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3-CYANO-4,6-DIMETHYL-5-R-PYRIDINE-2-SULFONYL CHLORIDES AND N-SUBSTITUTED SULFONYLAMIDES BASED ON THEM

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3-Cyanopyridine-2-sulfonyl chlorides were synthesized by the oxidative chlorination of the respective 3-cyanopyridine-2(1H)-2-thiones. It was established that 3-cyano-4,6-dimethylpyridine-2-sulfonyl chloride eliminates a SO_2 molecule at the isolation stage. N-Substituted sulfonylamides based on the latter were obtained by the reaction of the crude sulfonyl chloride with amines in an aqueous medium.

Keywords: sulfonylamides, sulfonyl chlorides, oxidative chlorination, synthesis, elimination.

Aryl- and heterylsulfonylamides have various types of biological activity, including pharmacological [1, 2], herbicidal [3], and fungicidal [4]. In order to extend the range of biologically active substances we made an attempt at the synthesis of new pyridyl-2-sulfonyl chlorides and N-substituted sulfonylamides based on them. One of the widely used methods for the production of aromatic sulfonyl chlorides is oxidative chlorination of the corresponding mercapto derivatives [5]. As starting compounds we used 3-cyanopyridine-2(1H)-thiones **1a**,**b**, the synthesis of which was described in [6].

Oxidative chlorination was realized in a 2 N solution of HCl in the range between -3 and 0°C. Here 5-chloro-4,6-dimethyl-2(1H)-pyridinethione (**1a**) gives the corresponding pyridine-2-sulfonyl chloride **2a** smoothly and with a good yield (85% theor.). 4,6-Dimethyl-2(1H)-pyridinethione (**1b**) also forms the required sulfonyl chloride **2b** in the reaction process. However, its subsequent behavior is unusual; at the drying stage (room temperature, atmospheric pressure or 5-10 mm Hg; distillation of the solvent from the dried extract of the product) the latter eliminates a molecule of SO_2, just as if it were "boiling". As a result 2-chloro-4,6-dimethyl-nicotinonitrile (**3**) is formed.

In order to avoid decomposition of the sulfonyl chloride **2b** the crude product was used straight away in the reactions with the amines. For this purpose a solution of the corresponding amine in acetone was added dropwise to an aqueous suspension of **2b** at 8-10°C, and after stirring for 2-4 h the sulfonylamides **4h-l** were isolated with fairly high yields (64-74%). The sulfonyl chloride **2b** was consequently unable to be hydrolyzed under the given conditions.

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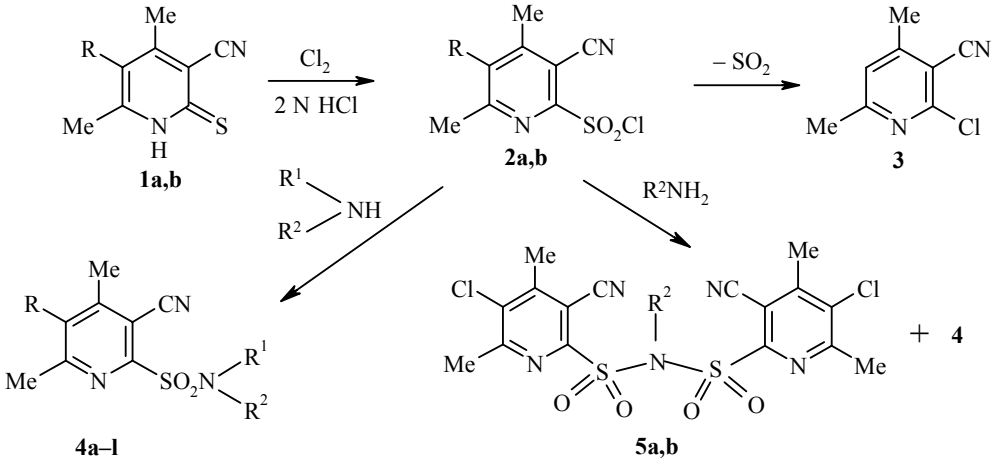


