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SYNTHESIS AND TRANSFORMATIONS OF SUBSTITUTED 4,6-DIMETHYLPYRAZOLO[3,4-*b*]PYRIDYL-3-AZIDES AND -SULFONYL CHLORIDES

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Diazotization of the amino group of 3-amino-4,6-dimethylpyrazolo[3,4-b]pyrimidines and subsequent replacement of the diazo group in the formed diazonium chlorides by an azide group gave the corresponding 3-azido derivatives. Their reactions with active methylene compounds have been studied. Substitution of the diazo group by a sulfo group gave the related 4,6-dimethylpyrazolo-[3,4-b]pyridyl-3-sulfonyl chlorides and sulfonylamides.

Keywords: azides, pyrazolo[3,4-*b*]pyrimidines, sulfonylamides, sulfonyl chlorides, diazotization, substitution, mass spectra, synthesis, elimination.

We have previously reported [1] the synthesis of the 3-aminopyrazolo[3,4-*b*]pyridines **1a-d** which can be used as starting materials in the synthesis of novel chemical materials with differently useful properties. With this in view we report in the current study an investigation of the possible diazotization of the amino group in compounds **1a-d** and subsequent substitution of the diazo group in the diazonium chlorides formed by an azide group to give azido derivatives and by a sulfo group to give the corresponding sulfonyl chlorides (Scheme 1).

The 3-aminopyrazolo[3,4-*b*]pyridines **1a-d** show aromatic amine properties and readily undergo diazotization in hydrochloric acid solution from -2 to 0°C to give the corresponding diazonium chlorides **2a-d**. Compounds **2a-c** react with a saturated sodium azide solution from -1 to +1°C (optimum conditions) to form the 3-azido-4,6-dimethylpyrazolo[3,4-*b*]pyridines **3a-c** in high yields (76-84%). When carrying out the reaction of salts **2a-c** with hydrazine under an analogous temperature regime according to a known method [2] the yield of the azide derivatives **3a-c** is significantly lower (54-67%).

It was found that the reaction of the diazonium chloride **2d** both with sodium azide and with hydrazine did not give the corresponding azido derivative but in both cases gave the 3,5-dichloro-4,6-dimethyl-(1H)pyrazolo[3,4-*b*]pyridine **4**. The reaction conditions could not be varied to yield the target 3-azido-5-chloro-4,6-dimethyl-(1H)pyrazolo[3,4-*b*]pyridine. In all likelihood the diazonium chloride **2d** is characterized by greater instability, the rate of elimination of the diazo group being greater than its substitution by the azide group.

Azides **3a-c** are colorless, crystalline materials stable to light but changing in color to a bright-yellow upon storage in light.

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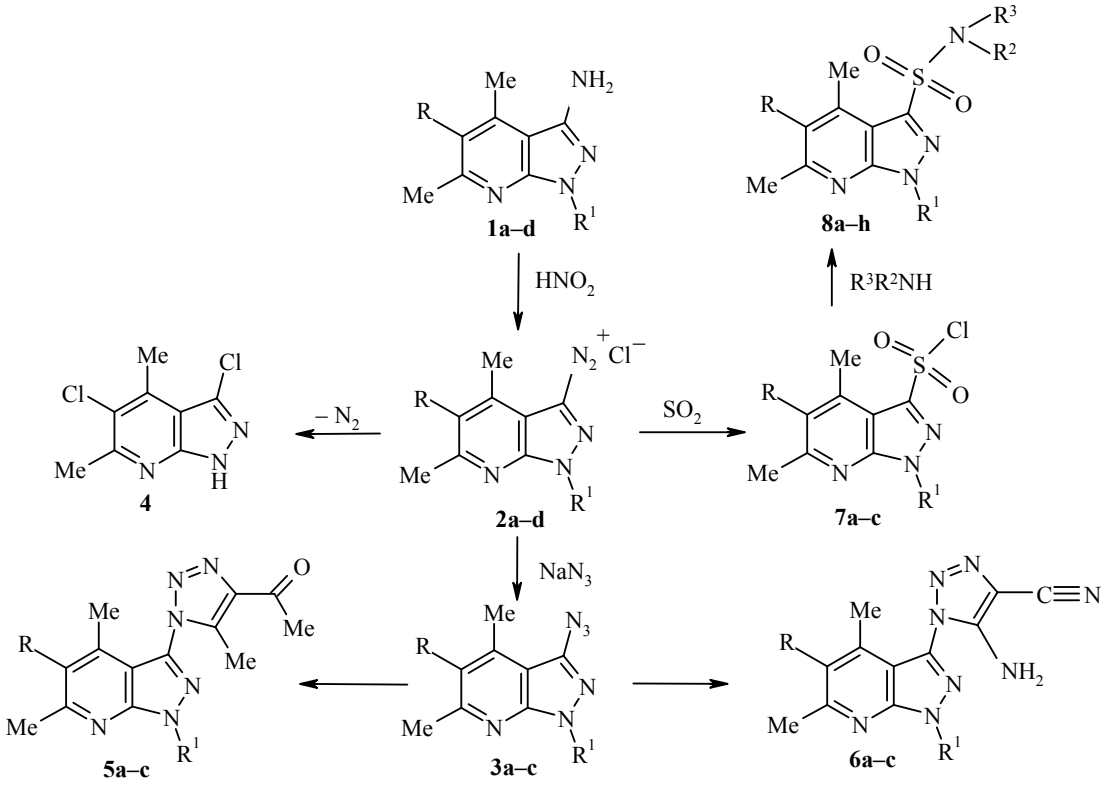
The physicochemical and spectroscopic characteristics, elemental analytical data, and the ^{1}H NMR spectra of azides **3a-c** are given in Table 1 and the mass spectra in Table 2.

