]pyridin-3(2*H*)-one 1-oxides **13a,b** and 2-aryl-4,6-dimethylthieno[2,3-*b*]-pyridin-3(2*H*)-one 1,1-dioxides **14a,b**, respectively, as the final products (Scheme 4).

Scheme 4



R = Ph (**a**), 4-Cl-C_6H_4 (**b**), Pr (**c**)

Compounds **13a,b** and **14a,b** possess typical acidic properties and react even with $NaHCO_3$ giving the corresponding salts.

We studied reaction of sulfide **9c**, sulfoxide **10c**, and sulfone **11c** with potassium *tert*-butoxide and found that the oxidation state of the sulfur atom considerably affects result of the reaction. Thus, during the reaction of methyl 2-(butylthio)-4,6-dimethylpyridine-3-carboxylate **9c** with potassium *tert*-butoxide, no considerable changes are observed and the starting substance can be recovered from the reaction mixture. The reaction of methyl 2-(butylsulfinyl)-4,6-dimethylpyridine-3-carboxylate **10c** with potassium *tert*-butoxide leads to decomposition of this compound and to formation of a complex mixture of substances. The reaction of methyl 2-(butylsulfonyl)-4,6-dimethylpyridine-3-carboxylate **11c** with potassium *tert*-butoxide results in the intramolecular cyclization to the corresponding 4,6-dimethyl-2-propylthieno[2,3-*b*]-pyridin-3(2*H*)-one 1,1-dioxide **14c** in good yield.

In conclusion, the method studied allows us to obtain in high yield earlier unavailable thieno[2,3-*b*]pyridines, thieno[2,3-*b*]pyridine 1-oxides, and thieno[2,3-*b*]pyridine 1,1-dioxides containing 2-aryl, 2-thienyl, and even 2-alkyl group.

Experimental

IR spectra were recorded on a Specord M82 instrument in KBr pellets for solid compounds and for neat liquids. ^{1}H NMR spectra were recorded on a Bruker AM 300 spectrometer (300 MHz) in DMSO-d_6.

4,6-Dimethyl-substituted 3-cyanopyridines 2a—e (general procedure). Powdered KOH (0.6 g, 11 mmol) was added to a suspension of 3-cyano-4,6-dimethylpyridine-2-thione (**1**)[22] (1.64 g, 10 mmol) in MeOH (15 mL) and the reaction mixture was stirred under heating until pyridinethione **1** was completely dissolved. Then, a halide (10 mmol) was added, the mixture was refluxed for 30 min, cooled to room temperature, diluted with water (100 mL), and the substance was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography on silica gel. The eluent was $CHCl_3$—hexane, 3 : 2. The eluate was concentrated and the substances were crystallized from appropriate solvent to obtain compounds **2a—e**.

3-Cyano-4,6-dimethyl-2-[(phenylmethyl)thio]pyridine (2a), the yield was 92%, m.p. 88—90 °C ($CHCl_3$—hexane). Found (%): C, 70.68; H, 5.62; S, 12.42. $C_{15}H_{14}N_2S$. Calculated (%): C, 70.83; H, 5.55; S, 12.60. IR, ν/cm^{-1}: 2224 (CN). ^{1}H NMR, δ: 2.37 (s, 3 H, CH_3); 2.50 (s, 3 H, CH_3); 4.50 (s, 2 H, CH_2S); 7.08 (s, 1 H, H(5) pyridine); 7.27 (m, 3 H, Ph); 7.42 (m, 2 H, Ph).

2-{[(4-Chlorophenyl)methyl]thio}-3-cyano-4,6-dimethylpyridine (2b), the yield was 93%, m.p. 143—144 °C ($CHCl_3$—hexane). Found (%): C, 62.49; H, 4.61; Cl, 12.13; S, 10.98. $C_{15}H_{13}ClN_2S$. Calculated (%): C, 62.39; H, 4.54; Cl, 12.28; S, 11.10. IR, ν/cm^{-1}: 2220 (CN). ^{1}H NMR, δ: 2.40 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3); 4.50 (s, 2 H, CH_2S); 7.10 (s, 1 H, H(5) pyridine); 7.33 (d, 2 H, aryl, J = 8.5 Hz); 7.47 (d, 2 H, aryl, J = 8.5 Hz).

3-Cyano-4,6-dimethyl-2-[(2-thienylmethyl)thio]pyridine (2c), the yield was 82%, m.p. 111—113 °C ($CHCl_3$—hexane). Found (%): C, 58.40; H, 4.18; S, 26.18. $C_{12}H_{10}N_2S_2$. Calculated (%): C, 58.51; H, 4.09; S, 26.03. IR, ν/cm^{-1}: 2220 (CN). ^{1}H NMR, δ: 2.40 (s, 3 H, CH_3); 2.57 (s, 3 H, CH_3); 4.74 (s, 2 H, CH_2S); 6.90 (m, 1 H, H(3) thiophene); 7.08 (m, 1 H, H(4) thiophene); 7.10 (s, 1 H, H(5) pyridine); 7.35 (d, 1 H, H(5) thienyl, J = 5 Hz).

