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THIONATION OF IMIDAZOPYRIDINES

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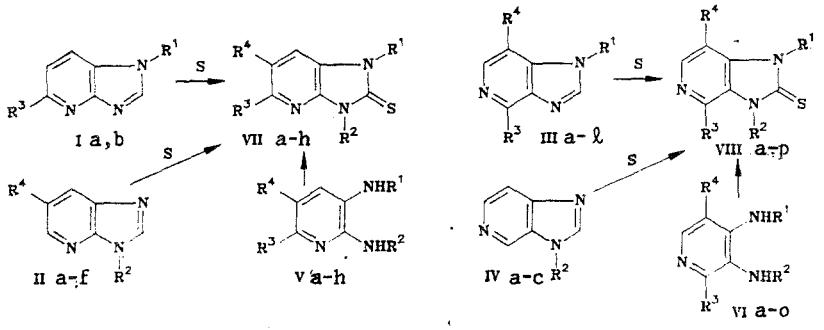
Direct thionation of imidazo[4,5-b]pyridines and imidazo[4,5-c]pyridines results in the formation of their 2-thioxo derivatives, usually in high yield. The thione structure of the imidazopyridines obtained has been confirmed from their IR spectra in the solid state and in solution. The general nature of the thionation of imidazole, benzimidazole, imidazo[4,5-b]pyridine, imidazo[4,5-c]pyridine, and purine has been noted as one of the distinctive chemical properties of compounds in this series of nitrogen heterocycles.

Imidazole when heated with sulfur is converted to its 2-mercapto derivative in "very good" yield [1]. Benzimidazole and its substituted derivatives [2, 3] and also purine [3] react with sulfur in a similar manner. Thionation of desazapurines such as imidazo[4,5-b]pyridine (IIa) and imidazo[4,5-c]pyridine (IIIa), which in structural terms are intermediate betweeen benzimidazole and purine, has not previously been studied.

We have shown [4] that when equivalent amounts of imidazopyridines I-IV are melted with sulfur, 1,3-dihydro-2H-imidazopyridine-2-thiones VII and VIII (Table 1) are formed, usually with high yields. Using the information in [5, 6] the same compounds were obtained from diamines V and VI and potassium ethylxanthate (method A) or carbon disulfide (method B) in the presence of pyridine (Table 2). Samples of compounds VIIa-h and VIIIa-n obtained by the two routes were found to be identical from the absence of any depression in the melting point of a mixed specimen and from their IR spectra. Other possible reaction products such as imidazo-[4,5-c]pyridine-4-thiones are probably not formed, at least not to any noticeable extent.



I a $R^1=CH_3$, $R^3=H$; b $R^1=CH_3$, $R^3=NO_2$; II a $R^2=R^4=H$; b $R^2=CH_3$, $R^4=H$; c $R^2=CH_2C_6H_5$, $R^4=H$; d $R^2=C_6H_5$, $R^4=H$; e $R^2=H$, $R^4=Cl$; f $R^2=H$, $R^4=Br$; III a $R^1=R^3=R^4=H$; b $R^1=CH_3$, $R^3=R^4=H$; c $R^1=i\text{-}C_3H_7$, $R^3=R^4=H$; d $R^1=C_4H_9$, $R^3=R^4=H$; e $R^1=C_6H_{11}$, $R^3=R^4=H$; f $R^1=CH_2C_6H_5$, $R^3=R^4=H$; g $R^1=C_6H_5$, $R^3=R^4=H$; h $R^1=R^4=H$; $R^3=Cl$; i $R^1=R^3=H$, $R^4=Br$; j $R^1=R^3=H$, $R^4=NO_2$; k $R^1=CH_3$, $R^4=H$, $R^3=Cl$; ℓ $R^1=CH_3$, $R^3=OCH_3$, $R^4=H$; IV a $R^2=CH_3$; b $R^2=CH_2C_6H_5$; c $R^2=C_2H_5$; V, VII a $R^1=R^2=R^3=R^4=H$; b $R^2=CH_3$, $R^1=R^3=R^4=H$; c $R^2=CH_2C_6H_5$, $R^1=R^3=R^4=H$; d $R^2=C_6H_5$, $R^1=R^3=R^4=H$; e $R^1=R^2=R^3=H$, $R^4=Cl$; f $R^1=R^2=R^3=H$, $R^4=Br$; g $R^1=CH_3$, $R^2=R^3=R^4=H$; h $R^1=CH_3$, $R^2=R^4=H$; $R^3=NO_2$; VI, VIII a $R^1=R^2=R^3=R^4=H$; b $R^1=CH_3$, $R^2=R^3=R^4=H$; c $R^1=i\text{-}C_3H_7$, $R^2=R^3=R^4=H$; d $R^1=C_4H_9$, $R^2=R^3=R^4=H$; e $R^1=C_6H_{11}$, $R^2=R^3=R^4=H$; f $R^1=CH_2C_6H_5$, $R^2=R^3=R^4=H$; g $R^1=C_6H_5$, $R^2=R^3=R^4=H$; h $R^1=R^2=R^4=H$, $R^3=Cl$; i $R^1=R^2=R^3=H$, $R^4=Br$; j $R^1=R^2=R^3=H$, $R^4=NO_2$; k $R^1=CH_3$, $R^2=R^4=H$, $R^3=Cl$; ℓ $R^2=CH_3$, $R^1=R^3=R^4=H$; m $R^2=CH_2C_6H_5$, $R^1=R^3=R^4=H$; n $R^2=C_2H_5$, $R^1=R^3=R^4=H$; o $R^1=C_{18}H_{37}$, $R^2=R^3=R^4=H$; p $R^2=R^3=R^4=H$; $R^1=CH_3$, $R^2=R^4=H$, $R^3=OCH_3$