1, 2 a R = Cl, **b** R = H; **4 a–g** R = Cl; **a** R^1 = H, R^2 = 2-ethylphenyl; **b** R^1 = H, R^2 = 3-chloro-4-methylphenyl; **c** R^1 = H, R^2 = furfuryl; **d** R^1 = H, R^2 = 4-chlorobenzyl; **e** R^1 = Et, R^2 = Ph; **f** R^1R^2 = $(CH_2CH_2)_2CHMe$; **g** R^1R^2 = $(CH_2CH_2)_2O$; **h–l** R = H, **h** R^1 = H, R^2 = 2-ethylphenyl; **i** R^1 = H, R^2 = cyclohexyl; **j** R^1 = H, R^2 = isopropyl; **k** R^1 = R^2 = allyl; **l** R^1 = Me, R^2 = Ph; **5 a** R^2 = 2-ethylphenyl, **b** R^2 = 3-chloro-4-methylphenyl

TABLE 1. The Physicochemical Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	S		
2a	$C_8H_6Cl_2N_2O_2S$	36.41 / 36.24	2.33 / 2.28	10.20 / 10.57	11.88 / 12.09	79-80 (hexane)	85
3	$C_8H_7ClN_2$	57.82 / 57.67	4.38 / 4.23	17.01 / 16.81	—	95-96 (hexane)	81
4a	$C_{16}H_{16}ClN_3O_2S$	55.12 / 54.93	4.65 / 4.61	11.88 / 12.01	9.24 / 9.17	181-182 (EtOAc)	71
4b	$C_{15}H_{13}Cl_2N_3O_2S$	48.80 / 48.66	3.47 / 3.54	11.11 / 11.35	8.89 / 8.66	198-200 (EtOH)	66
4c	$C_{13}H_{12}ClN_3O_3S$	48.59 / 47.93	3.86 / 3.71	13.01 / 12.90	10.03 / 9.84	138-139 (hexane + EtOAc)	69
4d	$C_{15}H_{13}Cl_2N_3O_2S$	48.41 / 48.66	3.31 / 3.54	11.18 / 11.35	8.74 / 8.66	179-180 (EtOAc)	56
4e	$C_{16}H_{16}ClN_3O_2S$	54.68 / 54.93	4.39 / 4.61	12.29 / 12.01	8.93 / 9.17	129-131 (cyclohexane)	69
4f	$C_{14}H_{18}ClN_3O_2S$	51.02 / 51.29	5.67 / 5.53	12.56 / 12.82	9.61 / 9.78	106-107 (hexane)	88
4g	$C_{12}H_{14}ClN_3O_3S$	45.83 / 45.64	4.26 / 4.47	13.12 / 13.31	10.22 / 10.15	154-156 (hexane + EtOAc)	76
4h	$C_{16}H_{17}N_3O_2S$	61.17 / 60.93	5.62 / 5.43	13.18 / 13.32	10.34 / 10.17	147-148 (hexane + EtOAc)	66
4i	$C_{14}H_{19}N_3O_2S$	57.12 / 57.31	6.41 / 6.53	14.17 / 14.32	11.08 / 10.93	151-152 (hexane + EtOAc)	74
4j	$C_{11}H_{15}N_3O_2S$	51.89 / 52.16	5.64 / 5.97	16.72 / 16.59	12.43 / 12.66	98-100 (hexane)	72
4k	$C_{14}H_{17}N_3O_2S$	57.58 / 57.71	5.69 / 5.88	14.57 / 14.42	11.14 / 11.00	52-53 (hexane)	70
4l	$C_{15}H_{15}N_3O_2S$	59.51 / 59.78	5.16 / 5.02	13.71 / 13.94	10.39 / 10.64	111-112 (cyclohexane)	64
5a	$C_{24}H_{21}Cl_2N_5O_4S_2$	50.02 / 49.83	3.60 / 3.66	12.23 / 12.11	10.89 / 11.09	248-251 (EtOH + DMF)	56
5b	$C_{23}H_{18}Cl_3N_5O_4S_2$	46.64 / 46.13	3.19 / 3.03	11.37 / 11.69	11.04 / 10.71	262-265 (EtOH + DMF)	44