3-Cyano-4,6-dimethyl-2-methylthiopyridine (2d), the yield was 89%, m.p. 88—90 °C (diethyl ether—hexane). Found (%): C, 61.03; H, 5,57; S, 18.22. $C_9H_{10}N_2S$. Calculated (%): C, 60.64; H, 5.65; S, 17.99. IR, ν/cm^{-1}: 2220 (CN). ^{1}H NMR, δ: 2.38 (s, 3 H, CH_3); 2.48 (s, 3 H, CH_3); 2.57 (s, 3 H, CH_3S); 7.06 (s, 1 H, H(5) pyridine).

2-Butylthio-3-cyano-4,6-dimethylpyridine (2e), the yield was 92%, m.p. 34.5—35.5 °C (diethyl ether—hexane). Found (%): C, 65.61; H, 7.47; S, 14.38. $C_{12}H_{16}N_2S$. Calculated (%): C, 65.42;

H, 7.32; S, 14.55. IR, ν/cm^{-1}: 2222 (CN). ^{1}H NMR, δ: 0.93 (t, 3 H, CH_3, J = 7.3 Hz); 1.42 (m, 2 H, CH_2); 1.63 (m, 2 H, CH_2); 2.40 (s, 3 H, CH_3); 2.48 (s, 3 H, CH_3); 3.23 (t, 2 H, CH_2S, J = 7.3 Hz); 7.08 (s, 1 H, H(5) pyridine).

2-(Organylsulfinyl)-substituted 3-cyano-4,6-dimethylpyridines 3a—e (general procedure). Hydrogen peroxide (30% aq., 1.2 mL, 12 mmol) was added to a suspension of compound **2a—e** (10 mmol) in AcOH (20 mL). The reaction mixture was stirred for 80 min at 65 °C, cooled to room temperature, and $CHCl_3$ (20 mL) was added to it. Acetic acid was neutralized by addition of aq. Na_2CO_3, the organic layer was separated, the aqueous layer was twice extracted with $CHCl_3$. The combined extracts were dried with $MgSO_4$ and concentrated and the residue was subjected to chromatography on silica gel. Eluent was $CHCl_3$, $CHCl_3$—acetone, 4 : 1. The eluate was concentrated, the substances were crystallized from acetone—diethyl ether to obtain compounds **3a—e**.

3-Cyano-4,6-dimethyl-2-[(phenylmethyl)sulfinyl]pyridine (3a), the yield was 68%, m.p. 172—174 °C. Found (%): C, 66.77; H, 5.14; S, 12.04. $C_{15}H_{14}N_2OS$. Calculated (%): C, 66.64; H, 5.22; S, 11.86 IR, ν/cm^{-1}: 2228 (CN), 1064 (SO). ^{1}H NMR, δ: 2.42 (s, 3 H, CH_3); 2.61 (s, 3 H, CH_3); 4.36 (d, 1 H, CH_2SO, J = 13 Hz); 4.44 (d, 1 H, CH_2SO, J = 13 Hz); 7.08 (m, 2 H, Ph); 7.30 (m, 3 H, Ph); 7.54 (s, 1 H, H(5) pyridine).

2-[(4-Chlorophenyl)methyl]sulfinyl-3-cyano-4,6-dimethylpyridine (3b), the yield was 65%, m.p. 126—128 °C. Found (%): C, 59.18; H, 4.22; Cl, 11.85; S, 10.72. $C_{15}H_{13}ClN_2OS$. Calculated (%): C, 59.11; H, 4.30; Cl, 11.63; S, 10.52. IR, ν/cm^{-1}: 2232 (CN), 1068 (SO). ^{1}H NMR, δ: 2.42 (s, 3 H, CH_3); 2.61 (s, 3 H, CH_3); 4.37 (d, 1 H, CH_2SO, J = 13 Hz); 4.48 (d, 1 H, CH_2SO, J = 13 Hz); 7.10 (d, 2 H, aryl, J = 8.5 Hz); 7.34 (d, 2 H, aryl, J = 8.5 Hz); 7.56 (s, 1 H, H(5) pyridine).

3-Cyano-4,6-dimethyl-2-[(2-thienylmethyl)sulfinyl]pyridine (3c), the yield was 60%, m.p. 161—162 °C. Found (%): C, 55.08; H, 4.01; S, 24.27. $C_{12}H_{10}N_2OS_2$. Calculated (%): C, 54.94; H, 3.84; S, 24.44. IR, ν/cm^{-1}: 2228 (CN), 1064 (SO). ^{1}H NMR, δ: 2.44 (s, 3 H, CH_3); 2.62 (s, 3 H, CH_3); 4.62 (d, 1 H, CH_2SO, J = 13 Hz); 4.72 (d, 1 H, CH_2SO, J = 13 Hz); 6.87 (d, 1 H, H(3) thiophene, J = 4 Hz); 6.98 (m, 1 H, H(4) thiophene); 7.46 (d, 1 H, H(5) thiophene, J = 5 Hz); 7.56 (s, 1 H, H(5) pyridine).