The IR spectra of compounds **3a-c** show a characteristic azide group absorption in the range 2121-2138 cm^{-1} [3]. The ^{1}H NMR spectra show signals for all of the protons of compounds **3a-c** in the corresponding regions.

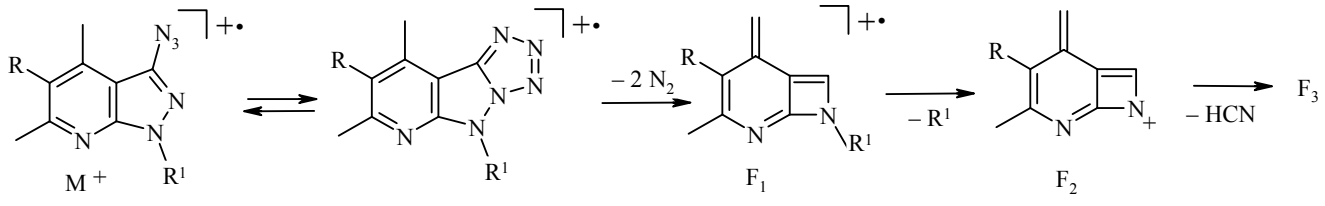
Scheme 1



2–7 a R = R^1 = H, **b** R = H, R^1 = Me, **c** R = Cl, R^1 = Me, **d** R = Cl, R^1 = H; **8 a–f** R = H, **a** R^1 = H, R^2, R^3 = $(CH_2CH_2)_2CH$–Me; **b** R^1 = H, R^2 = Me, R^3 = CH_2CH_2OH; **c** R^1 = R^2 = H, R^3 = 2-$ClC_6H_4CH_2$; **d** R^1= Me, R^2 = H, R^3 = furfuryl; **e** R^1 = Me; R^2 = R^3 = $CH_2CH{=}CH_2$; **f** R^1= R^2= Me; R^3 =$PhCH_2$; **g** R = Cl; R^1 = Me; R^2 = H, R^3 = 4-$MeOC_6H_4$; **h** R = Cl; R^1 = Me, R^2, R^3 = $(CH_2CH_2)_2CH$–Me

The mass spectra of azides **3a-c** show molecular ion peaks with relatively low intensities (3-19%). At the primary stage of fragmentation all three compounds **3a-c** show the elimination of two molecules of N_2 from the molecular ion to give the quite stable fragments F_1 which then undergo loss of an R^1 fragment and HCN molecule (Scheme 2).

Scheme 2



It is known that organic azides form 1,2,3-triazoles with 1,3-diketones and β-keto esters [4-6]. We have studied the reactions of the previously unreported azides **3a-c** with acetylacetone and malononitrile.