Unlike compound **2b** the sulfonyl chloride **2a** is fairly stable. After drying and purification it was therefore reacted with amines under traditional conditions, i.e., the sulfonylamides **4a-g** were synthesized in anhydrous benzene in the presence of triethylamine. It was found that the reaction of **2a** with primary amines takes place in different ways. If the primary amine is added to a solution of the sulfonyl chloride **2a** the bissulfonylamides **5a**,**b** are formed in addition to the required sulfonylamides **4a**,**b**. Conditions were found that make it possible to exclude the parallel competing reaction, and for this purpose a solution of the sulfonyl chloride **2a** was added dropwise to a solution of the primary amine at 10-15°C.

The results from elemental analysis are presented in Table 1. The structure of the synthesized compounds was confirmed by a combination of IR, ^{1}H NMR, and mass spectra (Tables 2 and 3, experimental section).

The ^{1}H NMR spectrum of the sulfonyl chloride **2a** only contains signals for the two methyl groups of pyridine at 2.80 and 2.85 ppm. In the mass spectrum there is a group of molecular ion peaks with relative intensity of 15%. Two primary fragmentation paths are observed, i.e., elimination of the SO_2 group and loss of the SO_2Cl group, and the fraction of the last fragment is maximum in the total ion current. The secondary dissociative ionization is characterized by loss of the CN, Cl, and other groups.

