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# UNEXPECTED FORMATION OF 4-ARYL-3-CYANO-6-PHENYLPYRIDINE-2(1H)-THIONES FROM THE REACTION OF ARYLMETHYLENECYANOTHIOACETAMIDES WITH BENZOYL-1,1,1-TRIFLUOROACETONE

**V. D. Dyachenko[1] and A. N. Chernega[2]**

*4-Aryl-3-cyano-6-phenylpyridine-2(1H)-thiones, used in the synthesis of substituted 2-alkylthiopyridines, thieno[2,3-b]pyridines, and 1,4-di(pyridin-2-ylthio)butane, have been synthesized by the condensation of arylmethylenecyanothioacetamides with benzoyl-1,1,1-trifluoroacetone. The reaction path includes the formation of the Michael adduct which undergoes loss of the acyl group. The structure of 3-cyano-2-methylthio-4-(1-naphthyl)-6-phenylpyridine has been studied by X-ray crystallography.*

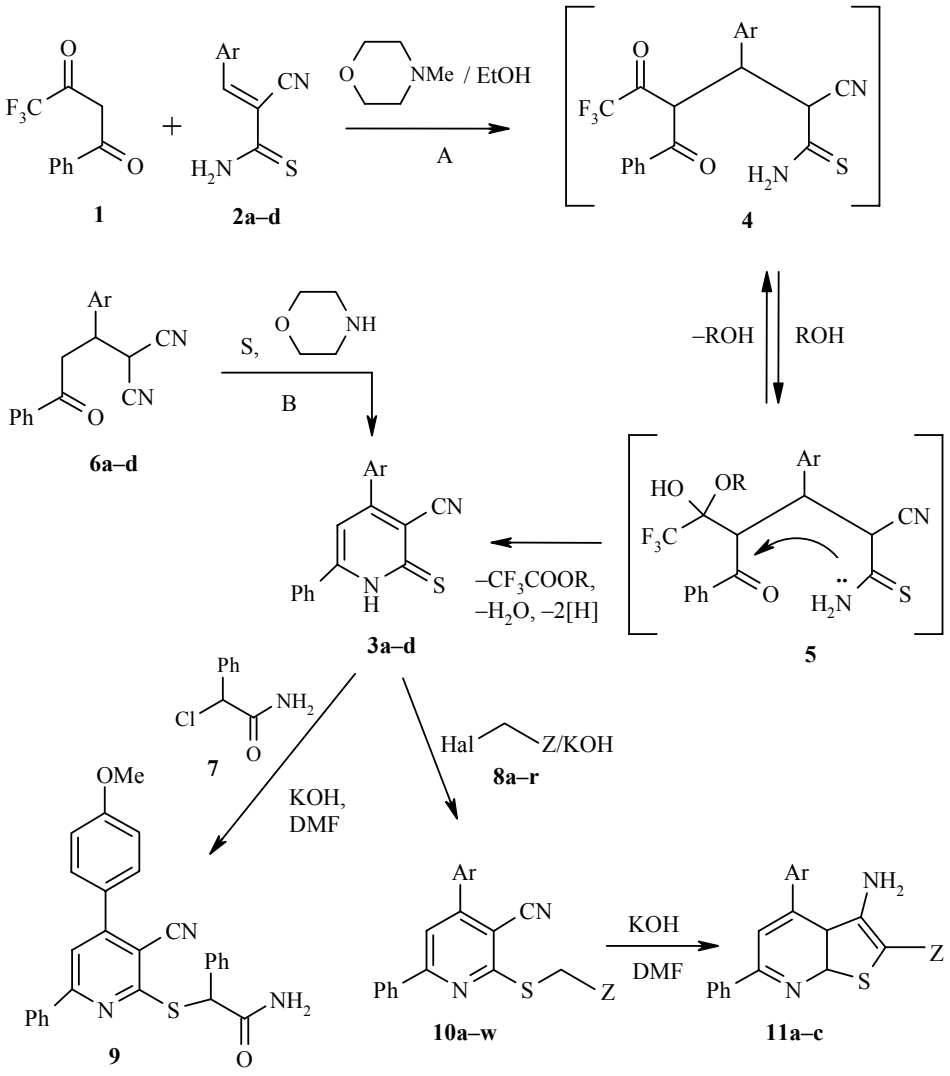
**Keywords:** Michael adducts, 2-alkylthiopyridines, arylmethylenecyanothioacetamides, 4-aryl-3-cyano-6-phenylpyridine-2(1H)-thiones, benzoyl-1,1,1-trifluoroacetones, 1,4-di(pyridin-2-ylthio)butane, alkylation, acyl cleavage, X-ray crystallography.