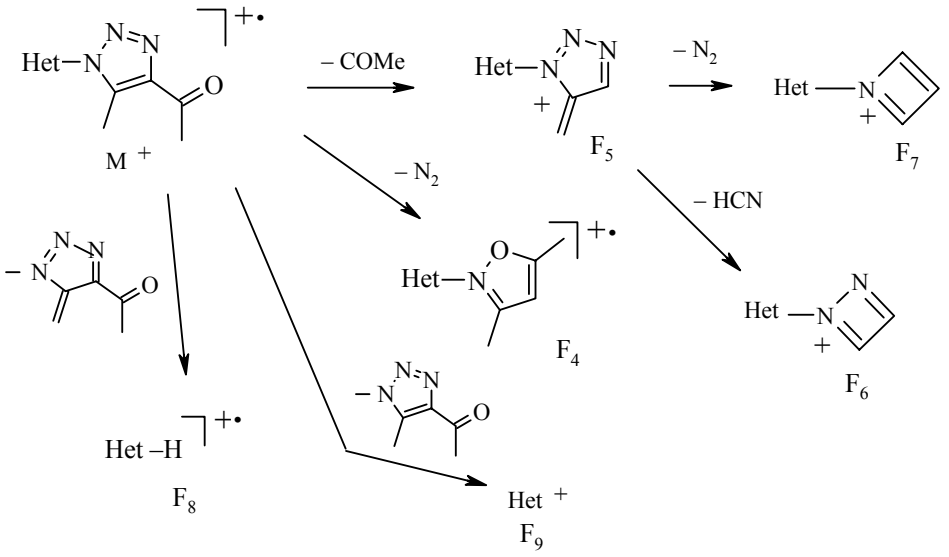
Heating the azides **3a-c** with excess acetylacetone in the presence of Et_3N base gave the 4,6-dimethyl-3-(1,2,3-triazolyl)pyrazolo[3,4-*b*]pyridines **5a-c** (Scheme 1). The reaction occurs upon refluxing in acetonitrile over 4-6 h. Reaction of azides **3a-c** under milder conditions occurs at 55-60ºC in a proton solvent medium in the presence of Et_3N base to give the 3-(5-amino-4-cyano-1,2,3-triazolyl)-4,6-dimethylpyrazolo[3,4-*b*]pyridines **6a-c**.

The cycloaddition of acetylacetone and malononitrile to the azido group occurs selectively to form single reaction products in agreement with literature data [4, 5]. The yield of addition products **5a-c**, **6a-c** was 56-81%. The structure was confirmed by mass and ^{1}H NMR spectroscopic data (Tables 1-3).

When compared with the starting azides **3a-c** the ^{1}H NMR spectra of compounds **5a-c** show signals for the protons of two methyl groups as singlets with δ 2.11-2.14 ppm (5-CH_3 triazole) and 2.69-2.72 ppm ($COCH_3$). The spectra of derivatives **6a-c** show NH_2 protons signals as a broadened singlet at 7.41-7.46 ppm.

The mass spectra of derivatives **5a-c, 6a-c** show molecular ion peaks with relative intensities 6-72%. Under electron impact conditions the triazole ring first undergoes destruction as reflected in the general fragmentation for compounds **5a-c** (Scheme 3). In addition, all of the compounds are also characterized by clevage of the C–N bond joining the pyrazole and triazole rings in the molecular ion with possible transfer of a hydrogen atom from the *ortho*-positioned methyl group to the pyrazole C(3).

Scheme 3



In order to synthesize the 4,6-dimethylpyrazolo[3,4-*b*]pyridyl-3-sulfonyl chlorides **7a-d** (Scheme 1) the diazonium chlorides **2a-d** were added dropwise to a saturated solution of SO_2 in glacial acetic acid. Anhydrous copper sulphate was used as the catalyst. The use of optimized conditions (0-4ºC) allowed the preparation of the sulfonyl chlorides **7a-c** in 68-93% yield. It was found that the diazonium chloride **2d** and SO_2 gave a mixture very difficult to resolve containing mainly the 3-chloro derivative **4** and a small amount of the target sulfonyl chloride (10-15% according to ^{1}H NMR spectroscopy), while a change in reaction conditions did not lead to a marked increase in the yield of the latter.

The synthesized sulfonyl chlorides **7a-c** are light-yellow crystalline materials hydrolyzing readily upon storage in air (Table 1).

As might be expected, the ^{1}H NMR spectra of the sulfonyl chlorides **7a-c** showed signals for the protons of the pyrazolopyridine system shifted to lower field when compared with the corresponding azides **3a-c** and this is explained by the effect of the strongly electron attracting SO_2Cl group (Table 2).

The mass spectrometric behavior of the products **7a-c** is similar. The spectra of all of the compounds (Table 3) show the presence of highly stable molecular ion peaks (54-100%). The initial fragmentation occurs in two directions, i.e. elimination of a chlorine molecular ion and the loss of the SO_2 molecule. The later stages of the fragmentation show the destruction of the pyrazole ring through the elimination of a N_2 molecule.

