2. A method for the preparation of higher unsaturated primary amines by the reduction of N-octadienylphthalimides by hydrazine hydrate has been developed.

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CONDENSED PYRIDINES

COMMUNICATION 3.* ARYLIDENETHIO(SELENO)ACETAMIDES IN THE SYNTHESIS

OF 4-ARYL-3-CYANO-2[1H]PYRIDINETHIONES AND 4-ARYL-3-CYANO-2[1H]PYRIDINESELENONES

UDC 542.91:547.83

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The known methods for the synthesis of substituted 4-aryl-3-cyano-2[lH]pyridinethiones are based on the exchange of the halogen atom in 2-halogeno-3-cyanopyridines in the interaction with thiourea or KHS [2], the condensation of 1,3-dicarbonyl or α,β -unsaturated carbonyl compounds with cyanothioacetamide [3-5], thiation of δ -ketonitriles with powered S [3, 6, 7], and recyclization of 4-amino-6-aryl-5-cyano-1,3-dithia-4-cyclohexenes [8, 9]. However, they all have certain limitations which are related, in a series of cases, to the complexity of realization or the difficult availability of the starting compounds. The selenium analogs were not described in the literature until recently.

We developed a sufficiently general method for the synthesis of substituted 4-aryl-3cyano-2[1H]pyridinethiones (VII) and the corresponding pyridineselenones (VIII) as a result of studying the interaction of carbonyl compounds of the type $R^1CH_2COR^2$ (III) containing a methylene or methyl group in the α -position, as well as their enamines (IV) with the arylidene derivatives of cyanothioacetamide (I) and cyanoselenoacetamide (II). The interaction of the carbonyl compounds (III) with the arylidenethio(seleno)acetamides (I), (II) proceeds readily under the action of organic bases as catalysts (piperidine, diethylamine, hexamethyleneimine, morpholine, etc.) with the formation of the pyridinethiones (VII) and pyridineselenones (VIII) (method a). The reaction probably proceeds through the stage of enamine formation, since the utilization of the enamines (IV) in this reaction (method b) leads to the salts (V) with good yields. It should be noted that the nature of the base has a significant influence on the yield of the salt: Higher yields are obtained in the formation of salts with piperidine and hexamethyleneimine. The presence of an electronegative substituent at position five stabilizes

*See [1] for Communication 2.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2101-2108, September, 1985. Original article submitted May 3, 1984. the salts (V). In the case of the alkyl substituents at positions five and six, the corresponding salts (V) could not be isolated on account of their ready oxidation