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TABLE 1. Thionation of Imidazopyridines Ia,b, IIa-f, IIIa-l, and IVa-c

Initial compound	Reaction conditions		Reaction product	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield
	temperature, °C	time, min			C	H	S		C	H	S	
IIa [16, 20]	245	60	VIIa†	315—316	47,5	3,5	21,0	$C_6H_5N_3S$	47,7	3,3	21,2	79
IIb [15, 20]	230	20	VII b [10]	265—266	—	—	—	—	—	—	—	76
IIc [14, 20]	240—245	30	VII c	209—210	64,8	4,5	13,2	$C_{13}H_{11}N_3S$	64,7	4,6	13,3	95
IId [14, 20]	240—245	30	VII d [11]	295—296	—	—	—	—	—	—	—	76
IIe [12, 20]	255—260	60	VII e [12]	354—355	—	—	—	—	—	—	—	98
IIf [17]	250—260	60	VII f†	>360	31,2	2,0	14,0	$C_6H_4BrN_3S$	31,3	1,7	13,9	99
Ia [15, 20]	235—240	35	VII g	234—235	51,0	4,1	19,5	$C_7H_7N_3S$	50,9	4,3	19,4	82
Ib	260	30	VII h	>350	39,8	3,0	15,4	$C_7H_6N_4O_2S$	40,0	2,9	15,2	93
IIIa [13]	245—250	25	VIIIa [6]	369—370	—	—	—	—	—	—	—	80
IIIb [15, 20]	235—240	30	VIIIb [6]	347—348	—	—	—	—	—	—	—	81
IIIc	230—240	60	VIIIc	264—265	55,7	5,9	16,4	$C_9H_{11}N_3S$	55,9	5,7	16,6	94
IIId	260	25	VIII d	209—210	58,1	6,1	15,7	$C_{10}H_{13}N_3S$	57,9	6,3	15,5	82
IIIe [20]	240—250	120	VIII e	301—302	61,5	6,3	13,4	$C_{12}H_{15}N_3S$	61,8	6,5	13,7	86
IIIf [20]	255—260	60	VIII f	297—298	64,5	4,6	13,2	$C_{13}H_{11}N_3S$	64,7	4,6	13,3	94
IIIg [14, 20]	230	20	VIII g	309—310	63,2	4,2	14,4	$C_{12}H_9N_3S$	63,4	4,0	14,1	83
IIIh [18]	255—260	60	VIII h	>360	38,6	2,4	17,5	$C_6H_4ClN_3S$	38,8	2,2	17,3	1,5
IIIi [17]	—	—	VIII i	>360	31,2	2,0	13,8	$C_6H_4BrN_3S$	31,3	1,8	13,9	99
IIIj [17]	260	30	VIII j	>360	37,0	1,9	16,5	$C_6H_4N_4O_2S$	36,8	2,1	16,3	99
IIIk [19]	235—240	30	VIII k	>360	41,8	2,9	15,9	$C_7H_6ClN_3S$	42,1	3,0	16,4	34
IIIl	255—260	30	VIII p	322—323	49,1	4,8	16,3	$C_8H_9N_3OS$	49,2	4,6	16,4	97
IVa [15, 20]	250—255	30	VIII l [6]	316—317	—	—	—	—	—	—	—	79
IVb [20]	235—240	20	VIII m	288—289	64,4	4,5	13,5	$C_{13}H_{11}N_3S$	64,7	4,6	13,3	98
IVc	240—245	40	VIII n	304—305	53,4	5,1	17,7	$C_8H_9N_3S$	53,6	5,1	17,9	60