By reaction of the sulfonyl chlorides **7a-c** with different amines we have prepared a series of N-alkyl(aryl, heteryl)-substituted pyrazolo[3,4-*b*]pyridyl-3-sulfonylamides **8a-h** (Scheme 1). The synthesis was carried out in anhydrous benzene medium in the presence of Et_3N as hydrogen chloride acceptor. The high reactivity of the sulfonyl chlorides even allowed the preparation of the substituted sulfonylamides **8a-h** at room temperature in quite high yields (64-88%) (Table 1).

TABLE 1. Physicochemical Characteristics of Compounds **3-8**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
3a	$C_8H_8N_6$	50.68 / 51.06	4.43 / 4.28	44.12 / 44.66	206-207 (EtOH)	76
3b	$C_9H_{10}N_6$	52.88 / 52.46	5.25 / 4.98	41.31 / 41.56	95-96 (hexane)	84
3c	$C_9H_9ClN_6$	45.41 / 45.68	4.20 / 3.83	35.19 / 35.51	115-116 (cyclohexane)	78
4	$C_8H_7Cl_2N_3$	44.16 / 44.47	3.40 / 3.27	19.64 / 19.44	188-190 (EtOH)	52
5a	$C_{13}H_{14}N_6O$	56.81 / 56.24	5.16 / 4.72	31.12 / 31.09	Dec. ≈280 (DMF)	56
5b	$C_{14}H_{16}N_6O$	58.60 / 59.14	6.02 / 5.67	29.41 / 29.56	156-158 (EtOAc)	81
5c	$C_{14}H_{15}ClN_6O$	52.58 / 52.75	5.16 / 4.74	25.99 / 26.36	197-199 (EtOH)	69
6a	$C_{11}H_{10}N_8$	51.39 / 51.96	4.30 / 3.96	43.82 / 44.07	Dec. ≈330 (DMF)	66
6b	$C_{12}H_{12}N_8$	53.49 / 53.72	4.80 / 4.51	41.34 / 41.77	Dec ≈290 (DMF)	80
6c	$C_{12}H_{11}ClN_8$	47.15 / 47.61	3.92 / 3.66	36.60 / 37.01	Dec 262-265 (DMF)	74
7a	$C_8H_8ClN_3O_2S$	39.40 / 39.11	3.14 / 3.28	17.29 / 17.10	238-240 (MeCN)	76
7b	$C_9H_{10}ClN_3O_2S$	41.89 / 41.62	3.71 / 3.88	15.97 / 16.18	108-109 (hexane)	68
7c	$C_9H_9Cl_2N_3O_2S$	36.46 / 36.75	3.18 / 3.08	14.03 / 14.28	115-116 (hexane)	93
8a	$C_{14}H_{20}N_4O_2S$	54.83 / 54.52	6.31 / 6.54	18.22 / 18.17	204-205 (EtOH)	81
8b	$C_{11}H_{16}N_4O_3S$	46.15 / 46.47	5.83 / 5.67	19.65 / 19.70	168-170 (EtOAc)	71
8c	$C_{15}H_{15}ClN_4O_2S$	51.58 / 51.35	4.16 / 4.31	15.82 / 15.97	198-200 (EtOH)	74
8d	$C_{14}H_{16}N_4O_3S$	52.23 / 52.49	4.88 / 5.03	17.60 / 17.49	96-97 (hexane)	64
8e	$C_{15}H_{20}N_4O_2S$	56.41 / 56.23	6.13 / 6.29	17.22 / 17.49	67-68 (hexane)	72
8f	$C_{17}H_{20}N_4O_2S$	58.99 / 59.28	5.74 / 5.85	16.34 / 16.27	92-93 (hexane)	76
8g	$C_{16}H_{17}ClN_4O_3S$	50.24 / 50.46	4.58 / 4.50	14.49 / 14.71	163-165 (EtOAc)	65
8h	$C_{15}H_{21}ClN_4O_2S$	50.69 / 50.48	6.08 / 5.93	15.54 / 15.70	151-152 (EtOAc)	69

The ^{1}H NMR spectra of the sulfonylamides **8a-h** showed both the signals for the pyrazolopyridine system protons and all of the protons signals corresponding to the amine component of the molecule (Table 2).