Benzoyl-1,1,1-trifluoroacetone has previously used successfully for the synthesis of substituted 6-trifluoromethylpyridinechalcogenones by the Michael reaction both as donor [1,2] and as acceptor (as the ethoxymethylene derivative) [3]. Absolute ethanol was used as the solvent and secondary or tertiary amines as the catalyst. Our invesigations have shown that carrying out the Michael reaction by the interaction of benzoyl-1,1,1-trifluoroacetone **1** with arylmethylenecyanothioacetamides **2** in ethanol in the presence of a two-fold excess of N-methylmorpholine gave rise to 4-aryl-3-cyano-6-phenylpyridine-2(1H)-thiones **3** which are potentially biologically active compounds (method A). In particular 4-(1-naphthyl)-substituted pyridine-2(1H)-chalcogenones appear to have antiasthmatic activity [4].

The reaction pathway apparently includes formation of the Michael adducts **4**. The latter undergo acyl cleavage [5] on the addition of water or ethanol as result of which products **5** are probably formed which then undergo heterocyclization into the substituted pyridine-2(1H)-thiones **3**. We note that fluorine-containing β-diketones have a tendency to acyl cleavage [6]. For example, 2-thienoyltrifluoroacetone reacts with arylmethylenemalononitrile in ethanol in the presence of morpholine to give 2-aryl-1,1-dicyano-3-(2-thienoyl)propanes and trifluoroacetic acid [7]. However acyl cleavage of benzoyl-1,1,1-trifluoroacetone in conditions of the Michael reaction is unknown.

[1] Taras Shevchenko Lugansk State Pedagogical University, Lugansk 91011, Ukraine; e-mail: dvd_lug@online.lg.ua. [2] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 02094, Ukraine; Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, 1821-1828, December 2005. Original article submitted July 15, 2003.




R = H or Et. **2,3,6 a** Ar = naphth-1-yl, **b** Ar = 4-$FC_6H_4$, **c** Ar = 4-$ClC_6H_4$, **d** Ar = 4-$MeOC_6H_4$;
**8 a** Hal = Cl, **b-l** Hal = Cl, **m-r** Hal = Br; **a** Z = H, **b** Z = $COOCH_2Ph$, **c** Z = COOEt, **d** Z = COOPr,
**e** Z = Ph, **f** Z = COOMe, **g** Z = $COO(CH_2)_8Me$, **h** Z = thiazol-2-ylcarbamoyl, **i** Z = $COO(CH_2)_7Me$, **j** Z = $CONH_2$,
**k** Z = 4-$BrC_6H_4NHCO$, **l** Z = CN, **m** Z = naphth-2-ylcarbonyl, **n** Z = 4-$EtOC_6H_4CO$, **o** Z = 2-$MeC_6H_4$, **p** Z = 4-$BrC_6H_4CO$,
**g** Z = $CH{=}CH_2$, **r** Z = coumarin-3-ylcarbonyl; **10, 11 a** Ar = 4-$ClC_6H_4$, Z = COOEt, **b** Ar = 4-$MeOC_6H_4$, Z = $COOCH_2Ph$,
**c** Ar = 4-$MeOC_6H_4$, Z = COOMe; **10 d-g** Ar = naphth-1-yl, **h-j** Ar = 4-$ClC_6H_4$, **k-w** Ar = 4-$MeOC_6H_4$; **d, k** Z = H,
**e,h** Z = $COOCH_2Ph$, **f** Z = naphth-2-ylcarbonyl, **g** Z = 4-$EtOC_6H_4CO$, **i** Z = COOPr, **j, n** Z = Ph, **l** Z = 2-$MeC_6H_4$,
**m** Z = $CONH_2$, **o** Z = 4-$BrC_6H_4NHCO$, **p** Z = 4-$BrC_6H_4CO$, **q** Z = CN, **r** Z = $CH{=}CH_2$, **s** Z = coumarin-3-ylcarbonyl,
**t** Z = COOEt, **u** Z = $COO(CH_2)_8Me$, **v** Z = thiazol-2-ylcarbamoyl, **w** Z = $COO(CH_2)_7Me$

The structures of compounds **3a-d** were shown by physicochemical and spectroscopic methods (Tables 1 and 2), direct synthesis by the interaction of δ-ketodinitriles **6** with elemental sulfur (method B) [8], and also by chemical transformations. In particular, the pyridinethiones **3** react readily with the alkyl halides **7** and **8** in basic medium to form the corresponding organic sulfides **9** and **10**. Compounds **10a-c** underwent intramolecular Thorpe–Ziegler cyclization under the influence of KOH solution to give substituted thieno-[2,3-*b*]pyridines **11** which confirmed the presence of the vicinal cyano group [9]. These compounds have potential as intermediates for creation of medicinal products [10, 11].