(III) = $R^{1}CH_{2}COR^{2}$, (IV) = $R^{1}CH=C(R^{2})NR^{3}R^{4}$. (I): Ar = Ph, (a); $Ar = 3-FC_6H_4(b)$; $Ar = 4-FC_6H_4$ (c); $Ar = 4-ClC_6H_4$ (d); $Ar = 2-ClC_6H_4$ (d); Arfuryl (e); $Ar = 4-BrC_6H_4$ (f); $Ar = 2-NO_2C_6H_4$ (g); Y = S. (II): Ar = Ph, Y = Se. (III): $R^1 = H$, $R^2 = Me$ (3); $R^1 = R^2 = Me$ (b); $R^1 = H$, $R^2 = Ph$ (c); $R^1 - R^2 =$ = $(CH_2)_3$ (d); $R^1 - R^2 = (CH_2)_4$ (e); $R^1 = Ac$, $R^2 = Me(f)$; $R^1 = COOEt$, $R^2 = Me(g)$. (IV): $R^1 = H$, $R^2 = Ph$, $R^3 - R^4 = (CH_2)_6$ (a); $R^1 - R^2 = (CH_2)_3$. $R^3 - R^4 = (CH_2)_6$ = $(CH_2)_2O(CH_2)_2$ (b); $R^1 - R^2 = (CH_2)_4$, $R^3 - R^4 = (CH_2)_2O(CH_2)_2$ (c); $R^1 = Ac$, $R^2 = Me, R^3 - R^4 = (CH_2)_5$ (d); $R^1 = Ac, R^2 = Me, R^3 - R^4 = (CH_2)_2O(CH_2)_2$ (e); $R^1 = Ac$, $R^2 = Me$, $R^3 - R^4 = (CH_2)_6$ (f); $R^1 = Ac$; $R^2 = Me$, $R^3 = R^4 = Et$ (g); $R^1 = COOEt$, $R^2 = Me$, $R^3 - R^4 = (CH_2)_5$ (h). (V): $Ar = R^2 = Ph$, $R^1 = H$, $R^3 - R^4 = (CH_2)_6$ (a); $Ar = 4-ClC_6H_4$, $R^1 = Ac$, $R^2 = R^2 = R^2 + R^2$ = Me, $R^3 - R^4 = (CH_2)_5$ (b); $Ar = 4 - ClC_6H_4$, $R^1 = Ac$, $R^2 = Me$, $R^3 - R^4 = R^4$ = $(CH_2)_2 O(CH_2)_2$ (c); Ar = 4-ClC₆H₄, R¹ = Ac, R² = Me, R³ - R⁴ = $(CH_2)_6$ (d); Ar = = $4-BrC_6H_4$, $R^1 = Ac$, $R^2 = Me$, $R^3 = R^4 = Et$ (e); $Ar = 2-NO_2C_6H_4$, $R^1 = Ac$, $R^2 = R^2$ = Me, $R^3 - R^4 = (CH_2)_2 O(CH_2)_2$ (f); Ar = 4-FC₆H₄, R¹ = COOEt, R² = Me, R³ - $- R^4 = (CH_2)_5$ (g). (VI): $Ar = R^2 = Ph$, $R^1 = H$ (a); $Ar = 4-FC_6H_4$, $R^1 = Ac$, $R^2 = Me$ (b); $Ar = R^2 = Me$ (c); $Ar = R^2 = Me$ (c); Ar = Me (c); Ar =4-ClC₆H₄, $R^1 = Ac$, $R^2 = Me$ (c). (VII): Ar = Ph, $R^1 = H$, $R^2 = Me$ (a); $Ar = 3-FC_6H_4$, $R^1 = H$, $R^2 = Me$ (b); Ar = (b)= 2- furyl , $R^1 = H$, $R^2 = Me$ (c); Ar = 4-ClC₆H₄, $R^1 = R^2 = Me$ (d); $Ar = R^2 = Ph$, $R^1 = H$ (e); Ar = 2-furyl, $R^1 - R^2 = (CH_2)_3$ (f); Ar = 4-FC₈H₄, $R^1 - R^2 = 1$ = $(CH_2)_4$ (g); Ar = 4-FC₆H₄, R¹ = Ac, R² = Me (h); Ar = 4-ClC₆H₄, R¹ = Ac, R² = = Me (i); Y = S. (VIII): $Ar = R^2 = Ph$, $R^1 = H$, Y = Se.

The structure of the salts (V) was confirmed by the data of IR, PMR, and ¹³C-NMR spectroscopy and by chemical conversions. In the IR spectra of the salts (V), the frequency of the vibrations of the CN group is considerably reduced (to 2161-2172 cm⁻¹) with a simultaneous increase in its intensity by comparison with the spectra of the thiones (VI). This can be explained by the increase in the degree of conjugation in the molecule due to the salt formation. Characteristic signals of the H⁴-proton of the pyridine nucleus in the region of 4.32-5.16 ppm are present in the PMR spectra of the salts (V) together with the signals of the aromatic and aliphatic protons. The position of the signal of the H⁴-proton depends significantly on the nature of the substituent in the aromatic nucleus and is practically independent of the nature of the cation (cf. Table 1). In the PMR spectrum of the salt (Va), the signals of the H^4 and H^5 protons are observed in the form of doublets in the region of 4.20 and 4.89 ppm correspondingly with a spin-spin coupling constant of 5.0 Hz. The singlet of the NH proton is thereby displaced to a region of high field (6.82 ppm) by comparison with the position of the corresponding signal in the salts (Vb-g) (8.27-8.40). The data of the ¹³C-NMR spectra of the salts (Vc, Vf) confirm their structure (Table 1). On the addition of an equimolar amount of 10% HCl under argon, the salts (V) are converted to 4-ary1-3-cyano-3,4-dihydro-2[1H]pyridinethiones (VI). The thione (VIa), obtained by such a route, is identical to the 4,6-dipheny1-3-cyano-3,4-dihydro-2[1H]pyridinethione described earlier [4]. The thione (VIb) can be obtained by the direct interaction of 4-fluorobenzylidenecyanothioacetamide with the enamine (IVe) (prepared from acetylacetone and morpholine) in the presence of 10% HC1.