The IR spectra of sulfonylamides **8a-h** showed the presence of two strong, characteristic bands in the regions 1315-1332 and 1149-1166 cm^{-1} which respectively correspond to the asymmetric and symmetric stretching absorption bands of the SO_2 group [3]. In addition the spectra contain medium intensity N–H absorption bands in the region 3174-3286 cm^{-1} (Experimental section).

By contrast to the sulfonyl chlorides **7a-c** under electron impact conditions the sulfonylamides Het–$SO_2NR^2R^3$ **8a-h** form very unstable molecule ions and in the majority of cases they are absent in the mass spectra. The typical direction of breakdown of the molecule ion is dissociation of the Het–S bond but the maximum intensity occurs for the fragment peaks $[NR^2N^3]^+$. Due to the low information available from the mass spectra of amides **8a-h** they are not reported in this publication.

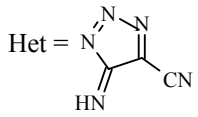
TABLE 2. ^{1}H NMR Spectra of Compounds **3-8**

Com-pound	Chemical shifts*, δ, ppm (*J*, Hz)
3a	13.16 (1H, br. s, N–H); 6.82 (1H, s, H-5); 2.61 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3)
3b	6.82 (1H, s, H-5); 3.93 (3H, s, N–CH_3); 2.56 (3H, s, 6-CH_3); 2.45 (3H, s, 4-CH_3)
3c	3.94 (3H, s, N–CH_3); 2.71 (3H, s, 6-CH_3); 2.62 (3H, s, 4-CH_3)
4	13.82 (1H, br. s, N–H); 2.74 (3H, s, 6-CH_3); 2.64 (3H, s, 4-CH_3)
5a	13.82 (1H, br. s, NH); 7.09 (1H, s, H-5); 2.72 (3H, s, $COCH_3$); 2.60 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3); 2.11 (3H, s, 5-CH_3 triazole)
5b	7.11 (1H, s, H-5); 4.12 (3H, s, N–CH_3); 2.72 (3H, s, $COCH_3$); 2.63 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3); 2.22 (3H, s, 5-CH_3 triazole)
5c	4.13 (3H, s, N–CH_3); 2.69 (3H, s, $COCH_3$); 2.62 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3); 2.14 (3H, s, 5-CH_3 triazole)
6a	14.08 (1H, br. s, N–H); 7.46 (2H, br. s, NH_2); 7.05 (1H, s, H-5); 2.66 (3H, s, 6-CH_3); 2.18 (3H, s, 4-CH_3)
6b	7.41 (2H, br. s, NH_2); 7.10 (1H, s, H-5); 4.09 (3H, s, N–CH_3); 2.62 (3H, s, 6-CH_3); 2.17 (3H, s, 4-CH_3)
6c	7.45 (2H, br. s, NH_2); 4.11 (3H, s, N–CH_3); 2.73 (3H, s, 6-CH_3); 2.22 (3H, s, 4-CH_3)
7a	15.05 (1H, br. s, N–H); 7.20 (1H, s, H-5); 2.96 (3H, s, 6-CH_3); 2.90 (3H, s, 4-CH_3)
7b	7.12 (1H, s, H-5); 4.48 (3H, s, N–CH_3); 2.62 (3H, s, 6-CH_3); 2.51 (3H, s, 4-CH_3)
7c	4.48 (3H, s, N–CH_3); 2.92 (3H, s, 6-CH_3); 2.80 (3H, s, 4-CH_3)
8a	14.21 (1H, br. s, N–H); 7.08 (1H, s, H-5); 2.70 (3H, s, 6-CH_3); 2.55 (3H, s, 4-CH_3 Py); piperidine ring: 3.78 (m); 3.16 (m), 1.74 (m), 1.53 (m), 1.18 (m), 0.94 (3H, m, 4-CH_3)
8b	14.19 (1H, br. s, N–H); 7.08 (1H, s, H-5); 4.82 (1H, br. s, OH); 3.88 (2H, t, *J* = 5.8, $\underline{CH_2}$OH); 3.62 (2H, t, *J* = 5.8, NCH_2); 3.08 (3H, s, N–CH_3); 2.68 (3H, s, 6-CH_3); 2.56 (3H, s, 4-CH_3)
8c	14.18 (1H, br. s, N–H); 8.78 (1H, br. s, SO_2NH); 7.30-7.55 (4H, m, Ar); 7.07 (1H, s, H-5); 4.43 (2H, s, CH_2); 2.72 (3H, s, 6-CH_3); 2.56 (3H, s, 4-CH_3)
8d	8.54 (1H, br. s, NH); 7.11 (1H, s, H-5 Py); furan ring: 7.52 (1H, d, $J_{5,4}$ = 1.8, H-5); 6.32 (1H, dd, $J_{3,4}$ = 3.5, $J_{5,4}$ = 1.8, H-4); 6.23 (1H, d, $J_{3,4}$ = 3.5, H-3); 4.27 (2H, s, CH_2); 4.04 (3H, s, N–CH_3); 2.71 (3H, s, 6-CH_3); 2.57 (3H, s, 4-CH_3)
8e	7.09 (1H, s, H-5); 5.82-5.94 (2H, m, $CH_2\underline{CH}$=CH_2); 5.18-5.30 (4H, m, CH_2CH=$\underline{CH_2}$); 4.08 (3H, s, N–CH_3); 3.96 (4H, d, *J* = 6.2, $\underline{CH_2}CH$=CH_2); 2.81 (3H, s, 6-CH_3); 2.68 (3H, s, 4-CH_3)
8f	7.32-7.45 (5H, m, C_6H_5); 7.05 (1H, s, H-5 Py); 4.52 (2H, s, CH_2); 4.11 (3H, s, N–CH_3); 2.94 (3H, s, $\underline{CH_3}$–N–CH_2–Ar); 2.82 (3H, s, 6-CH_3); 2.71 (3H, s, 4-CH_3)
8g	10.50 (1H, br. s, N–H); 7.03 (2H, d, *J* = 8.9, H-2,4 Ar); 6.83 (2H, d, *J* = 8.9, H-3,5 Ar); 4.04 (3H, s, N–CH_3); 3.68 (3H, s, OCH_3); 2.79 (3H, s, 6-CH_3); 2.71 (3H, s, 4-CH_3)
8h	4.09 (3H, s, N–CH_3); 2.82 (3H, s, 6-CH_3); 2.70 (3H, s, 4-CH_3); piperidine ring: 3.77 (m), 3.04 (m), 1.73 (m), 1.55 (m), 1.21 (m), 0.95 (3H, m, 4-CH_3)