*Compounds VIIc, g, and VIIIf, l-n were recrystallized from water; VIIb and VIIIb were recrystallized from ethanol; VIId was recrystallized from water—ethanol (1:1); VIIIc, d were recrystallized from DMF; VIIIe, g, o, were recrystallized from water—DMF (1:1); VIIa, e, f, h and VIIIh-k were reprecipitated by ammonia from an aqueous solution of dilute acid.

†According to [9], mp >300°C.

TABLE 2. 1,3-Dihydro-2H-imidazopyridine-2-thiones VIIa-h and VIIIa-o Obtained by Cyclization of Diaminopyridines Va-h and VIa-o

Compound	Initial diamine	Reaction time, h		mp, °C	Yield, %	
		method A	method B		A	B
VIIa	Va [22]	5	5	315—316	92	98
VIIb	Vb [15]	4	5	264—265	92	96
VIIc	Vc [22]	6	5,5	209—210	87	93
VIId	Vd [22]	6	5	295—296	80	82
VIIe*	Ve [12]	—	5	354—355	—	98
VIIf	Vf [9]	—	6	>360	—	95
VIIg	Vg [15]	4	5,5	234—235	90	99
VIIh	Vh [27]	—	6	>350	—	99
VIIIa	VIa [25]	5	5	>370	90	99
VIIIb	VIb [15]	5	5,5	347—348	94	99
VIIIc	VIc [23]	6	5,5	264—265	79	99
VIIId	VId [24]	—	6	209—210	—	80
VIIIe	VIe [26]	6	5,5	301—302	83	90
VIIIf	VIf [24]	4	5	297—298	98	99
VIIIg	VIg [14]	—	5,5	309—310	—	97
VIIIh	VIh [18]	—	6	>360	—	95
VIIIi	VIi [17, 21]	—	6	>360	—	99
VIIIk	VIj [17]	6	5,5	>360	84	99
VIIIl	VIk [22]	—	6	>360	—	96
VIIIm	VIl [15]	5	5,5	316—317	82	90
VIIIn	VIm [28]	4	5,5	288—289	87	99
VIIIo	VIn [22]	—	5,5	304—305	—	66
		—	—	154—155†	—	94

*In [12] the preparation of compound VIIe from diamine Ve and phosgene in 5% yield is reported.
†From alcohol. Found: C 71.4; H 10.4; S 7.8%. $C_{24}H_{41}N_3S$. Calculated: C 71.4; H 10.2; S 7.9%.

It is appropriate to mention here that the thionation reaction of other heterocycles has been suggested as having a homolytic character [7]. It is known, however, that during radical C-alkylation of 1-methylimidazo[4,5-c]pyridine, its 4-substituted derivatives are mainly formed [8].

Thionation of imidazopyridines occurs at 230-260°C and is complete after 15-60 min. When the temperature is lowered to 210-220°C there is a sharp decrease in the yield of thiones. The difference in relative orientation of the imidazole and pyridine rings in structures I-IV does not affect the course of the reaction of the yields of the products formed.

Introduction of substituents into the molecules of bases IIa and IIIa can have a considerable effect on the completeness of this reaction, but this effect is not so obvious. For example, unsubstituted imidazopyridines IIa and IIIa undergo thionation similarly to the N-methyl and phenyl derivatives Ia, IIb, d, IIIb, g, and IVa with yields close to 80%, but the yields of N-benzyl substituted thiones VIIc and VIIIf, m are almost quantitative. An almost complete conversion to 2-thioxo derivatives VIIh and VIIIj is observed when nitro compounds Ib and IIIj are melted with sulfur, and also when thiones VIIe, f and VIIIp are formed from chloro-, bromo- and methoxy-imidazopyridines IIe, f and IIIl. On the other hand, thionation of chloroimidazopyridines IIIk, h proceeds with difficulty, thione VIIIh, which is not substituted in the imidazole ring, being formed in extremely low yield.