TABLE 1. Characteristics of the Compounds Synthesized, **9, 10a-w, 11a-c, 12**

| Compound | Empirical formula | Found, % / Calculated, % | | | mp, °C* | Yield, % |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| **9** | $C_{27}H_{21}N_3O_2S$ | 71.70 / 71.82 | 4.58 / 4.69 | 9.20 / 9.31 | 303-305 (DMF) | 84 |
| **10a** | $C_{22}H_{17}ClN_2O_2S$ | 64.50 / 64.62 | 3.95 / 4.19 | 6.74 / 6.85 | 191-193 (BuOH) | 71 |
| **10b** | $C_{28}H_{22}N_2O_3S$ | 71.86 / 72.08 | 4.60 / 4.75 | 6.14 / 6.00 | 132-134 (EtOH) | 69 |
| **10c** | $C_{28}H_{18}N_2O_3S$ | 67.73 / 67.68 | 4.51 / 4.65 | 7.02 / 7.17 | 148-151 (MeOH) | 78 |
| **10d** | $C_{23}H_{16}N_2S$ | 78.21 / 78.38 | 4.40 / 4.58 | 8.11 / 7.95 | 150-152 (AcOH) | 77 |
| **10e** | $C_{31}H_{22}N_2O_2S$ | 76.39 / 76.52 | 4.42 / 4.56 | 5.68 / 5.76 | 176-177 (AcOH) | 87 |
| **10f** | $C_{34}H_{22}N_2OS$ | 80.79 / 80.61 | 4.21 / 4.38 | 5.42 / 5.53 | 114-116 (AcOH) | 84 |
| **10g** | $C_{32}H_{24}N_2O_2S$ | 76.63 / 76.78 | 4.70 / 4.83 | 5.52 / 5.60 | 165-166 (AcOH) | 78 |
| **10h** | $C_{27}H_{19}ClN_2O_2S$ | 68.91 / 68.86 | 3.84 / 4.07 | 6.14 / 5.95 | 195-198 (EtOH) | 65 |
| **10i** | $C_{23}H_{19}ClN_2O_2S$ | 65.19 / 65.32 | 4.61 / 4.53 | 6.50 / 6.62 | 175-178 (*i*-PrOH) | 70 |
| **10j** | $C_{25}H_{17}ClN_2S$ | 72.50 / 72.72 | 4.02 / 4.15 | 6.85 / 6.78 | 194-196 (AcOH) | 63 |
| **10k** | $C_{20}H_{16}N_2OS$ | 72.11 / 72.26 | 4.70 / 4.85 | 8.55 / 8.43 | 144-146 (BuOH) | 66 |
| **10l** | $C_{27}H_{22}N_2OS$ | 76.60 / 76.75 | 5.32 / 5.25 | 6.54 / 6.63 | 163-165 (BuOH) | 71 |
| **10m** | $C_{21}H_{17}N_3O_2S$ | 66.95 / 67.18 | 4.62 / 4.56 | 11.02 / 11.19 | 251-253 (BuOH) | 78 |
| **10n** | $C_{26}H_{20}N_2OS$ | 76.32 / 76.44 | 5.11 / 4.93 | 6.70 / 6.86 | 169-172 (AcOH) | 69 |
| **10o** | $C_{27}H_{20}BrN_3O_2S$ | 60.96 / 61.14 | 3.75 / 3.80 | 8.07 / 7.92 | 227-228 (BuOH) | 70 |
| **10p** | $C_{27}H_{19}BrN_2O_2S$ | 63.02 / 62.92 | 3.60 / 3.72 | 5.29 / 5.44 | 229-231 (BuOH) | 82 |
| **10q** | $C_{21}H_{15}N_3OS$ | 70.42 / 70.57 | 4.11 / 4.23 | 11.85 / 11.76 | 161-163 (BuOH) | 85 |
| **10r** | $C_{22}H_{18}N_2OS$ | 73.58 / 73.72 | 4.92 / 5.06 | 7.90 / 7.81 | 110-111 (BuOH) | 67 |
| **10s** | $C_{30}H_{20}N_2O_4S$ | 71.20 / 71.41 | 4.12 / 3.99 | 5.38 / 5.55 | 235-237 (DMF) | 73 |
| **10t** | $C_{23}H_{20}N_2O_3S$ | 68.14 / 68.30 | 4.80 / 4.98 | 6.72 / 6.93 | 191-193 (BuOH) | 80 |
| **10u** | $C_{30}H_{34}N_2O_3S$ | 71.50 / 71.68 | 6.74 / 6.82 | 5.40 / 5.57 | 122-124 (EtOH) | 64 |
| **10v** | $C_{24}H_{18}N_4O_2S_2$ | 62.71 / 62.86 | 4.12 / 3.96 | 12.05 / 12.22 | 239-241 (AcOH) | 77 |
| **10w** | $C_{29}H_{32}N_2O_3S$ | 71.12 / 71.28 | 6.72 / 6.60 | 5.59 / 5.73 | 133-134 (*i*-PrOH) | 68 |
| **11a** | $C_{22}H_{17}ClN_2O_2S$ | 64.40 / 64.62 | 3.95 / 4.19 | 7.02 / 6.85 | 274-276 (BuOH) | 69 |
| **11b** | $C_{28}H_{22}N_2O_3S$ | 71.85 / 72.08 | 4.60 / 4.75 | 5.84 / 6.00 | 248-250 (AcOH) | 75 |
| **11c** | $C_{22}H_{18}N_2O_3S$ | 67.74 / 67.68 | 4.42 / 4.65 | 7.02 / 7.17 | 215-217 (AcOH) | 66 |
| **12** | $C_{42}H_{34}N_4O_2S_2$ | 73.18 / 73.02 | 5.15 / 4.96 | 7.90 / 8.11 | 118-124 (BuOH) | 67 |