* ^{1}H NMR spectra were recorded in DMSO-d_6 (compounds **3-6, 8**) or $CDCl_3$ (compound **7**).

TABLE 3. Electron Impact Mass Spectra of Compounds **3a-c, 4, 5a-c, 6a-c**

Compound*	Mass-spectrum, *m/z* (I_{rel}, %)
3a	188 $[M]^+$ (19), 132 $[F_1]^+$ (100), 131 $[F_2]^+$ (12), 117 $[F_1–CH_3]^+$ (15), 104 $[F_3]^+$ (22)
3b	202 $[M]^+$ (6), 146 $[F_1]^+$ (31), 131 $[F_2]^+$ (29), 104 $[F_3]^+$ (32)
3c	236 $[M]^+$ (3), 180 $[F_1]^+$ (21), 165 $[F_2]^+$ (21), 145 $[F_1–Cl]$ (25), 103 $[F_2–Cl, –HCN]^+$ (11)
4	215 $[M]^+$ (100), 180 $[M–Cl]^+$ (58), 152 $[180–N_2]^+$ (20), 117 $[152–Cl]^+$ (16), 90 $[117–HCN]^+$ (16)
5a	270 $[M]^+$ (23), 242 $[F_4]^+$ (49), 227 $[F_5]^+$ (61), 200 $[F_6]^+$ (88), 199 $[F_7]^+$ (100), 147 $[F_8]^+$ (37), 146 $[F_9]^+$ (10)
5b	284 $[M]^+$ (24), 256 $[F_4]^+$ (25), 241 $[F_5]^+$ (26), 214 $[F_6]^+$ (97), 213 $[F_7]^+$ (84), 161 $[F_8]^+$ (21), 160 $[F_9]^+$ (32)
5c	318 $[M]^+$ (6), 290 $[F_4]^+$ (29), 275 $[F_5]^+$ (19), 248 $[F_6]^+$ (37), 247 $[F_7]^+$ (26), 195 $[F_8]^+$ (23), 194 $[F_9]^+$ (10)
6a*	254 $[M]^+$ (72), 226 $[M–N_2]^+$ (53), 225 $[M–H, –N_2]^+$ (13), 211 $[226–CH_3]^+$ (23), 200 $[226–CN]^+$ (14), 199 $[226–HCN]^+$ (50), 198 $[225–HCN]^+$ (31), 184 $[200–NH_2]^+$ (28), 147 $[M–Het]^+$ (26)
6b*	268 $[M]^+$ (28), 240 $[M–N_2]^+$ (77), 239 $[M–H, –N_2]^+$ (100), 225 $[M–CH_3N_2]^+$ (12), 199 $[225–CN]^+$ (28), 160 $[M–Het]^+$ (21), 133 $[160–HCN]^+$ (33)
6c*	302 $[M]^+$ (36), 274 $[M–N_2]^+$ (31), 273 $[M–H, –N_2]^+$ (100), 233 $[M–CN, –CH_3N_2]^+$ (34), 198 $[233–Cl]^+$ (22), 195 $[M–Het]^+$ (24), 167 $[198–N_2]^+$ (22)
7a	245 $[M]^+$ (59), 210 $[M–Cl]^+$ (23), 181 $[M–SO_2]^+$ (25), 146 $[210–SO_2]^+$ (48), 118 $[146–N_2]^+$ (82), 105 $[146–CN_2H]^+$ (31), 78 $[105–HCN]^+$ (100)
7b	259 $[M]^+$ (85), 224 $[M–Cl]^+$ (59), 176 $[224–SO]^+$ (48), 160 $[224–SO_2]^+$ (100), 132 $[160–N_2]^+$ (54), 117 $[160–N_2, –CH_3]^+$ (8)
7c	293 $[M]^+$ (54), 258 $[M–Cl]^+$ (28), 229 $[M–SO_2]^+$ (33), 210 $[258–SO]^+$ (28), 194 $[258–SO_2]^+$ (100), 166 $[194–N_2]^+$ (37), 131 $[166–Cl]^+$ (28)