3-Cyano-4,6-dimethyl-2-(methylsulfinyl)pyridine (3d), the yield was 60%, m.p. 103—105 °C. Found (%): C, 55.41; H, 5.26; S, 16.33. $C_9H_{10}N_2OS$. Calculated (%): C, 55.65; H, 5.19; S, 16.50. IR, ν/cm^{-1}: 2228 (CN), 1040 (SO). ^{1}H NMR, δ: 2.53 (s, 3 H, CH_3); 2.60 (s, 3 H, CH_3); 2.90 (s, 3 H, CH_3SO); 7.58 (s, 1 H, H(5) pyridine).

2-(Butylsulfinyl)-3-cyano-4,6-dimethylpyridine (3e), the yield was 63%, m.p. 88—89 °C. Found (%): C, 61.16; H, 6.97; S, 13.41. $C_{12}H_{16}N_2OS$. Calculated (%): C, 60.99; H, 6.82; S, 13.57. IR, ν/cm^{-1}: 2232 (CN), 1048 (SO). ^{1}H NMR, δ: 0.93 (t, 3 H, CH_3, J = 7.3 Hz); 1.42 (m, 2 H, CH_2); 1.63 (m, 2 H, CH_2); 2.52 (s, 3 H, CH_3); 2.58 (s, 3 H, CH_3); 3.08 (t, 2 H, CH_2SO, J = 7.5 Hz); 7.56 (s, 1 H, H(5) pyridine).

2-(Organylsulfonyl)-substituted 3-cyano-4,6-dimethylpyridines 4a—d (general procedure). Powdered $KMnO_4$ (1.26 g, 8 mmol) was added to a solution or suspension of sulfide **2a,b,d,e** (5 mmol) in AcOH (20 mL) with stirring, keeping the temperature within 20—25 °C. The reaction mixture was stirred for another 40 min, discolored by addition of aq. Na_2SO_3, and poured into a separation funnel with water (100 mL). The substance was extracted with $CHCl_3$. The extract was washed with aq. $NaHCO_3$, dried with $MgSO_4$, concentrated, and the substances were crystallized from appropriate solvent to obtain compounds **4a—d**.

3-Cyano-4,6-dimethyl-2-[(phenylmethyl)sulfonyl]pyridine (4a), the yield was 78%, m.p. 193—195 °C (chloroform—methanol). Found (%): C, 63.06; H, 5.05; S, 11.08. $C_{15}H_{14}N_2O_2S$. Calculated (%): C, 62.92; H, 4.93; S, 11.20. IR, ν/cm^{-1}: 2232 (CN), 1320, 1132 (SO_2). ^{1}H NMR, δ: 2.50 (s, 3 H, CH_3); 2.64 (s, 3 H, CH_3); 4.95 (s, 2 H, CH_2SO_2); 7.32 (m, 5 H, Ph), 7.73 (s, 1 H, H(5) pyridine).

2-{[(4-Chlorophenyl)methyl]sulfonyl}-3-cyano-4,6-dimethylpyridine (4b), the yield was 75%, m.p. 195—196 °C (chloroform—methanol). Found (%): C, 55.98; H, 4.16; Cl, 11.23; S, 10.12. $C_{15}H_{13}ClN_2O_2S$. Calculated (%): C, 56.16; H, 4.08; Cl, 11.05; S, 9.99. IR, ν/cm^{-1}: 2232 (CN), 1316, 1130 (SO_2). ^{1}H NMR, δ: 2.53 (s, 3 H, CH_3); 2.66 (s, 3 H, CH_3); 5.00 (s, 2 H, CH_2SO_2); 7.34 (d, 2 H, aryl, J = 9 Hz); 7.42 (d, 2 H, aryl, J = 9 Hz); 7.74 (s, 1 H, H(5) pyridine).

3-Cyano-4,6-dimethyl-2-(methylsulfonyl)pyridine (4c), the yield was 81%, m.p. 111—112 °C (methanol). Found (%): C, 51.30; H, 4.88; S, 15.17. $C_9H_{10}N_2O_2S$. Calculated (%): C, 51.41; H, 4.79; S, 15.25. IR, ν/cm^{-1}: 2238 (CN), 1320, 1130 (SO_2). ^{1}H NMR, δ: 2.57 (s, 3 H, CH_3); 2.61 (s, 3 H, CH_3); 3.43 (s, 3 H, CH_3SO_2); 7.74 (s, 1 H, H(5) pyridine).

2-(Butylsulfonyl)-3-cyano-4,6-dimethylpyridine (4d), the yield was 72%, m.p. 59—60 °C (methanol). Found (%): C, 57.02; H, 6.51; S, 12.55. $C_{12}H_{16}N_2O_2S$. Calculated (%): C, 57.12; H, 6.39; S, 12.71. IR, ν/cm^{-1}: 2236 (CN), 1320, 1128 (SO_2). ^{1}H NMR, δ: 0.90 (t, 3 H, CH_3, J = 7.5 Hz); 1.42 (m, 2 H, CH_2); 1.65 (m, 2 H, CH_2); 2.57 (s, 3 H, CH_3); 2.61 (s, 3 H, CH_3); 3.60 (t, 2 H, CH_2SO_2, J = 7.3 Hz); 7.74 (s, 1 H, H(5) pyridine).