* Solvent for crystallization in brackets.

TABLE 2. Spectroscopic Characteristics of Compounds **9, 10a-w, 11a-c, 12**

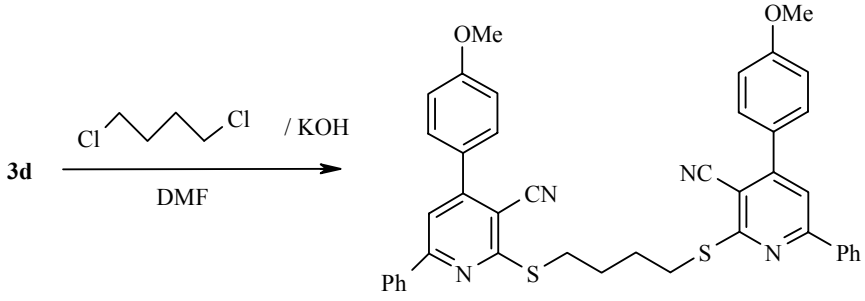
| Compound | IR spectrum, ν, $cm^{-1}$ (C≡N, C=O) | $^1$H NMR spectrum, δ, ppm (*J*,Hz) | |
|---|---|---|---|
| | | $C_{(5)}H$, s, $SCH_2$, s, or $NH_2$, br. s | others signals |
| 1 | 2 | 3 | 4 |
| **9** | 2218, 1664 | 7.86, 5.84 | 3.86 (3H, s, $CH_3O$); 7.07 and 8.32 (2H each, both d, *J* = 8.0, $C_6H_4$); 7.37-7.72 [11H, m, $(C_6H_5)_2$ and $NH_2$], 8.06 (1H, br. s, $NH_2$) |
| **10a** | 2224, 1714 | 7.95, 4.27 | 1.18 (3H, t, *J* = 6.7, $CH_2\underline{CH_3}$); 4.10 (2H, q, $\underline{CH_2}CH_3$); 7.58 (3H, m, $C_6H_5$); 7.65 and 7.81 (2H each, both d, *J* = 8.7, $C_6H_4$); 8.22 (2H, m, $C_6H_5$) |
| **10b** | 2221, 1705 | 7.89, 4.37 | 3.83 (3H, s, $CH_3O$); 5.15 (2H, s, $OCH_2$); 7.15 and 7.75 (2H each, both d, *J* = 8.1, $C_6H_4$); 7.29 (5H, s, $C_6H_5$); 7.49 (3H, m, $C_6H_5$); 8.21 (2H, m, $C_6H_5$) |
| **10c** | 2214, 1709 | 7.90, 4.27 | 3.67 (3H, s, $COOCH_3$); 3.86 (3H, s, $OCH_3$); 7.15 and 7.77 (2H each, both d, *J* = 7.8, $C_6H_4$); 7.53 (3H, m, $C_6H_5$); 8.21 (2H, m, $C_6H_5$) |
| **10d** | 2224 | 7.99, 3.35 | 7.35-7.78 (8H, m, $H_{arom,}$); 8.10 (2H, m, $H_{arom,}$); 8.33 (2H, m, $H_{arom,}$) |
| **10e** | 2225, 1716 | 7.82, 4.32 | 5.16 (2H, s, $OCH_2$); 7.25-7.69 (13H, m, $H_{arom,}$); 8.05 (4H, m, $H_{arom,}$) |
| **10f** | 2234, 1700 | —*, 5.13 | 6.99 (2H, t, *J* = 7.9, $H_{arom,}$); 7.21 (1H, m, $H_{arom,}$); 7.51-8.14 (16H, m, $H_{arom,}$)*; 8.88 (1H, s, $C_{(1)}H$ naphthyl) |
| **10g** | 2210, 1675 | 7.76, 4.95 | 1.46 (3H, t, *J* = 6.7, $CH_3$); 4.17 (2H, q, $CH_2$); 7.04 and 7.87 (2H each, both d, *J* = 8.1, $C_6H_4$); 7.22 (2H, m, $H_{arom,}$); 7.35 (1H, m, $H_{arom,}$); 7.59 (5H, m, $H_{arom,}$); 8.09 (4H, m, $H_{arom,}$) |
| **10h** | 2225, 1698 | 7.95, 4.27 | 5.14 (2H, s, $CH_2$); 7.48-7.60 (8H, m, $H_{arom,}$); 7.64 and 7.80 (2H each, both d, *J* = 8.10, $C_6H_4$); 8.24 (2H, m, $H_{arom,}$) |
| **10i** | 2217, 1695 | 7.98, 4.25 | 0.81 (3H, t, *J* = 8.4, $CH_3$); 1.55 (2H, m, $CH_2$); 4.08 (2H, t, *J* = 7.9, $OCH_2$); 7.54 (3H, m, $C_6H_5$); 7.67 and 7.79 (2H each, both d, *J* = 8.5, $C_6H_4$); 8.24 (2H, m, $C_6H_5$) |