In the IR spectra of the thiones, recorded in petrolatum oil or as KBr pellets, a broad band can be found at 150-200 cm^{-1} in the region of stretching vibrations of the N—H bond; however, it is masked to a large extent by the considerable background absorption due to strong intermolecular association involving hydrogen bonds. It was virtually impossible to detect this band in the spectra of unsubstituted imidazopyridine-2-thiones VIIa and VIIIa and of some of their N-methyl and N-benzyl derivatives (VIIb, c and VIIIb, f) in petrolatum oil. It is interesting that 3-benzylimidazo[4,5-c]pyridine-2-thione (VIIIm), which is isomeric to compound VIIIf, has a sharply defined absorption at 3435 cm^{-1} in its IR spectrum in KBr (it does not appear in petrolatum oil). But the most intense and relatively narrow (half-width 100 cm^{-1}) symmetrical band at 3400 cm^{-1} (in petrolatum oil) appears in the spectrum of compound VIIIe, which has a cyclohexyl substituent at $N_{(1)}$.

The band due to stretching vibrations of the S—H bond relating to a possible thiol tautomeric form was not found in the IR spectra of the compounds studied in the solid phase, possibly because of the strong background absorption already mentioned. In this connection, the spectra of solutions of thiones in carbon tetrachloride or other neutral solvents that are transparent in the region 2400-3600 cm^{-1} would be of considerable interest. However, it was not possible to obtain such solutions since imidazopyridine-2-thiones even with N-benzyl or cyclohexyl substituents are virtually insoluble not only in the solvents mentioned but also in many other organic solvents.

In order to make one of the thiones sufficiently soluble in a solvent such as carbon tetrachloride, we introduced an octadecyl substituent into the 1-position of imidazo[4,5-c]pyridine-2-thione. In order to do this, 3-nitro-4-ethoxypyridine and octadecylamine were reacted to give 3-nitro-4-octadecylaminopyridine (IX), which was reduced to 3-amino-4-octadecylaminopyridine (VIo). Conversion of diamine VIo to 1-octadecylimidazo[4,5-c]pyridine-2-thione (VIIIo) was achieved using the general procedure (method B) given in the Experimental section. It transpired that thione VIIIo obtained had fairly good solubility in CCl_4, $CHCl_3$, and other organic solvents. In the IR spectrum of its solution in CCl_4 (thickness of layer 1.0 cm) recorded at 50°C there is a fairly strong, sharp (half-width 15 cm^{-1}) band due to the NH group at 3456 cm^{-2}, but the absorption in the region of the S—H group stretching vibrations was not detected again. The data given on the IR spectra of these sulfur derivative of imidazopyridines provide a sufficiently reliable confirmation that they have a thione structure in both the solid state and solution.

Thus, like purine and benzimidazole, imidazopyridines can undergo a reaction with elemental sulfur and be converted to imidazopyridine-2-thiones. This conversion, which occurs with a high selectivity, can now be grouped among the most typical and general chemical properties not only of imidazopyridines but also of a whole series of compounds from imidazole and benzimidazole to imidazo[4,5-b]pyridine, imidazo[4,5-c]pyridine, and purine.

EXPERIMENTAL

IR spectra of imidazopyridine-2-thiones were recorded on a UR-20 spectrometer in petrolatum oil, as KBr pellets, or in carbon tetrachloride.

3-Ethyl-3H-imidazo[4,5-c]pyridine (IVc). This was obtained according to the method in [20] by boiling a mixture of 1.37 g (10 mmole) of 4-amino-3-ethylaminopyridine (VIn) [22] and 6 g of pentyl formate for 3.5 h under a reflux condenser. After distilling off excess pentyl formate and the reaction by-products (water and pentyl alcohol) under vacuum using a water-jet pump, the residue was crystallized from hexane. Yield 1.32 g (90%), mp 52-53°C. Found: C 65.3; H 6.1; N 28.4%. $C_8H_9N_3$. Calculated: C 65.3; H 6.2; N 28.6%.

1-Isopropyl-1H-imidazo[4,5-c]pyridine (IIIc). This was obtained in a similar manner to the above compound from 1.51 g (10 mmole) of diamine VIc [23] and 6 g of pentyl formate. Yield of oily reaction product was 1.35 g (84%). Picrate, mp 188°C (from alcohol). Found: C 46.2; H 3.9; N 21.7%. $C_9H_{11}N_3 \cdot C_6H_3N_3O_7$. Calculated: C 46.2; H 3.6; N 21.5%.

1-Butyl-1H-imidazo[4,5-c]pyridine (IIId). This was prepared by the same method from 3.3 g (20 mmole) of diamine VId [24] and 12 g of pentylformate. The yield of the oily residue was 3.3 g. Picrate, mp 198°C (from alcohol). Found: C 47.5; H 4.2; N 20.6%. $C_{10}H_{13}N_3 \cdot C_6H_3N_3O_7$. Calculated: C 47.5; H 4.0; N 20.8%.