2-Aryl(2-thienyl)-substituted 3-amino-4,6-dimethylthieno-[2,3-*b*]pyridines 5a—c (general procedure). Potassium *tert*-butoxide (1.12 g, 10 mmol) was added to a solution of sulfide **2a—c** (10 mmol) in *tert*-butanol (20 mL) at 50 °C with stirring. The reaction mixture was stirred for 30 min, cooled, and poured into water (100 mL). The substance was extracted with $CHCl_3$. The extract was dried with $MgSO_4$ and concentrated and the residue was subjected to chromatography on silica gel. Eluent was $CHCl_3$. After evaporation of the solvent, the substances were crystallized from appropriate solvent to obtain compounds **5a—c**.

3-Amino-4,6-dimethyl-2-phenylthieno[2,3-*b*]pyridine (5a), the yield was 75%, m.p. 74—76 °C (acetone—hexane). Found (%): C, 70.65; H, 5.47; S, 12.81. $C_{15}H_{14}N_2S$. Calculated (%): C, 70.83; H, 5.55; S, 12.60. IR, ν/cm^{-1}: 3418, 3364 (NH). ^{1}H NMR, δ: 2.50 (s, 3 H, CH_3); 2.76 (s, 3 H, CH_3); 4.83 (s, 2 H, NH_2); 7.00 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.32 (t, 1 H, Ph, J = 8 Hz); 7.48 (t, 2 H, Ph, J = 8 Hz); 7.57 (d, 2 H, Ph, J = 8 Hz).

3-Amino-2-(4-chlorophenyl)-4,6-dimethylthieno[2,3-*b*]pyridine (5b), the yield was 72%, m.p. 197—198 °C (acetone—hexane). Found (%): C, 62.23; H, 4.67; Cl, 12.42; S, 11.22. $C_{15}H_{13}ClN_2S$. Calculated (%): C, 62.39; H, 4.54; Cl, 12.28; S, 11.10. IR, ν/cm^{-1}: 3436, 3336 (NH). ^{1}H NMR, δ: 2.50 (s, 3 H, CH_3); 2.76 (s, 3 H, CH_3); 4.95 (s, 2 H, NH_2); 6.98 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.50 (d, 2 H, aryl, J = 8.5 Hz); 7.57 (d, 2 H, aryl, J = 8.5 Hz).

3-Amino-4,6-dimethyl-2-(2-thienyl)thieno[2,3-*b*]pyridine (5c), the yield was 70%, m.p. 144—146 °C (acetone—hexane). Found (%): C, 58.63; H, 4.13; S, 26.18. $C_{12}H_{10}N_2S_2$. Calculated (%): C, 58.51; H, 4.09; S, 26.03. IR, ν/cm^{-1}: 3428, 3348 (NH). ^{1}H NMR, δ: 2.48 (s, 3 H, CH_3); 2.75 (s, 3 H, CH_3); 5.00 (s, 2 H, NH_2); 7.00 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.18 (t, 1 H,

H(3) thiophene, J = 4 Hz); 7.27 (d, 1 H, H(4) thiophene, J = 4 Hz); 7.58 (d, 1 H, H(5) thiophene, J = 5 Hz).

2-Aryl(2-thienyl)-substituted 3-amino-4,6-dimethylthieno-[2,3-*b*]pyridine 1-oxides 6a—c (general procedure). Potassium *tert*-butoxide (1.12 g, 10 mmol) was added to a solution of sulfoxide **3a—c** (10 mmol) in *tert*-butanol (25 mL) at 50 °C and with stirring. The reaction mixture was stirred for 10 min, cooled, and poured into water (100 mL). After several hours, the substance was filtered off, dried in air, and crystallized from appropriate solvent to obtain compounds **6a—c**.

3-Amino-4,6-dimethyl-2-phenylthieno[2,3-*b*]pyridine 1-oxide (6a), the yield was 80%, m.p. 202—204 °C (DMF—MeOH). Found (%): C, 66.73; H, 5.30; S, 11.75. $C_{15}H_{14}N_2OS$. Calculated (%): C, 66.64; H, 5.22; S, 11.86. IR, ν/cm^{-1}: 3412 (NH), 1012 (SO). ^{1}H NMR, δ: 2.54 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 6.05 (s, 2 H, NH_2); 7.30 (m, 2 H, Ph); 7.50 (m, 3 H, Ph); 7.60 (s, 1 H, H(5) thieno[2,3-*b*]pyridine).

3-Amino-2-(4-chlorophenyl)-4,6-dimethylthieno[2,3-*b*]pyridine 1-oxide (6b), the yield was 82%, m.p. 220—222 °C (decomp.) (DMF—MeOH). Found (%): C, 59.02; H, 4.38; S, 11.70. $C_{15}H_{13}ClN_2OS$. Calculated (%): C, 59.11; H, 4.30; Cl, 11.63; S, 10.52. IR, ν/cm^{-1}: 3412 (NH), 1012 (SO). ^{1}H NMR, δ: 2.53 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 6.23 (s, 2 H, NH_2); 7.30 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.50 (d, 2 H, aryl, J = 7.5 Hz); 7.58 (d, 2 H, aryl, J = 7.5 Hz).