| **10j** | 2220 | 7.93, 4.72 | 7.30-7.54 (8H, m, $H_{arom,}$); 7.65 and 7.80 (2H each, both d, *J* = 8.5, $C_6H_4$); 8.28 (2H, m, $H_{arom,}$) |
| **10k** | 2218 | 7.78, 2.73 | 3.84 (3H, s, $OCH_3$); 7.70 and 8.25 (2H each, both d, *J* = 8.4, $C_6H_4$); 7.60 (5H, m, $C_6H_5$) |
| **10l** | 2215 | 7.81, 4.72 | 2.42 (3H, s, $CH_3$); 3.85 (3H, m, $OCH_3$); 7.08 and 8.27 (2H each, both d, *J* = 8.5, $C_6H_4$); 7.20 (2H, m, $H_{arom,}$); 7.38-7.74 (7H, m, $H_{arom,}$) |
| **10m** | 2224, 1670 | 7.88, 4.08 | 3.85 (3H, s, $OCH_3$); 7.05 and 8.29 (2H each, both d, *J* = 8.5, $C_6H_4$); 7.25 (1H, br. s, $NH_2$); 7.52-7.79 (6H, m, $C_6H_5$ and $NH_2$) |
| **10n** | 2221 | 7.85, 4.70 | 3.31 (3H, s, $OCH_3$); 7.11 and 7.71 (2H each, both d, *J* = 8.5, $C_6H_4$); 7.29 (2H, m, $H_{arom,}$); 7.56 (6H, m, $H_{arom,}$); 8.25 (2H, m, $H_{arom,}$) |
| **10o** | 2218, 1674 | 7.82, 4.31 | 3.78 (3H, s, $OCH_3$); 6.81 and 8.19 (2H each, both d, *J* = 8.0, $C_6H_4$); 7.46-7.70 (9H, m, $H_{arom,}$); 10.61 (1H, br. s, NH) |
| **10p** | 2227, 1705 | 7.90, 5.00 | 3.81 (3H, s, $OCH_3$); 6.75 and 8.05 (2H each, both d, *J* = 8.5, $C_6H_4$); 7.52-7.80 (9H, m, $H_{arom,}$) |
| **10q** | 2252, 2217 | 7.93, 4.50 | 3.84 (3H, s, $OCH_3$); 7.08 and 8.34 (2H each, both d, *J* = 8.5, $C_6H_4$); 7.50-7.78 (5H, m, $C_6H_5$) |
| **10r** | 2218 | 7.82, 4.08 (d, *J* = 6.9), | 3.83 (3H, s, $OCH_3$); 5.16 (1H, d, $J_{cis}$ = 9.1, $=CH_2$); 5.37 (1H, d, $J_{trans}$ = 16.9, $=CH_2$); 6.05 (1H, m, CH=); 7.04 and 8.25 (2H each, both d, *J* = 8.0, $C_6H_4$); 7.61 (5H, m, $C_6H_5$) |
| **10s** | 2220, 1698 | 7.95, 4.98 | 3.69 (3H, s, $OCH_3$); 6.77 and 8.04 (2H each, both d, *J* = 8.0, $C_6H_4$); 7.32-7.78 (9H, m, $H_{arom,}$); 8.61 (1H, s, $H_{(3)}$ coumarinyl) |
| **10t** | 2214, 1717 | 7.84, 4.24 | 1.19 (3H, s, *J* = 6.9, $CH_2\underline{CH_3}$); 3.85 (3H, s, $OCH_3$); 4.13 (2H, q, $OCH_2$); 7.07 and 8.20 (2H each, both d, *J* = 8.2, $C_6H_4$); 6.61 (5H, m, $C_6H_5$) |
| **10u** | 2206, 1690 | 7.75, 4.14 | 0.82 (3H, t, *J* = 4.02, $CH_3$); 1.19 [12H, m, $(CH_2)_6$], 1.55 (2H, m, $CH_2$); 3.88 (3H, s, $OCH_3$); 4.06 (2H, t, *J* = 6.66, $OCH_2$); 7.08 and 7.69 (2H each, both d, *J* = 8.7, $C_6H_4$); 7.50 (3H, m,$C_6H_5$); 8.13 (2H, m, $C_6H_5$) |