TABLE 2. The ^{1}H NMR Spectra of Compounds **2-5**

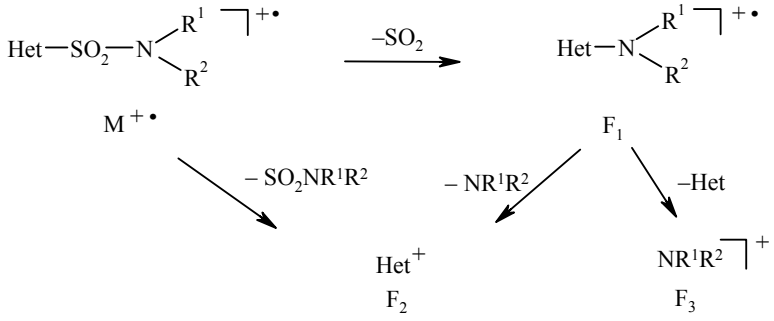
Com-pound	Chemical shifts, δ, ppm (*J*, Hz)
2a	2.85 (3H, s, 6-CH_3); 2.80 (3H, s, 4-CH_3)
3	7.45 (1H, s, H-5); 2.62 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3)
4a	7.78 (1H, br. s, NH); 7.62-7.30 (4H, m, Ar); 3.00 (3H, s, 6-CH_3); 2.85 (3H, s, 4-CH_3); 2.62 (2H, q, *J* = 7.6, C<u>H</u>$_2$CH$_3$); 1.22 (3H, t, *J* = 7.6, CH$_2$C<u>H</u>$_3$)
4b	8.02 (1H, br. s, NH); 7.89 (1H, s, H-2 Ar); 7.64 (1H, d, *J* = 8.3, H-5 Ar); 7.55 (1H, d, *J* = 8.3, H-6 Ar); 2.94 (3H, s, 6-CH_3 Py); 2.82 (3H, s, 4-CH_3 Py); 2.35 (3H, s, 4-CH_3 Ar)
4c	8.85 (1H, s, NH), furane ring: 7.45 (1H, d, $J_{5,4}$ = 1.8, H-5); 6.30 (1H, dd, $J_{3,4}$ = 3.5, $J_{5,4}$ = 1.8, H-4); 6.20 (1H, d, $J_{3,4}$= 3.5, H-3); 4.27 (2H, s, CH_2); 2.65 (3H, s, 6-CH_3 Py); 2.60 (3H, s, 4-CH_3 Py)
4d	8.70 (1H, br. s, NH); 7.32-7.21 (4H, m, Ar); 4.25 (2H, s, CH_2); 2.85 (3H, s, 6-CH_3 Py); 2.75 (3H, s, 4-CH_3 Py)
4e	7.41-7.30 (5H, m, Ar); 3.95 (2H, q, *J* = 7.2, C<u>H</u>$_2$CH$_3$); 2.80 (3H, s, 6-CH_3 Py); 2.65 (3H, s, 4-CH_3 Py); 1.15 (3H, t, *J* = 7.2, CH$_2$C<u>H</u>$_3$)
4f	3.84 (1H, m, CH_2 piperidine); 3.01 (1H, m, CH_2 piperidine); 2.72 (3H, s, 6-CH_3 Py); 2.62 (3H, s, 4-CH_3 Py); 1.75 (1H, m, CH_2 piperidine); 1.62 (1H, m, CH_2 piperidine); 1.30 (1H, m, CH piperidine); 1.02 (3H, m, CH_3)
4g	3.73 (4H, m, OCH_2); 3.43 (4H, m, NCH_2); 2.78 (3H, s, 6-CH_3 Py); 2.70 (3H, s, 4-CH_3 Py)
4h	10.24 (1H, br. s, NH); 7.70 (1H, s, H-5 Py); 7.24-7.05 (4H, m, Ar); 2.66 (2H, q, *J* = 7.5, C<u>H</u>$_2$CH$_3$); 2.60 (3H, s, 6-CH_3 Py); 2.55 (3H, s, 4-CH_3 Py); 1.08 (3H, t, *J* = 7.5, CH$_2$C<u>H</u>$_3$)
4i	8.30 (1H, br. s, NH); 7.65 (1H, s, H-5), cyclohexane ring: 3.18 (1H, m, CHN); 1.81 (2H, m, H*e*-2,6); 1.75 (3H, m, H*e*-3,4,5); 1.48 (2H, m, H*a*-2,6); 1.21 (1H, m, H*a*-4); 1.10 (2H, m, H*a*-3,5); 2.62 (3H, s, 6-CH_3 Py); 2.55 (3H, s, 4-CH_3 Py)
4j	8.18 (1H, d, *J* = 6.8, NH); 7.66 (1H, s, H-5); 3.52 (1H, m, C<u>H</u>(CH$_3$)$_2$); 2.60 (3H, s, 6-CH_3 Py); 2.55 (3H, s, 4-CH_3 Py); 1.12 (6H, d, *J* = 6.8, CH(C<u>H</u>$_3$)$_2$)
4k	7.69 (1H, s, H-5); 5.77 (2H, ddd, *J* = 15.0, *J* = 11.0, *J* = 17.0, CH$_2$C<u>H</u>=CH$_2$); 5.26-5.15 (4H, m, CH$_2$CH=C<u>H</u>$_2$); 3.93 (4H, d, *J* = 4.8, C<u>H</u>$_2$CH=CH$_2$); 2.62 (3H, s, 6-CH_3 Py); 2.57 (3H, s, 4-CH_3 Py)
4l	7.72 (1H, s, H-5); 7.40-7.25 (5H, m, Ar); 3.48 (3H, s, N-CH_3); 2.68 (3H, s, 6-CH_3 Py); 2.57 (3H, s, 4-CH_3 Py)
5a	7.55-7.25 (4H, m, Ar); 2.92 (2H, q, *J* = 7.6, C<u>H</u>$_2$CH$_3$); 2.75 (6H, s, 6-CH_3 Py); 2.70 (6H, s, 4-CH_3 Py); 1.22 (3H, t, *J* = 7.6, CH$_2$C<u>H</u>$_3$)
5b	7.82 (1H, s, H-2 Ar); 7.60 (1H, d, *J* = 8.3, H-5 Ar); 7.51 (1H, d, *J* = 8.3, H-6 Ar); 7.82-7.51 (3H, m, Ar); 2.82 (6H, s, 6-CH_3 Py); 2.72 (6H, s, 4-CH_3 Py); 2.41 (3H, s, 4-CH_3 Ar)

TABLE 3. The Electron-Impact Mass Spectra of Compounds **2a**, **3**, **4a-l**, **5a**,**b**