3-Amino-4,6-dimethyl-2-(2-thienyl)thieno[2,3-*b*]pyridine 1-oxide (6c), the yield was 68%, m.p. 214—216 °C (decomp.) (DMF—MeOH). Found (%): C, 54.76; H, 3.96; S, 24.61. $C_{12}H_{10}N_2OS_2$. Calculated (%): C, 54.94; H, 3.84; S, 24.44. IR, ν/cm^{-1}: 3492, 3308 (NH), 1020 (SO). ^{1}H NMR, δ: 2.53 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 6.23 (s, 2 H, NH_2); 7.18 (t, 1 H, H(3) thiophene, J = 4 Hz); 7.27 (d, 1 H, H(4) thiophene, J = 4 Hz); 7.30 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.58 (d, 1 H, H(5) thiophene, J = 5 Hz).

2-Aryl-substituted 3-amino-4,6-dimethylthieno[2,3-*b*]pyridine 1,1-dioxides 7a,b (general procedure). Potassium *tert*-butoxide (1.12 g, 10 mmol) was added to a solution of sulfone **4a,b** (10 mmol) in *tert*-butanol (40 mL) at 50 °C and with stirring. The reaction mixture was stirred for 10 min followed by addition of MeOH (100 mL), and placed into a refrigerator. After several hours, the substance precipitated was filtered off and washed with cold MeOH.

3-Amino-4,6-dimethyl-2-phenylthieno[2,3-*b*]pyridine 1,1-dioxide (7a), the yield was 92%, m.p. 292—294 °C (DMF—MeOH). Found (%): C, 63.03; H, 5.01; S, 11.33. $C_{15}H_{14}N_2O_2S$. Calculated (%): C, 62.92; H, 4.93; S, 11.20. IR, ν/cm^{-1}: 3508, 3408 (NH), 1268, 1136 (SO_2). ^{1}H NMR, δ: 2.56 (s, 3 H, CH_3); 2.73 (s, 3 H, CH_3); 6.37 (s, 2 H, NH_2); 7.37 (s, 1 H, H(5) thieno[2,3-*b*]-pyridine); 7.42 (m, 1 H, Ph); 7.55 (m, 4 H, Ph),

3-Amino-2-(4-chlorophenyl)-4,6-dimethylthieno[2,3-*b*]pyridine 1,1-dioxide (7b), the yield was 94%, m.p. 272—274 °C (DMF—MeOH). Found (%): C, 56.22; H, 4.11; Cl, 10.96; S, 9.92. $C_{15}H_{13}ClN_2O_2S$. Calculated (%): C, 56.16; H, 4.08; Cl, 11.05; S, 9.99. IR, ν/cm^{-1}: 3468, 3356 (NH), 1260, 1132 (SO_2). ^{1}H NMR, δ: 2.55 (s, 3 H, CH_3); 2.71 (s, 3 H, CH_3); 6.55 (s, 2 H, NH_2); 7.40 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.60 (s, 4 H, aryl).

Methyl 4,6-dimethyl-2-thioxopyridine-3-carboxylate (8) was obtained similarly to ethyl 4,6-dimethyl-2-thioxopyridine-3-carboxylate.[23] A mixture of methoxycarbonylthioacetamide[24] (7.8 g, 0.058 mol), acetylacetone (11.7 g, 0.117 mol), and triethylamine (2 g) was heated for 5 h at 50 °C and kept at room temperature for 16 h. Then, MeOH (20 mL) and AcOH (1.5 mL) were added to the reaction mixture followed by keeping for 2 h at −15 °C. The substance precipitated was filtered off and washed with cold MeOH to obtain ester **8** (9 g, 78%), m.p. 187—189 °C (acetone—hexane). Found (%): C, 54.68; H, 5.70; S, 16.41. $C_9H_{11}NO_2S$. Calculated (%): C, 54.80; H, 5.62; S, 16.25.

Methyl 2-organylthio-4,6-dimethylpyridine-3-carboxylates 9a—c (general procedure). Halide (12 mmol) was added to a solution of thione **8** (1.97 g, 10 mmol) and triethylamine (1.4 g, 14 mmol) in $CHCl_3$ (10 mL). The reaction mixture was refluxed for 1 h, the solvent was evaporated *in vacuo*, and the residue was subjected to chromatography on silica gel. Eluent was hexane—$CHCl_3$, 1 : 1. The eluate was concentrated, the substance obtained was dried *in vacuo* or crystallized from appropriate solvent.

Methyl 4,6-dimethyl-2-[(phenylmethyl)thio]pyridine-3-carboxylate (9a), the yield was 92%, oil. Found (%): C, 66.72; H, 6.03; S, 11.22. $C_{16}H_{17}NO_2S$. Calculated (%): C, 66.87; H, 5.96; S, 11.16. IR, ν/cm^{-1}: 1732 (CO). ^{1}H NMR, δ: 2.22 (s, 3 H, CH_3); 2.45 (s, 3 H, CH_3); 3.81 (s, 3 H, $COOCH_3$); 4.40 (s, 2 H, CH_2S); 6.95 (s, 1 H, H(5) pyridine); 7.25 (m, 3 H, Ph); 7.38 (d, 2 H, Ph, J = 7.5 Hz).