The band of the stretching vibrations of the CN group, of low intensity at ~2258 cm⁻¹ is present in the IR spectra of the compounds (VIa-VIc). The PMR spectrum of 5-acety1-6-methy1-

4-(4-fluorophenyl)-3-cyano-3,4-dihydro-2[1H]pyridinethione (VIb) contains characteristic signals of the protons in the region (δ , ppm): 2.12 singlet (3H, COCH₃), 2.53 doublet (3H, CH₃) with ${}^{5}J_{Me}, {}_{H^{4}} = 0.7$ Hz, 4.20 doublet (1H, C³H-pyridine), 4.37 doublet (1H, C⁴H-pyridine) with ${}^{3}J = 2.7$ Hz, and 7.0-7.3 multiplet (4H, 4-FC₆H₄). On irradiation at the frequency of H⁴, the doublets at 4.20 and 2.53 ppm unite into singlets. Irradiation at the frequency of the protons of the CH₃ group significantly constricts the components of the doublet of the H⁴ proton. This assumes the presence of a homoallyl interaction with ${}^{5}J_{Me}, H^{4} = 0.7$ Hz. From the magnitude of the vicinal spin-spin coupling constant, ${}^{3}J_{H^3}, H^{4}$ is ~3 Hz for the trans conformer. The character of the PMR spectrum of 3,4-dihydro-2-[1H]pyridinethione (VIc) is identical to that presented above for the thione (VIb).

The structure of the dihydropyridinethiones (VI) was also confirmed by the data of mass spectrometric investigation. In the mass spectra of the compounds (VIb, VIc), the intensity of the peaks of the molecular ions $(M^{+\circ})$ is sufficiently high, and the stability to electron impact W_M amounts to 8.0 and 7.8%, correspondingly. The main processes of decomposition of the $M^{+\bullet}$ ions are the competing processes of the elimination of a molecule of HCN and the CH_3CO^{\bullet} radical with the formation of possible structures having a high degree of nonsaturation relative to the $M^{+\bullet}$ ions



The processes of dehydrogenation of the pyridinethiones (VIb, c) under the action of electron impact are weakly expressed and constitute about 10% of the intensity of the peaks of the M^{+•} ions. The peak of maximum intensity in the mass spectra of (VIb, VIc) is due to the acetyl radicals with m/z 43.

The dihydro-2[1H]pyridinethiones (VI) are readily oxidized to the corresponding 4-aryl-3-cyano-2[1H]pyridinethiones (VIIa-i) in solutions of alcohol or DMSO. The pyridinethiones (VIIa-i) can also be obtained without the intermediate separation of their hydrogenated analogs (VI) by increasing the time of holding or raising the temperature of the reaction mixture. Analogous methods (method a and b) were utilized to synthesize 4,6-diphenyl-3-cyano-2-[1H]pyridineselenone (VIII). The structure of the isolated pyridinethiones (VII) and the pyridineselenone (VIII) was confirmed by UV, IR, PMR (Table 2), and ¹³C-NMR (Table 1) spectral data.

The use of substituted 3-cyano-2[1H]pyridinethiones in the synthesis of different 3-aminothieno(2,3-b)pyridines was previously described [1, 2, 4, 6-9]. However, the production of their hydrogenated analogs has not been reported up to the present time. For the first time, we obtained 3-amino-5-acetyl-6-methyl-4-(2-nitrophenyl)-2-cyano-4,7-dihydrothieno(2,3-b)pyridine (IX) by the alkylation of the salt (Vf) with chloroacetonitrile in DMF with subsequent addition of an aqueous solution of KOH