Compound	*m*/*z* (I_{rel},%)
2a	264 $[M]^+$ (15), 200 $[M–SO_2]^+$ (18), 165 $[M–SO_2C1]^+$ (100), 138 $[165–HCN]^+$ (34), 130 $[165–Cl]^+$ (25), 102 $[138–HCl]^+$ (55)
3	166 $[M]^+$ (100), 130 $[M–HCl]^+$ (30), 104 $[130–CN]^+$ (24), 103 $[130–HCN]^+$ (26)
4a	349 $[M]^+$ (10), 320 $[M–C_2H_5]^+$ (22), 285 $[F_1]^+$ (14), 270 $[285–CH_3]^+$ (30), 256 $[320–SO_2]^+$ (19), 165 $[F_2]^+$ (11), 120 $[F_3]^+$ (100)
4b	305 $[F_1]^+$ (8), 270 $[305–Cl]^+$ (24), 165 $[F_2]^+$ (51), 140 $[F_3]^+$ (100), 105 $[140–Cl]^+$ (44)
4c	261 $[F_1]^+$ (10), 232 [M–CN, –furyl]$^+$ (17), 165 $[F_2]^+$ (100), 138 $[165–HCN]^+$ (18), 96 $[F_3]^+$ (56)
4d	369 $[M]^+$ (2), 305 $[F_1]^+$ (6), 165 $[F_2]^+$ (51), 140 $[F_3]$]$^+$ (100), 125 $[F_3–NH]^+$ (23)
4e	349 $[M]^+$ (2), 334 $[M–CH_3]^+$ (4), 285 $[F_1]^+$ (4), 165 $[F_2]^+$ (11), 120 $[F_3]^+$ (100)
4f	327 $[M]^+$ (2), 263 $[F_1]^+$ (5), 165 $[F_2]^+$ (23), 98 $[F_3]^+$ (100)
4g	251 $[F_1]^+$ (3), 165 $[F_2]^+$ (14), 130 $[165–Cl]^+$ (10), 86 $[F_3]^+$ (100)
4h	315 $[M]^+$ (23), 251 $[F_1]^+$ (16), 236 $[251–CH_3]^+$ (23), 222 $[251–C_2H_5]^+$ (27), 131 $[F_2]^+$ (11), 120 $[F_3]^+$ (100)
4i	293 $[M]^+$ (2), 250 $[M–C_3H_7]^+$ (57), 186 $[F_1]^+$ (28), 159 $[186–HCN]^+$ (38), 131 $[F_2]^+$ (49), 98 $[F_3]^+$ (100)
4j	238 $[M–CH_3]^+$ (61), 174 $[F_1]^+$ (42), 131 $[F_2]^+$ (84), 104 [131–HCN]$^+$ (37), 58 $[F_3]^+$ (100)
4k	186 [M–SO_2, $–CH_2CH=CH_2$]$^+$ (8), 171 $[186–CH_3]^+$ (5), 131 $[F_2]^+$ (23), 96 $[F_3]^+$ (100)
4l	301 $[M]^+$ (5), 237 $[F_1]^+$ (27), 222 $[237–CH_3]^+$ (11), 131 $[F_2]^+$ (16), 106 $[F_3]^+$ (100), 77 $[C_6H_5]^+$ (87)
5a	449 $[M–2SO_2]^+$ (3), 348 $[M–2SO_2–Het]^+$ (45), 284 $[M–HetSO_2]^+$ (100), 165 $[Het]^+$ (20), 129 $[Het–HCl]^+$ (10), 119 $[M–2HetSO_2]^+$ (80)
5b	469 $[M–2SO_2]^+$ (3), 368 $[M–2SO_2–Het]^+$ (18), 304 $[M–HetSO_2]^+$ (10), 269 $[M–HetSO_2–Cl]^+$ (18), 165 $[Het]^+$ (32), 139 $[M–2HetSO_2]^+$ ((100)

The sulfonyl chloride **2b** was identified by the N-substituted sulfonylamides **4h**,**l** produced from it. In the IR spectra of the sulfonylamides **4a-l** there are two characteristic absorption bands in the regions of 1134-1157 and 1358-1377 cm^{-1}, corresponding to the symmetrical and asymmetrical vibrations of the SO_2 group, and also an absorption band for the cyano group at 2222-2231 cm^{-1} [7]. The ^1H NMR spectra of compounds **4a-l** contain all the necessary signals (Table 2).