Methyl 2-{[(4-chlorophenyl)methyl]thio}-4,6-dimethylpyridine-3-carboxylate (9b), the yield was 90%, m.p. 43—44 °C (hexane). Found (%): C, 59.87; H, 5.07; Cl, 11.14; S, 10.06. $C_{16}H_{16}ClNO_2S$. Calculated (%): C, 59.72; H, 5.01; Cl, 11.02; S, 9.96. IR, ν/cm^{-1}: 1700 (CO). ^{1}H NMR, δ: 2.20 (s, 3 H, CH_3); 2.45 (s, 3 H, CH_3); 3.81 (s, 3 H, $COOCH_3$); 4.36 (s, 2 H, CH_2S); 6.93 (s, 1 H, H(5) pyridine); 7.30 (d, 2 H, aryl, J = 8.0 Hz); 7.38 (d, 2 H, aryl, J = 8.0 Hz).

Methyl 2-butylthio-4,6-dimethylpyridine-3-carboxylate (9c), the yield was 90%, oil, Found (%): C, 61.80; H, 7.62; S, 12.72. $C_{13}H_{19}NO_2S$. Calculated (%): C, 61.63; H, 7.56; S, 12.65. IR, ν/cm^{-1}: 1736 (CO). ^{1}H NMR, δ: 0.88 (s, 3 H, CH_3, J = 7.5 Hz); 1.42 (m, 2 H, CH_2); 1.63 (m, 2 H, CH_2); 2.20 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 3.10 (t, 2 H, CH_2S, J = 7.5 Hz); 3.83 (s, 3 H, $COOCH_3$); 6.90 (s, 1 H, H(5) pyridine).

Methyl 2-organylsulfinyl-4,6-dimethylpyridine-3-carboxylate 10a—c (general procedure). Hydrogen peroxide (30% aq., 0.5 mL, 5 mmol) was added to a solution of **9a—c** (4 mmol) in AcOH (10 mL). The reaction mixture was heated for 30 min at 60 °C and cooled to room temperature followed by addition of $CHCl_3$ (15 mL). Acetic acid was neutralized by aq. Na_2CO_3. Compounds **10a—c** were isolated as described for sulfoxides **3**.

Methyl 4,6-dimethyl-2-[(phenylmethyl)sulfinyl]pyridine-3-carboxylates (10a), the yield was 80%, m.p. 102.5—103.5 °C (acetone—hexane). Found (%): C, 63.51; H, 5.79; S, 10.37. $C_{16}H_{17}NO_3S$. Calculated (%): C, 63.35; H, 5.65; S, 10.57. IR, ν/cm^{-1}: 1732 (CO), 1064 (SO). ^{1}H NMR, δ: 2.30 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3); 4.27 (d, 1 H, CH_2SO, J = 13 Hz); 4.36 (d, 1 H, CH_2SO, J = 13 Hz); 7.20 (m, 2 H, Ph); 7.33 (m, 3 H, Ph); 7.38 (s, 1 H, H(5) pyridine).

Methyl 2-{[(4-chlorophenyl)methyl]sulfinyl}-4,6-dimethylpyridine-3-carboxylate (10b), the yield was 85%, 110—112 °C (acetone—hexane). Found (%): C, 56.76; H, 4.71; Cl, 10.62; S, 9.60. $C_{16}H_{16}ClNO_3S$. Calculated (%): C, 56.89; H, 4.77; Cl, 10.49; S, 9.49. IR, ν/cm^{-1}: 1732 (CO), 1060 (SO). ^{1}H NMR, δ: 2.28 (s, 3 H, CH_3); 2.50 (s, 3 H, CH_3); 3.77 (s, 3 H, $COOCH_3$); 4.28 (d, 1 H, CH_2SO, J = 13 Hz); 4.40 (d, 1 H, CH_2SO, J = 13 Hz); 7.16 (d, 2 H, aryl, J = 7.5 Hz); 7.35 (d, 2 H, aryl, J = 7.5 Hz); 7.38 (s, 1 H, H(5) pyridine).

Methyl 2-(butylsulfinyl)-4,6-dimethylpyridine-3-carboxylate (10c), the yield was 82%, oil. Found (%): C, 58.13; H, 7.04; S, 11.73. $C_{13}H_{19}NO_3S$. Calculated (%): C, 57.97; H, 7.11; S, 11.90. IR, ν/cm^{-1}: 1736 (CO), 1044 (SO). ^{1}H NMR, δ: 0.88 (s, 3 H, CH_3, J = 7.5 Hz); 1.42 (m, 2 H, CH_2); 1.63 (m, 2 H, CH_2); 2.30 (s, 3 H, CH_3); 2.60 (s, 3 H, CH_3); 3.00 (t, 2 H, CH_2S, J = 7.5 Hz); 3.83 (s, 3 H, $COOCH_3$); 7.36 (s, 1 H, H(5) pyridine).