* Het = 

Hence we have found optimum conditions for the synthesis of the 3-azido-4,6-dimethylpyrazolo-[3,4-*b*]pyridines **3a-c** and 4,6-dimethylpyrazolo[3,4-*b*]pyridine-3-sulfonyl chlorides **7a-d** and prepared derivatives based on them. Amongst the sulfonylamides **8a-h** synthesized there were discovered compound having antidotal and growth regulating activity.

EXPERIMENTAL

IR spectra were recorded for KBr tablets on an Infra LUM FT-02 instrument. ^{1}H NMR spectra were obtained on a Bruker WM-500 radio spectrometer (500 MHz) using TMS as internal standard. Electron impact mass spectra were recorded on a Finnigan MAT INCOS 50 instrument (ionization energy 70 eV). CHN elemental analysis was performed on a Carol-Erba model 1106 analyzer. Monitoring of the reaction course and the purity of the products obtained was carried out by TLC on Silufol UV-254 plates using the system hexane–acetone (1:1) and revealed using iodine vapor.

The solvents used in the synthesis were purified from admixtures and dehydrated using known methods [7].

The starting 3-amino-4,6-dimethylpyrazolo[3,4-*b*]pyridines **1a-d** were prepared by method [1].

4,6-Dimethyl(1H)pyrazolo[3,4-*b*]pyridyl-3-azide (3a). A solution of sodium nitrite (0.73 g, 9.3 mmol) in water (2 ml) was added dropwise with stirring to a solution of 3-amino-4,6-dimethyl(1H)pyrazolo-

[3,4-*b*]pyridine (**1a)**, (1.0 g, 6.2 mmol) in conc. HCl (8 ml) at -5ºC, the reaction mixture temperature being held in the range -1 to +1ºC. At the end of the addition the product was stirred at 0°C for a further 20-30 min and the 4,6-dimethyl(1H)pyrazolo[3,4-*b*]pyridine-3-yl diazonium salt **2a** formed was added in small portions with vigorous stirring of the reaction mixture to an aqueous solution of sodium azide (2.0 g, 31 mmol) cooled to -5ºC (the temperature must not exceed 4ºC). To complete the reaction the temperature was slowly raised to room temperature and the precipitate formed was filtered off, washed with water, and dried. Recrystallization from ethanol gave the target product **3a** (0.88 g, 76%) as colorless crystals. IR spectrum, ν, cm^{-1}: 2952, 2927 (C–H Me), 2131 (N_3), 1614, 1606 (C=C, C=N).