mbound Arvi Pyridine Arvi Acetyl Morpholinium	10nes (Vc, VI) and 5-Acety1-6-methy1-4-(4-chloropheny1)-3-cyano-2[1E]pyridinernione (VIII) in u6-DHDO 0, ppm (Ji3CiH, 112)	("II) TALES IN THE STATES INTERPORT IN THE STATES INTO STATES IN THE STATES INTO STATES I	Morpholinium	C C	6-Me	Acetyl	Aryl	Pyridine	Aryl	punoduu
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 $\frac{42.9}{(143,3)}$ 43,3 115,6107,2108,5 19.8 (129,5) 17.6 (131,3) 19,6199.9195, 2194,7 $\begin{array}{c} 30.3 \\ (126,7) \\ 31.4 \\ (129,5) \end{array}$ 29,7 126,5 133,1 130,4 127,8 *133,2 *135,2 * 130,0 124,5 130,0 *(164,6) 128,3 * 147,2 128,9 * (170,2) 143,1146,5 125,3 146,8 124,5 147,1 126,5 151,0 152.4(3,7) 37,0 (135,0) 42.3(132,2) 79,3 78,8 4-CIPh 177,8 113,8 164,62-NO₂Ph 165,4 4-ClPh (VI) (VIII) (Vc)

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*Signals were not taken.

EXPERIMENTAL

The UV spectra were taken on a Specord UV-VIS spectrophotometer in ethanol. IP. Spectra were recorded on a UR-20 spectrometer in KBr pellets. PMR Spectra were taken on "Bruker WM-250" (250 MHz) and Varian FT-80A (80 MHz) instruments in solutions of d_6 -DMSO and CDCl₃ with TMS as the internal standard. The ¹³C-NMR spectra were taken on a Bruker WM-250 instrument in a solution of d_6 -DMSO. The mass spectra were obtained on an MX-1310 mass-spectrometer with the direct introduction of the sample into the ion source. The temperature of the ionization chamber was 150°C. The ionizing voltage was 70 eV. The emission current was 100 µA.* The temperature of heating of the samples varied in the range of 50-150°C; and the mass spectra were unchanged for the varying temperature of heating. Thin layer chromatography was accomplished in the systems acetone-hexane (3:5) and acetone-benzene (1:3) on plates of Silufol UV-254.

Salts of the Substituted 4-Aryl-3-cyano-3,4-dihydro-2[1H]pyridinethiones (V). a) To a mixture of 10 mmoles of the arylidenecyanothioacetamide (I) and 10 mmoles of the β -diketone (III) in 20-25 ml of abs. ethanol was added, with stirring, 20 mmoles of the freshly distilled secondary amine (piperidine, diethylamine, hexamethyleneamine, and morpholine). The mixture was stirred for 1 h at ~20°C. The residue was filtered off and washed with ethanol and hexane. The yields, constants, and the data of elemental analysis for the compounds (V) are presented in Table 3.

b) A mixture of 10 mmoles of the arylidenecyanothioacetamide (I) and 10 mmoles of the β enaminoketone (IV) in 20 ml of abs. ethanol was stirred at ~20°C for 2-3 h. The residue was filtered off and washed with ethanol and hexane. The salt (Va) was recrystallized from nitromethane. The salts (Vb-g) were recrystallized from ethanol.

4-Aryl-3-cyano-3,4-dihydro-2[1H]pyridinethiones (VIa-c). These were obtained by the acidification of a suspension of 10 mmoles of the salts (V) in 25 ml of ethanol by an equimolar amount of a 10% aqueous solution of HCl in ethanol under argon.

4,6-Dipheny1-3-cyano-3,4-dihydro-2[1H]pyridinethione (VIa). This was obtained with a yield of 67% and mp 158-160°C (from ethanol). According to the data of the PMR spectrum and the mp, it is identical to the previously described (VIa) [5].

 $\frac{5-\text{Acetyl-6-methyl-4-}(4-\text{fluorophenyl})-3-\text{cyano-3},4-\text{dihydro-2[1H]pyridinethione (VIb)}. This was obtained with a yield of 73% and mp 191-192°C (from ethanol). The IR spectrum had (v, cm⁻¹): 1680 (CO), 2258 (CN), and 3318 (NH). The mass spectrum had m/z (relative intensity,%): 290 (3), 289 (9), 288 (45), 287 (6), 286 (4), 261 (54), 246 (34), 245 (88), 57 (17), 55 (11), 43 (100), and 42 (31). W_M = 8.0%. The mol. wt. was 288. Found: C 62.53, H 4.42, F 6.33, N 9.64, and S 11.08%. C₁₅H₁₃FN₂OS. Calculated: C 62.49, H 4.54, F 6.59, N 9.72, and S 11.12%.$