Methyl 2-organylsulfonyl-4,6-dimethylpyridine-3-carboxylates 11a—c (general procedure). Powdered $KMnO_4$ (1 g, 6.3 mmol) was added to a solution of **9a—c** (4 mmol) in AcOH (15 mL) with such a rate that to keep the temperature within 20—25 °C. The reaction mixture was stirred for another 30 min and treated as described for sulfones **4** to obtain compounds **11a—c**.

Methyl 4,6-dimethyl-2-(phenylmethylsulfonyl)pyridine-3-carboxylate (11a), the yield was 85%, m.p. 111—112 °C ($CHCl_3$—hexane). Found (%): C, 60.28; H, 5.46; S, 10.11. $C_{16}H_{17}NO_4S$. Calculated (%): C, 60.17; H, 5.37; S, 10.04. IR, ν/cm^{-1}: 1740 (CO), 1320, 1148 (SO_2). ^{1}H NMR, δ: 2.25 (s, 3 H, CH_3); 2.58 (s, 3 H, CH_3); 3.77 (s, 3 H, $COOCH_3$); 4.82 (s, 2 H, CH_2SO_2); 7.26 (m, 2 H, Ph); 7.33 (m, 3 H, Ph); 7.57 (s, 1 H, H(5) pyridine).

Methyl 2-{[(4-chlorophenyl)methyl]sulfonyl}-4,6-dimethylpyridine-3-carboxylate (11b), the yield was 83%, m.p. 131—132 °C ($CHCl_3$—hexane). Found (%): C, 54.19; H, 4.63; Cl, 10.12; S, 9.15. $C_{16}H_{16}ClNO_4S$. Calculated (%): C, 54.31; H, 4.56; Cl, 10.02; S, 9.06. IR, ν/cm^{-1}: 1736 (CO), 1320, 1140 (SO_2). ^{1}H NMR, δ: 2.28 (s, 3 H, CH_3); 2.50 (s, 3 H, CH_3); 3.77 (s, 3 H, $COOCH_3$); 4.85 (s, 2 H, CH_2SO_2); 7.26 (d, 2 H, aryl, J = 7.5 Hz); 7.40 (d, 2 H, aryl, J = 7.5 Hz); 7.58 (s, 1 H, H(5) pyridine).

Methyl 2-(butylsulfonyl)-4,6-dimethylpyridine-3-carboxylate (11c), the yield was 80%, oil. Found (%): C, 54.88; H, 6.65; S, 11.31. $C_{13}H_{19}NO_4S$. Calculated (%): C, 54.72; H, 6.71; S, 11.24. IR, ν/cm^{-1}: 1744 (CO), 1320, 1140 (SO_2). ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3, J = 6.5 Hz); 1.42 (m, 2 H, CH_2); 1.63 (m, 2 H, CH_2); 2.30 (s, 3 H, CH_3); 2.55 (s, 3 H, CH_3); 3.43 (t, 2 H, CH_2SO_2, J = 7.5 Hz); 3.83 (s, 3 H, $COOCH_3$); 7.58 (s, 1 H, H(5) pyridine).

2-Aryl-3-hydroxy-4,6-dimethylthieno[2,3-*b*]pyridines 12a,b (general procedure). Potassium *tert*-butoxide (0.7 g, 6 mmol) was added to a solution of compound **9a,b** (4 mmol) in *tert*-butanol (12 mL) at 50 °C with stirring. The reaction mixture was stirred for 1 h, cooled, and diluted with water (50 mL) followed by addition of AcOH (0.5 g). The substance was extracted with $CHCl_3$, the extract was dried with $MgSO_4$ and concentrated, and the residue was subjected to chromatography on silica gel. Eluent was $CHCl_3$—hexane, 3 : 1. The eluate was concentrated and the substances were crystallized from appropriate solvent to obtain compounds **12a,b**.

3-Hydroxy-4,6-dimethyl-2-phenylthieno[2,3-*b*]pyridine (12a), the yield was 54%, m.p. 156—158 °C (acetone—hexane). Found (%): C, 70.48; H, 5.08; S, 12.68. $C_{15}H_{13}NOS$. Calculated (%): C, 70.56; H, 5.13; S, 12.56. IR, ν/cm^{-1}: 3450—3300 (OH). ^{1}H NMR, δ: 2.50 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 7.04 (s, 1 H, H(5) thieno[2,3-*b*]pyridine); 7.23 (t, 1 H, Ph, J = 7.5 Hz); 7.46 (t, 2 H, Ph, J = 7.5 Hz); 7.74 (d, 2 H, Ph, J = 7.5 Hz); 9.40 (br.s, 1 H, OH).

2-(4-Chlorophenyl)-3-hydroxy-4,6-dimethylthieno[2,3-*b*]-pyridine (12b), the yield was 51%, m.p. 152—154 °C (acetone—hexane). Found (%): C, 62.02; H, 4.23; Cl, 12.05; S, 10.90. $C_{15}H_{12}ClNOS$. Calculated (%): C, 62.17; H, 4.17; Cl, 12.23; S, 11.06. IR, ν/cm^{-1}: 3450—3300 (OH). ^{1}H NMR, δ: 2.50 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 7.05 (s, 1 H, H(5) thieno[2,3-*b*]-pyridine); 7.52 (d, 2 H, aryl, J = 7.5 Hz); 7.78 (d, 2 H, aryl, J = 7.5 Hz); 9.42 (br.s, 1 H, OH).