TABLE 2 (continued)

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| **10v** | 2216, 1660 | 7.70, 4.33 | 3.89 (3H, s, $OCH_3$); 7.02 and 7.39 (1H each, both d, $J$ = 3.54, $H_{(5)}$ and $H_{(4)}$ thiazolyl); 7.10 and 7.69 (2H each, both d, $J$ = 8.0, $C_6H_4$); 7.32 (3H, m, $C_6H_5$); 8.05 (2H, d, $J$ = 7.04, $C_6H_5$); 12.51 (1H, br. s, NH) |
| **10w** | 2220, 1704 | 7.75, 4.12 | 0.83 (3H, t, $J$ = 4.02, $CH_3$); 1.20 [10H, m, $(CH_2)_5$], 1.56 (2H, m, $CH_2$); 3.89 (3H, s, $OCH_3$); 4.05 (2H, t, $J$ = 4.98, $OCH_2$); 7.08 and 7.65 (2H each, both d, $J$ = 6.76, $C_6H_4$); 7.46 (3H, m, $C_6H_5$); 8.14 (2H, m, $C_6H_5$) |
| **11a** | 1713 | 7.80, 5.86 | 1.30 (3H, t, $J$ = 6.7, $CH_2\underline{CH_3}$); 4.27 (2H, q, $\underline{CH_2}CH_3$); 7.53 (3H, m, $C_6H_5$); 7.66 (4H, s, $C_6H_4$); 8.21 (2H, m, $C_6H_5$) |
| **11b** | 1705 | 7.72, 5.84 | 3.82 (3H, s, $OCH_3$); 5.31 (2H, s, $CH_2$); 7.04 and 8.18 (2H each, both d, $J$ = 8.1, $C_6H_4$); 7.40 (5H, s, $C_6H_5$); 7.59 (5H, s, $C_6H_5$) |
| **11c** | 1714 | 7.74, 5.79 | 3.78 (3H, s, $COOCH_3$); 3.83 (3H, s, $OCH_3$); 7.04 and 8.18 (2H each, both d, $J$ = 8.0, $C_6H_4$); 7.60 (5H, s, $C_6H_5$) |
| **12** | 2219 | 7.70, 3.45 (m,) | 2.00 [4H, m, $(CH_2)_2$], 3.75 [6H, s, $(OCH_3)_2$], 6.94 and 8.13 [4H each, both d, $J$ = 8.0, $(C_6H_4)_2$], 7.59 [10H, m, $(C_6H_5)_2$] |

* Signals are overlapped.

Alkylation of the pyridinethione **3d** with 1,4-dichlorobutane with a reagent ratio of 2:1 gave 1,4-di(pyridin-2-ylthio)butane **12**.