 $\frac{5-\text{Acetyl-6-methyl-4-(4-chlorophenyl)-3-cyano-3,4-dihydro-2[1H]pyridinethione (VIc).}}{(VIc).}$ This was obtained with a yield of 77% and mp 188-190°C (from ethanol), The IR spectrum had (v, cm⁻¹): 1676 (CO), 2258 (CN), and 3310 (NH). The mass spectrum had m/z (relative intensity, %): 307 (2), 306 (14), 305 (8), 304 (35), 303 (3), 302 (2), 279 (17), 278 (11), 277 (43), 264 (15), 263 (32), 262 (28), 261 (85), 245 (5), 222 (11), 193 (21), 128 (11), 84 (14), 75 (12), 43 (100), and 42 (38). W_M = 7.8%. The peaks of the ions with an intensity of <10%, besides those close to the molecular ion as well as those mentioned in the discussion, are excluded. The mol. wt. was 304 (in conversion to ³⁵Cl). Found: C 58.93, H 4.17, Cl 11.42, N 9.25, and S 10.50%. C₁₅H₁₃ClN₂OS. Calculated: C 59.11, H 4.30, Cl 11.63, N 9.19, and S 10.52%.

<u>Substituted 4-Aryl-3-cyano-2[1H]pyridinethiones (VII) and the Selenone (VIII).</u> a) A mixture of 100 mmoles of the arylidenethio(seleno)acetamide (I), (II), and 10 mmoles of the carbonyl compound (III) and 10-15 mmoles of morpholine or pyridine in 20-30 ml of ethanol was stirred at 25-50°C for 5-8 h (control by thin layer chromatography). The mixture was acidified with a 10% solution of HCl. The residue was filtered off and washed with ethanol and hexane. The pyridinethiones (VIIa-g) and the selenone (VIII) were obtained after recrystallization from glacial AcOH or nitromethane with a yield of 58-77%.

b) A mixture of 10 mmoles of (I), (II) and 10 mmoles of the enamine (IV) in 25-30 ml of ethanol was stirred at 25-50°C for 5-8 h. After analogous treatment, the pyridinethiones (VII) and the pyridineselenone (VIII) were obtained with yields of 62-93%. The data are presented in Tables 2 and 3.

*As in Russian original - Translator.

TABLE 2. UV, IR, and PMR Spectra of the Salts of 5,6-Disubstituted 4-Aryl-3-cyano-3,4-dihydro-2[IH]pyri-dinethiones (V), 5,6-Disubstituted 4-Aryl-3-cyano-2[IH]pyridinethiones (VII), and 4,6-Diphenyl-3-cyano-2[1H]pyridineselenone (VIII)

	IIV spectrum	IR spectrum	(v, cm ⁻¹)		a na an	PMR	spectrum (6,	ppm)		
pound	Amax, nm (lg s)	co	CN	(s) HN	Ar(m)	5H-Py(S)	4H-Py(S)	B(M)*	R ² (S)	R ³ (S)
(Va)			2472	6,82	7,15-744	4,89 đ	4,20 d	3,06, 1,74,		
(qA)		1708	2461	8,35	7,31 d,		4,32	+ 57 + 98 58	2,26	1,98
(Vc)		1704	2468	8,32	7,30 d. d		4,32	004 100 100	2,24	1,96
(pA)		17112	21.65	8,34	7,31 d, 7,10 d,		4,32	3,06, 1,746,	2,25	1,98
(ve)		1696	2165	8,33	7,43 đ		4,32	2,91 q.	2,25	1,98
(tt)		1648	2/170	8,40	7,15-7,80		5,16	3,69 2,69 2,04	2,25	2,01
(Vg)		1745	2/163	8,27	7,08		4,26	20°4	3,89 d, 1.06 t	2,21
(dIIV)	259(4,24), 314(4,26),		2229	13,87	7,42	6,77		20.4	- 00'r	2,40
(VIIc)	268(3,59) 268(3,62), 317(4,13)		2220	13,83	7,97 q 7,60 q.	6,95				2,33
(pIIV)	258(3,97), $318(3,96)$		2222	13,95	6,75 q 7,54d, 7,564				1,74	2,42
(VIIg)	264(4,22), 314(4,14),		2227	13,98	7,34				2,75 t,	2,05 t
(UIIV)	251 (4,05), 278 (4,30) 400 (2,90)		2207	14,38	7,30-8,00	7,10			1,01	