2-Aryl-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1-oxides 13a,b (general procedure). Potassium *tert*-butoxide (0.7 g, 6 mmol) was added to a solution of compound **10a,b** (4 mmol) in *tert*-butanol (12 mL) at 50 °C with stirring. The reaction mixture was stirred for 30 min, cooled, and diluted with water (50 mL) followed by addition of AcOH (0.5 g). The substance was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, concentrated, and compounds **13a,b** were crystallized from appropriate solvent.

4,6-Dimethyl-2-phenylthieno[2,3-*b*]pyridin-3(2*H*)-one 1-oxide (13a), the yield was 62%, m.p. 126—129 °C (acetone—diethyl ether). Found (%): C, 66.51; H, 4.88; S, 11.90. $C_{15}H_{13}NO_2S$. Calculated (%): C, 66.40; H, 4.83; S, 11.82. IR, ν/cm^{-1}: 1712 (C=O), 1048 (SO). ^{1}H NMR, δ: 2.65 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 5.52 (s, 0.5 H, CHSO); 5.74 (s, 0.5 H, CHSO); 7.25 (m, 1 H, Ph); 7.42 (m, 4 H, Ph); 7.62 (s, 1 H, H(5) thieno-[2,3-*b*]pyridine).

2-(4-Chlorophenyl)-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1-oxide (13b), the yield was 61%, m.p. 141—144 °C (acetone—diethyl ether). Found (%): C, 58.81; H, 4.02; Cl, 11.70; S, 10.57. $C_{15}H_{12}ClNO_2S$. Calculated (%): C, 58.92; H, 3.96; Cl, 11.59; S, 10.48. IR, ν/cm^{-1}: 1704 (C=O), 1044 (SO). ^{1}H NMR, δ: 2.63 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 5.58 (s, 0.5 H, CHSO); 5.77 (s, 0.5 H, CHSO); 7.28 (d, 1 H, aryl, J = 7.5 Hz); 7.50 (m, 3 H, aryl); 7.60 (s, 1 H, H(5) thieno[2,3-*b*]pyridine).

2-Organyl-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxides 14a—c (general procedure). Potassium *tert*-butoxide (0.7 g, 6 mmol) was added to a solution of compound **11a—c** (4 mmol) in *tert*-butanol (18 mL) at 50 °C with stirring. The reaction mixture was stirred for 20 min, cooled, and treated as described for compounds **13a,b** to obtain compounds **14a—c**.

4,6-Dimethyl-2-phenylthieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxide (14a), the yield was 75%, m.p. 185—188 °C (acetone—hexane). Found (%): C, 62.78; H, 4.61; S, 10.03. $C_{15}H_{13}NO_3S$. Calculated (%): C, 62.70; H, 4.56; S, 9.96. IR, ν/cm^{-1}: 1720 (C=O), 1320, 1132 (SO_2). ^{1}H NMR, δ: 2.70 (s, 6 H, CH_3); 6.08 (s, 1 H, $CHSO_2$); 7.23 (m, 2 H, Ph); 7.47 (m, 3 H, Ph); 7.74 (s, 1 H, H(5) thieno[2,3-*b*]pyridine).

2-(4-Chlorophenyl)-4,6-dimethylthieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxide (14b), the yield was 70%, m.p. 177—178 °C (acetone—hexane). Found (%): C, 55.83; H, 3.69; Cl, 10.91; S, 9.86. $C_{15}H_{12}ClNO_3S$. Calculated (%): C, 55.99; H, 3.76; Cl, 11.02; S, 9.96. IR, ν/cm^{-1}: 1716 (C=O), 1340, 1132 (SO_2). ^{1}H NMR, δ: 2.70 (s, 6 H, CH_3); 6.12 (s, 1 H, $CHSO_2$); 7.38 (d, 2 H, aryl, J = 7.5 Hz); 7.54 (d, 2 H, aryl, J = 7.5 Hz); 7.75 (s, 1 H, H (5) thieno[2,3-*b*]pyridine).

4,6-Dimethyl-2-propylthieno[2,3-*b*]pyridin-3(2*H*)-one 1,1-dioxide (14c), the yield was 68%, m.p. 98.5—100 °C (acetone—hexane). Found (%): C, 56.77; H, 5.93; S, 12.52. $C_{12}H_{15}NO_3S$. Calculated (%): C, 56.90; H, 5.97; S, 12.66. IR, ν/cm^{-1}: 1716 (C=O), 1316, 1140 (SO_2). ^{1}H NMR, δ: 0.97 (t, 3 H, CH_3, J = 7.5 Hz); 1.62 (m, 2 H, CH_2); 1.87 (m, 1 H, CH_2); 2.03 (m, 1 H, CH_2); 2.62 (s, 3 H, CH_3); 2.67 (s, 3 H, CH_3); 4.47 (dd, 1 H, $CHSO_2$, J_1 = 12 Hz, J_2 = 4 Hz); 7.65 (s, 1 H, H(5) thieno[2,3-*b*]pyridine).

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