**12**

TABLE 3. Mass Spectra of Compounds **10d-g, 10u-w**

| Compound | *m/z* ($I_{rel}$, %) |
|---|---|
| **10d** | 352 $[M]^+$ (58), 351 $[M–1]^+$ (100), 305 (6), 277 (8), 77 (4) |
| **10e** | 486 $[M]^+$ (65), 485 $[M–1]^+$ (45), 441 (12), 351 (52), 337 (28), 318 (13), 277 (14), 239 (6), 91 (100), 77 (8), 65 (7) |
| **10f** | 506 $[M]^+$ (10), 351 (18), 296 (7), 155 (100), 127 (64), 77 (3) |
| **10g** | 500 $[M]^+$ (8), 351 (7), 149 (100), 121 (39), 77 (4), 65 (6) |
| **10u** | 502 $[M]^+$ (47), 501 $[M–1]^+$ (88), 487 (21), 469 (13), 331 (100), 317 (16), 300 (8), 288 (12), 242 (15), 77 (6), 69 (14), 55 (26), 43 (65), 41 (39) |
| **10v** | 458 $[M]^+$ (14), 457 $[M–1]^+$ (6), 385 (10), 359 (52), 331 (100), 317 (24), 303 (7), 288 (17), 242 (23), 214 (13), 127 (76), 100 (19), 77 (18), 55 (16), 45 (18) |
| **10w** | 488 $[M]^+$ (49), 487 $[M–1]^+$ (77), 473 (18), 331 (100), 317 (16), 300 (10), 288 (14), 242 (15), 214 (10), 77 (8), 69 (12), 55 (22), 43 (57) |

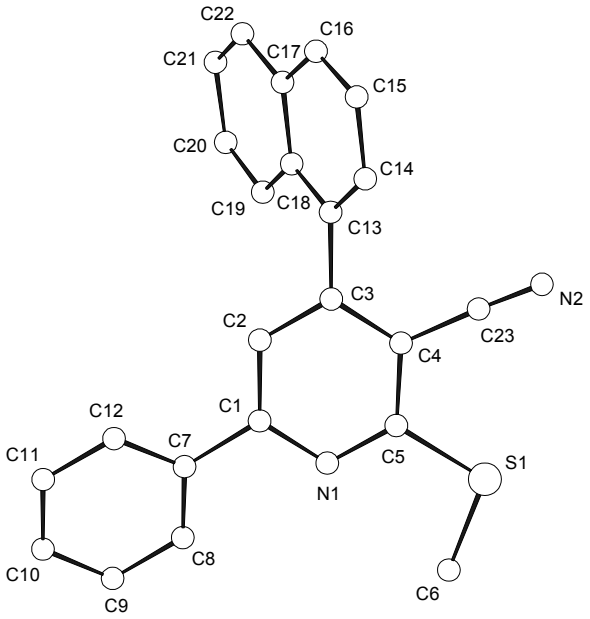



Fig. 1. General view of the molecule **10d** with numbering of the atoms (H atoms are not shown). Principal bond lengths and angles: $S_{(1)}$–$C_{(5)}$ 1.754(5), $S_{(1)}$–$C_{(6)}$ 1.781(6), $N_{(1)}$–$C_{(1)}$ 1.349(6), $N_{(1)}$–$C_{(5)}$ 1.331(5) Å; $C_{(5)}$–$S_{(1)}$–$C_{(6)}$ 101.3(3), $C_{(1)}$–$N_{(1)}$–$C_{(5)}$ 118.4(4) deg. The remaining bond lengths and angles are comparable with standard values [12].

To establish unambiguously the structure of the products of the interaction of benzoyl-1,1,1-trifluoroacetone with arylmethylencyanothioacetamides under the conditions of the Michael reaction and the regioselectivity of their alkylation compound **10d** (Fig. 1) was studied by X-ray crystallography. The benzene ring $C_{(7-12)}$ and the $C_{(13-22)}$ group form dihedral angles of 25.5 and 60.0° with the central pyridine ring $N_{(1)}C_{(1-5)}$. The S–Me substituent is practically coplanar with the pyridine ring – the torsion angle $N_{(1)}$–$C_{(5)}$–$S_{(1)}$–$C_{(6)}$ is only 11.6°.

So condensation of benzoyl-1,1,1-trifluoroacetone with arylmethylencyanothioacetamides include acyl cleavage from the Michael adducts to give substituted 4-aryl-3-cyano-6-phenylpyridine-2(1H)-thiones.

## EXPERIMENTAL

A monocrystal of compound **10d** was initially rolled into a sphere of diameter 0.19 mm.

**X-ray Crystallography** was carried out at room temperature on an automatic four circle Enraf-Nonius CAD-4 diffractometer (CuKα radiation, λ = 1.54178 A, with relative scanning rate 2θ/ω = 1.2, $\theta_{max}$ = 60°, segment of the sphere $0 \le h \le 9$, $0 \le k \le 15$, $0 \le l \le 16$). A total of 1592 reflexions were collected. Crystalls of compound **10d** are rhombic, $a$ = 8.849(2), $b$ = 14.795(3), $c$ = 14.004(5) Å; $V$ = 1833.5(9) Å$^3$; M = 352.45; $Z$ = 4; $d_{calc}$ = 1.28 g/cm$^3$; μ = 15.72 cm$^{-1}$; $F$(000) = 739.0; space group $Pna2_1$ (No. 33). The structures was refined by the direct method by least squares analysis in the complete matrix anisotropic approximation using the CRYSTALS suite of programs [13]. In the refinement 1415 reflexions with $I > 1.5\sigma(I)$ (235 calculated parameters with 6.0 reflexions per parameter). About half the hydrogen atoms were found from electron density difference syntheses, while the rest were placed in calculated positions. All the hydrogen atoms were included in the refinement at fixed positions with fixed thermal parameters. Absorption by the crystal was calculated with