*B is base.

c) A solution of 1.4 g (5 mmole) of the dihydropyridinethione (VIb) in 25 ml of ethanol and 2 ml of conc. HCl was boiled for 30 min. After cooling, the residue was separated and recrystallized from glacial AcOH. We obtained 0.9 g (63%) of 5-acetyl-6-methyl-4-(4-fluorophen-yl)-3-cyano-2[1H]pyridinethione (VIIh) having mp 272-273°C (with decomposition). The IR spectrum had (ν , cm⁻¹): 1693 (CO) and 2240 (CN). The PMR spectrum had (DMSO-d₆, δ , ppm): 7.38-7.62 (4H, 4-FC₆H₄), 2.73 s (3H, CH₃), and 1.82 (3H, COCH₃). Found: C 62.73, H 7.32, F 6.40, N 9.70, and S 11.08%. C₁₅H₁₁FN₂OS. Calculated: C 62.92, H 3.87, F 6.63, N 9.78, and S 11.20%.

By analogy, we obtained 5-acetyl-6-methyl-4-(4-chlorophenyl)-3-cyano-2[1H]pyridinethione (VIIi) with a yield of 53% and mp 270-271°C (with decomposition). The IR spectrum had (ν , cm⁻¹): 1720 (CO) and 2236 (CN). The PMR spectrum had (DMSO-d₆, δ , ppm): 7.63, 7.44 doublets (4H, 4-ClC₆H₄), 2.38 singlet (3H, CH₃), and 1.86 singlet (3H, COCH₃). Found: C 59.62, H 3.74, Cl 11.80, N 9.14, and S 10.45%. C₁₅H₁₁ClN₂OS. Calculated: C 59.90, H 3.66, Cl 11.71, N 9.25, and S 10.59%.

3-Amino-5-acetyl-6-methyl-4-(2-nitrophenyl)-2-cyano-4,7-dihydrothieno(2,3-b)pyridine (IX). To a solution of 1.21 g (3 mmole) of the morpholinium salt (Vf) in 15 ml of DMF was added, with stirring, 0.23 g (3 mmole) of chloroacetonitrile. The mixture was stirred at 25°C for 30 min

Com-	- Po	1, %	mn °C	Empirical	I I	ound /C	alculate	ed, %	
pound	Meth	Yield		formula	С	н	Hal	N	s
(Va)	a b	52 54	134-137	$\mathrm{C}_{24}\mathrm{H}_{27}\mathrm{N}_3\mathrm{S}$	73,84 74,00	$\begin{array}{r} 6,78\\\hline 6,99\end{array}$		10,63	<u>8,20</u> 8,23
(Vb)	a b	87 74	134-135	C ₂₀ H ₂₄ ClN ₃ OS	$\frac{61,52}{61,60}$	$\frac{6,02}{6,20}$	9,17	10,64 10,78	8,08
(Vc)	a b	70 62	125-126	C ₁₉ H ₂₂ ClN ₃ O ₂ S	$\frac{58,17}{58,23}$	5,58	9,05	10,85	<u>8,27</u> 8,18
(Vd)	a b	98 83	123124	C ₂₁ H ₂₆ ClN ₃ OS	$\frac{62,53}{62,44}$	$\frac{-6,57}{-6,49}$	8,85	$\frac{10,53}{10,40}$	7,79
(Ve)	a b	82 70	124-125	C ₁₉ H ₂₂ BrN ₃ OS	54,30	5,33 5,28	<u>19,20</u> 19.01	10,08	7,77
(Vf)	a b	78 84	191-192	$C_{19}H_{22}N_4O_4S$	56,83	5,50 5,51		<u>13,95</u> 13,92	7,97
(Vg)	a b	74 72	168	$C_{21}H_{26}FN_3O_2S$	$\tfrac{62,42}{62,51}$	<u>6,38</u> 6,50	4,62	$\frac{10,22}{10,41}$	7,78
(VIIa)*	а	72	271-273 (with decomp.)	$\mathrm{C_{13}H_{10}N_{2}S}$					
(VIIb)	a	74	250-252	$C_{13}H_9FN_2S$	<u>63,84</u> 63,92	$\frac{3,62}{3,71}$		<u>11,32</u> 11,47	$\frac{12,98}{13,12}$
(VIIc)	a	62	291-293 (with	$C_{11}H_8N_2OS$	<u>61,12</u> 61,09	$\frac{3,60}{3,73}$		$\frac{12,72}{12,95}$	$\frac{14,64}{14,83}$
(VIId)	a	7 0	decomp.) 269-270	$C_{14}H_{11}ClN_2S$	$\tfrac{61,28}{61,20}$	$\begin{array}{c} 3,92 \\ \hline 4,04 \end{array}$	$\frac{12,24}{12,40}$	<u>10,08</u> 10,19	$\frac{11,54}{11,67}$
(VIIe) *	a b	63 78	228229	$C_{18}H_{12}N_2S$					
(VIIf) *	a b	75 88	236237	$C_{13}H_{10}N_2OS$					
(VIIg)	a b	82 93	262-264	$\mathrm{C_{16}H_{13}FN_{2}S}$	$\tfrac{67,38}{67,59}$	4,72 4,61	$\frac{-6,52}{-6,68}$	<u>9,92</u> 9,85	<u>11,30</u> 11,27
(VIII)	a	$\begin{array}{c} 58 \\ 62 \end{array}$	280283	$\mathrm{C_{18}H_{12}N_2Se}$	$\tfrac{64,24}{64,48}$	$\frac{3,50}{3,61}$		$\underbrace{8,42}_{8,36}$	23,50 [†] 23,55