Compounds 3b,c were prepared similarly. **Compound 3b**. IR spectrum, ν, cm^{-1}: 2952, 2925 (C–H, Me), 2854 (N–Me), 2138 (N_3), 1598, 1581 (C=C, C=N). **Compound 3c**. IR spectrum, ν, cm^{-1}: 2958, 2923 (C–H, Me), 2851 (N–Me), 2121 (N_3), 1594, 1571 (C=C, C=N).

2,5-Dichloro-4,6-dimethyl-(1H)pyrazolo[3,4-*b*]pyridine (4). The 2,5-dichloro-3-amino-4,6-dimethyl-(1H)pyrazolo[3,4-*b*]pyridine (**1b**) (1.0 g, 5.1 mmol) was diazotized similarly to the above and the solution of the diazonium chloride **2b** obtained was treated with an aqueous solution of sodium azide. The precipitate was filtered off, washed with water, and dried. Recrystallization from benzene gave product **4** (0.57 g, 52%) as pale-yellow crystals.

3-(4-Acetyl-5-methyl-1,2,3-triazol-1-yl)-1,4,6-trimethylpyrazolo[3,4-*b*]pyrimidine (5b). A solution of acetylacetone (0.93 g, 9.3 mmol) and triethylamine (0.93 g, 9.3 mmol) in acetonitrile (3 ml) was added to a suspension of the 1,4,6-trimethylpyrazolo[3,4-*b*]pyridyl-3-azide **3b** in acetonitrile (9 ml) and refluxed for 5.5-6 h. The reaction product was evaporated to dryness, washed with water, and dried. Recrystallization from a mixture of hexane and ethyl acetate (1:3) gave the target product **5b** (0.85 g, 81%) as colorless crystals.

Compounds 5a,c were prepared similarly.

3-(5-Amino-4-cyano-1,2,3-triazol-1-yl)-5-chloro-1,4,6-trimethylpyrazolo[3,4-*b*]pyridine (6c). 5-Chloro-1,4,6-trimethyl-pyrazolo[3,4-*b*]pyridyl-3-azide (**3c**) (1.0 g, 4.2 mmol), malononitrile (0.55 g, 8.4 mmol), and triethylamine (0.85 g, 8.4 mmol) were mixed in ethanol (10 ml) and heated at 55-60ºC for 3.5-4 h. The reaction product was doubly diluted with water and the precipitate formed was filtered off, washed with water, and dried. Recrystallization from acetone gave the target product **6c** (0.95 g, 74%) as an amorphous, pink powder.

Compounds 6a,b were prepared similarly.

4,6-Dimethyl(1H)pyrazolo[3,4-*b*]pyridyl-3-sulfonyl Chloride (7a). The 3-amino-4,6-dimethyl-(1H)pyrazolo[3,4-*b*]pyridine **1a** (5.0 g, 31 mmol) was diazotized as described above. Anhydrous copper sulphate (0.85 g) was added to a previously prepared saturated solution of SO_2 in glacial acetic acid (30 ml) and then, with vigorous stirring, a solution of 4,6-dimethyl(1H)pyrazolo[3,4-b]pyridyl-3-diazonium chloride was added dropwise such that the temperature remained at 0-4ºC. At the end of the nitrogen evolution the flask contents were poured into a 5% NaCl solution (100 ml), cooled to 0ºC, and the precipitate formed was filtered off, washed with iced water, dried in air, and then in a vacuum desiccator (5-10 mm Hg). Recrystallization from anhydrous acetonitrile gave the product **7a** (5.8 g, 76%) as light-yellow crystals.

Compounds 7b-c were prepared similarly.

N-(2-Chlorobenzyl)-4,6-dimethyl(1H)pyrazolo[3,4-*b*]pyridyl-3-sulfonylamide (8c). A solution of 2-chlorobenzylamine (0.62 g, 4.4 mmol) and triethylamine (0.4 g, 4.0 mmol) in benzene (10 ml) was added at room temperature with stirring to a suspension of compound **7a** (1.0 g, 4.0 mmol) in anhydrous benzene (20 ml). At the end of the addition stirring was continued for a further 3 h and the precipitate was filtered off, liberally washed with warm water, and dried. Recrystallization from ethanol gave the product **8c** (1.05 g, 74%) as light-yellow crystals. IR spectrum, ν, cm^{-1}: 3286 (N–H), 1618, 1583 (C=C, C=N arom.), 1332, 1449 (SO_2).

Compounds 8a,b,d-h were prepared similarly.

Compound 8j. IR spectrum, ν, cm^{-1}: 3174 (N–H), 1581, 1564 (C=C, C=N arom.), 1326, 1155 (SO_2).

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