The molecular ions of the sulfonylamides **4a-l** are extremely unstable. In most of the compounds the intensities of the molecular ion peaks amount to 2-5%, and only in individual cases are they 10 (**4a**) and 23% (**4i**). There are no molecular ion peaks in the mass spectra of the sulfonylamides **4b**,**c**,**g**,**j** and **4k**. The subsequent fragmentation has much in common and can be represented by the following scheme:



In the IR spectra of compounds **5a**,**b** the absorption band of the NH group disappears compared with the spectra of **4a,b**.

The mass spectra of compounds **5a**,**b** do not contain molecular ion peaks but do contain peaks of the $[M-SO_2]^+$ fragments. The fragmentation paths are presented in Table 3.

Compounds with antidote and growth-regulating activity are found among the newly synthesized sulfonylamides **4a-l**.

EXPERIMENTAL

The IR spectra were recorded for suspensions in vaseline oil on a Specord-71 UR-20 spectrophotometer. The ^1H NMR spectra were obtained for solutions of the substances in DMSO-d_6 on a Bruker WM-500 radiospectrometer (500 MHz) with TMS as internal standard. The electron-impact mass spectra were recorded on a Finnigan MAT INCOS 50 instrument (ionization energy 70 eV). Elemental analysis of the synthesized compounds for C, H, N, and S was performed on a Carlo-Erba analyzer (model 1106). The reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates in the 1:1 hexane–acetone system with iodine vapor as developer.

The benzene used as solvent in the synthesis was purified from impurities and made absolute by known methods [8].

The initial 3-cyanopyridine-2-thiones **1a**,**b** were prepared by the method in [6] from the corresponding 2-chloronicotinonitriles, the synthesis of which was described in [9].

5-Chloro-3-cyano-4,6-dimethylpyridine-2-sulfonyl Chloride (2a). Chlorine was bubbled into a suspension of the thione **1a** (2.0 g, 10 mmol) in 2 N HCl (20 ml) with stirring for 1 h while the temperature of the reaction mixture was kept in the range between -2 and 0°C. After the flow of chlorine had stopped the mixture was stirred at the same temperature for a further 20 min. The precipitate was filtered off, washed on the filter with iced water to a neutral reaction, pressed, and dried in a vacuum desiccator at 5-10 mm Hg. After recrystallization from anhydrous hexane we obtained 2.27 g (85%) of the product in the form of light-yellow shiny crystals; mp 79-80°C.

3-Cyano-4,6-dimethylpyridine-2-sulfonyl Chloride (2b). This compound was obtained similarly to **2a**, but the drying stage was omitted, and the product was used straight away in the reaction with the amine.

2-Chloro-4,6-dimethylnicotinonitrile (3). A. The product **2b** after washing with iced water was dried in a vacuum desiccator at 5-10 mm Hg, and the nitrile **3** was obtained with a yield of 81%.

B. The product **2b** after washing with iced water was extracted with benzene, the extract was dried with Na_2SO_4, the solvent was distilled on a rotary evaporator, and the nitrile **3** was obtained with a yield of 73%.

All the physicochemical characteristics of the product **3** were identical with those of the compound described in [9].

N-(2-Ethylphenyl)-5-chloro-3-cyano-4,6-dimethylpyridine-2-sulfonylamide (4a). To a solution of 2-ethylaniline (0.47 g, 4.0 mmol) and triethylamine (0.38 g, 3.8 mmol) in anhydrous benzene (15 ml) with stirring we added dropwise a solution of the sulfonyl chloride **2a** (1.0 g, 3.8 mmol) while keeping the temperature of the mixture in the range of 10-15°C. The mixture was then stirred at the same temperature for 0.5 h and then at room temperature for a further 2-3 h. The precipitate was filtered off, washed from the $Et_3N{\cdot}HCl$ on the filter with water, combined with the residue obtained after evaporation of the mother solution, and recrystallized from ethyl acetate. We obtained 0.94 g (71%) of the required sulfonylamide **4a**; mp 181-182°C. IR spectrum, ν, cm^{-1}: 1144, 1362 (SO_2), 1482, 1548, 1589 (C=C, C=N arom.), 2227 (C≡N), 3348 (N–H).