TABLE 3. Salts of 5,6-Disubstituted 4-Ary1-3-cyano-3,4-dihydro-2-[1H]pyridinethiones (V), 5,6-Disubstituted 4-Ary1-3-cyano-2[1H]pyridinethiones (VII), and 4,6-Dipheny1-3-cyano-2[1H]pyridineselenone (VIII)

*The compounds (VIIa, VIIe, VIIf) have the identical mp values and IR spectra to the pyridinethiones described in [4, 9]. [†]Data for Se. prior to the addition of 2 ml of a 10% solution of HCl. The mixture was stirred for 1 h. To the reaction mixture was added 5 ml of water. The precipitated residue was filtered off and washed with ethanol and hexane. The yield of (IX) was 0.8 g (75%). It had mp 243-244°C (from ethanol). The IR spectrum had (ν , cm⁻¹): 2186 (CN), 3236, 3348, and 3449 (NH₂). The PMR spectrum had (DMSO-d₆, δ , ppm): 6.11 singlet (2H, NH₂), 5.44 singlet (1H, CH), 2.32 singlet (3H, CH₃), and 2.16 singlet (3H, COCH₃). Found: C 57.43, H 3.72, N 15.80, and S 9.18%. C₁₇H₁₄N₄-O₃S. Calculated: C 57.62, H 3.98, N 15.81, and S 9.05%.

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CONCLUSIONS

1. A general method for the synthesis of substituted 4-aryl-3-cyano-2[1H]pyridinethiones and the corresponding selenones was developed. The method was based on the interaction of carbonyl compounds of the type $R^1CH_2COR^2$, where $R^1 = H$, Me, Ac, and COOEt; $R^2 = Me$ and Ph or R^1 - $R^2 = (CH_2)_3$ and $(CH_2)_4$, and also of their enamines with the arylidene derivatives of cyanothio-(seleno)acetamides.

2. The salts of the substituted 4-aryl-3-cyano-3,4-dihydro-2[1H]pyridinethiones with organic bases were obtained and characterized.

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VINYLATION OF ALCOHOLS BY 10-VINYLPHENOTHIAZINE

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Previously we detected an unusual mechanism of hydrolytic cleavage of 10-vinylphenothiazine (I) in the presence of organic π -electron acceptors [1] occurring via a step of formation of a vinyl cation. It was also assumed that compound (I) reacts similarly with alcohols. The reaction occurs in the presence of p-benzoquinone (II), 2,4,7-trinitrofluorenone (III), p-chloranil (IV), and 7,7,8,8-tetracyanoquinodimethane (V) with formation of unsubstituted phenothiazine and vinyl alkyl ether. In addition, it was assumed that the formation of the final products was preceded by steps of formation and ionization of a donor-acceptor complex with subsequent solvolysis of the unstable radical cation of compound (I) into a vinyl cation and a phenothiazine radical

^{*}Deceased.

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