the help of azimuthal scanning [14]. The Chebyshev weighting scheme [15] with five parameters: 0.92, 0.12, 0.80, 0.01, and 0.25, was used in the refinement. The final values of the residual factors were $R = 0.038$ and $R_w = 0.036$, $GOF = 1.217$. Coordinates of the non-hydrogen atoms may be obtained from the authors.

IR spectra of nujol mulls of the synthesized compounds were recorded with an IKS-29 instrument. $^1$H NMR spectra of DMSO-$d_6$ solutions with $Me_4Si$ as internal standard were recorded with the following instruments: Bruker WP-100 SY (100 MHz) (compounds **9, 10a-c, h-t**), Gemini -200 (200 MHz) (compounds **10e-g, v**), Bruker WM-250 (250 MHz) (compound **3a**), Varian Mercury-400 (400 MHz) (compound **10d**) and Bruker DR 500 (500 MHz) (compounds **10u,w**). Mass spectra were taken with a Kratos MS-890 machine with direct introduction of the sample into the ion source (70 eV). Melting points were determined with a Kofler block. The course of reactions and the purity of the compounds obtained were monitored by TLC (Silufol UV 254, 3:5 acetone–hexane, detection with iodine vapor).

**4-Aryl-3-cyano-6-phenylpyridine-2(1H)-thiones 3a-d.** Method A. The corresponding arylmethylencyanothioacetamide **2** (10 mmol) and N-methylmorpholine (2.2 ml, 10 mmol) were added to a solution of benzoyl-1,1,1-trifluoroacetone (2.16 g, 10 mmol) in ethanol (25 ml) and the mixture was stirred for 4 h. The mixture was then kept for 1 d, then diluted with 10% hydrochloric acid to pH 5 and kept for 48 h. The precipitate which formed was separated and washed with water and hexane. Compounds **3a-d** were formed and were crystallized from glacial acetic acid.

**3-Cyano-4-(1-naphthyl)-6-phenylpyridine-2(1H)-thione (3a).** Yield 2.37 g (70%); mp 228-230°C. IR spectrum (nujol mull), ν, cm$^{-1}$: 2212 (C≡N). $^1$H NMR spectrum, δ, ppm: 7.14 (1H, s, $C_{(5)}H$); 7.49-8.18 (12H, m, $H_{arom}$); 14.23 (1H, br. s, NH). Mass spectrum, *m/z*, ($I_{rel}$): 338 $[M]^+$(47), 337 $[M-1]^+$ (100), 277 (9), 177 (18), 175 (25), 169 (47), 77 (20). Found, %: C 77.89; H 4.02; N 8.36. $C_{22}H_{14}N_2S$. Calculated, %: C 78.08; H 4.17; N 8.28.

**3-Cyano-4-(4-fluorophenyl)-6-phenylpyridine-2(1H)-thione (3b)**. Yield 68%; mp199-204°C (200-202°C [16]). The spectroscopic characteristics corresponded to those in the literature [16].

**4-(4-Chlorophenyl)-3-cyano-6-phenylpyridine-2(1H)-thione (3c)**. Yield 74%; mp 233-236°C (233-234°C [8]). The spectroscopic characteristics corresponded to those in the literature [8].

**3-Cyano-4-(4-methoxyphenyl)-6-phenylpyridine-2(1H)-thione (3d).** Yield 65%; mp 219-224°C (223-225°C [8]). The spectroscopic characteristics corresponded to those in the literature [8].

Method B was described in the literature [8, 17]. The yields of compounds **3a-d** were 75, 60, 79, and 66% respectively.

**2-(1-Carbamoyl-1-phenylmethylthio)-3-cyano-4-(4-methoxyphenyl)-6-phenylpyridine (9), 4-Aryl-3-cyano-2-*Z*-methyl-6-phenylthiopyridines 10a-w, 6-Amino-4-aryl–6-phenyl-2-*Z*-thieno[2,3-*b*]pyridines 11a-c, and 1,4-Di[3-cyano-4-(4-methoxyphenyl)-6-phenylpyrin-2-ylthio]butane (12)** were obtained by a known method [18] (see Tables 1 and 2).

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