Compounds **4b-d** were obtained similarly.

5-Chloro-3-cyano-4,6-dimethylpyridine-2-sulfonylmorpholine (4g). Into a solution of compound **2a** (0.90 g, 3.4 mmol) in anhydrous benzene (15 ml) we poured a solution of morpholine (0.31 g, 3.57 mmol) and triethylamine (0.34 g, 3.4 mmol) in anhydrous benzene (10 ml). The mixture was left at room temperature

for 3-4 h. The reaction mass was then filtered from the precipitate ($Et_3N \cdot HCl$), the solution was evaporated, the residue was recrystallized from a 1:1 mixture of hexane and ethyl acetate, and 0.81 g (76%) of the sulfonylamide **4g** was obtained in the form of white crystals; mp 154-156°C. IR spectrum, ν, cm^{-1}: 1162, 1373 (SO_2), 1562, 1558 (C=C, C=N arom.), 2230 (C≡N).

Compounds **4e**,**f** were obtained similarly.

N-Methyl-N-phenyl-3-cyano-4,6-dimethylpyridine-2-sulfonylamide (4l). To a suspension of moist sulfonyl chloride **2b** (1.0 g, 4.3 mmol) in water (6 ml) at 8-10°C we added dropwise a solution of N-methylaniline (0.50 g, 4.3 mmol) and triethylamine (0.43 g, 4.3 mmol) in acetone (2 ml) while keeping the temperature constant. When all the amines had been added the mixture was stirred at the same temperature for 1.5-2 h. The temperature was then raised gradually to room temperature, and the mixture was stirred for a further 1.5-2 h. The reaction mass was acidified to pH 3-4 with concentrated hydrochloric acid, and the precipitate was filtered off, washed with water, and dried. After recrystallization from cyclohexane we obtained 0.84 g (64%) of the product (**4l**); mp 111-112°C. IR spectrum, ν, cm^{-1}: 1134, 1377 (SO_2), 1458, 1527, 1591 (C=C, C=N arom.), 2226 (C≡N).

Compounds **4h-k** were obtained similarly.

N-(2-Ethylphenyl)-5-chloro-3-cyano-4,6-dimethylpyridine-2-sulfonylamide (4a) and N-(2-Ethylphenyl)-N,N-bis(4,6-dimethyl-5-chloro-3-cyanopyridine-2-sulfonyl)amine (5a). To a solution of the sulfonyl chloride **2a** (1.20 g, 4.5 mmol) in anhydrous benzene (15 ml) at 10-15°C we added dropwise a solution of 2-ethylaniline (0.57 g, 4.7 mmol) and triethylamine (0.48 g, 4.5 mmol) in anhydrous benzene (10 ml). When all the amines had been added the mixture was stirred at the same temperature for 0.5 h and then at room temperature for a further 2-3 h. The precipitate was filtered off, washed copiously with water, and dried. We obtained a mixture of products with R_f 0.46 (**4a**) and 0.21 (**5a**) by TLC. The precipitate was heated to boiling with ethyl acetate (15 ml) and filtered from the undissolved part. The extract was combined with the residue obtained after evaporation of the mother solution and recrystallized twice from ethyl acetate. We obtained 0.38 g (29%) of the product **4a**; mp 181-182°C. The residue undissolved in ethyl acetate was recrystallized from a 1:1 mixture of ethanol and DMF, and 0.55 g (56%) of the product **5a** was obtained in the form of white crystals; mp 248-251°C. IR spectrum, ν, cm^{-1}: 1138, 1360 (SO_2), 1464, 1541, 1580 (C=C, C=N arom.), 2226 (C≡N).

Compound **5b** was obtained similarly.

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