1-Methyl-5-nitro-1H-imidazo[4,5-b]pyridine (Ib). A mixture of 1.7 g (10 mmole) of 2-amino-3-methylamino-6-nitropyridine (Vh) [27], 12 ml (72 mmole) of triethyl orthoformate, and 5.3 ml (0.14 mole) of anhydrous formic acid was heated for 4 h at 120-130°C under a reflux condenser. The excess reagents were distilled off under vacuum using a water-jet pump, and the residue was mixed with 4 ml of water and neutralized with ammonia. Yield 1.24 g (69%), mp 253-254°C (from dioxane). Found: C 47.0; H 3.6; N 31.2%. $C_7H_6N_4O_2$. Calculated: C 47.2; H 3.4; N 31.4%.

1-Methyl-4-methoxy-1H-imidazo[4,5-c]pyridine (IIIl). A mixture of 0.5 g (3 mmole) of 1-methyl-4-chloro-1H-imidazo[4,5-c]pyridine (IIIk) and a solution of 0.47 g (9 mmole) of sodium methoxide in 6 ml of methanol was boiled for 2 h. The solvent was distilled off and the reaction product extracted from the residue with hot benzene (3 × 2 ml). After evaporation of the benzene, 0.4 g (81%) of colorless needles was obtained, mp 156-157°C (from benzene). Found: C 59.0; H 5.8; N 25.6%. $C_8H_9N_3O$. Calculated: C 58.9; H 5.6; N 25.8%.

General Method for Thionation of Imidazopyridines Ia, b, IIa-f, IIIa-l, IVa-c (Table 1). A mixture of 10 mmole of imidazopyridines I-IV and 10.5 mmole of sulfur was heated in a flask at 230-260°C (in a bath). The solidified mass was cooled, ground up, and purified by reprecipitation or by crystallization from a suitable solvent. In certain cases it was sufficient to wash the precipitate with carbon disulfide (0.5-1 ml).

3-Nitro-4-octadecylaminopyridine (IX). A mixture of 5.1 g (30 mmole) of 3-nitro-4-ethoxypyridine [29] and 8.1 g (30 mmole) of octadecylamine was heated in an open flask for 2 h at 150-155°C. After cooling, the mass crystallized out. Yield 11.6 g (99%) of light yellow prisms, mp 53-54°C (from alcohol). Found: C 70.3; H 10.8; N 10.5%. $C_{23}H_{41}N_3O_2$. Calculated: C 70.5; H 10.6; N 10.7%.

3-Amino-4-octadecylaminopyridine (VIo). To a boiling solution of 3.9 g (10 mmole) of nitro compound IX mixed with 15 ml of alcohol, 6 ml of water, and 5 drops of concentrated hydrochloric acid was added 2.8 g (50 mmole) of iron carbonyl in small portions with vigorous agitation. The reaction mixture was boiled for another 2-3 h, filtered when hot, and the residue on the filter was washed with hot alcohol (3 × 5 ml) and hot water (2 × 3 ml). The filtrate was evaporated to a quarter of its original volume and a 40% solution of alkali was added until pH 10 was reached. The precipitate was filtered off, washed with water (3 × 3 ml), and dried. Yield 2.7 g (75%) of colorless prisms, mp 76-77°C (from alcohol). Found: C 76.2; H 12.2; N 11.5%. $C_{23}H_{43}N_3$. Calculated: C 76.4; H 12.0; N 11.6%.

General Method for Obtaining 1,3-Dihydro-2H-imidazopyridine-2-thiones (Table 2). A. A mixture of 0.1 mole of o-diaminopyridine V or VI, 200-250 ml of pyridine, 0.2-0.25 mole of potassium or sodium ethylxanthate, and 20-25 ml of water was boiled for 4-6 h. Pyridine was distilled off as completely as possible from the reaction mixture under vacuum using a water-jet pump, and 20-25 ml of water was added to the residue, which was acidified to pH 5 with hydrochloric or acetic acid. The precipitate was filtered off, washed with water, dried, and purified by reprecipitation or crystallization from a suitable solvent.

B. A solution of 0.1 mole of o-diaminopyridine in 200-250 ml of pyridine was boiled with 20-28 ml (0.2-0.3 mole) of carbon disulfide. The reaction product was isolated using method A.

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CYCLIZATION REACTIONS OF NITRILS.

29.* REGIOSELECTIVE SYNTHESIS OF 6-ARYL-3-CYANO-2(1H)-PYRIDINETHIONES AND THE CORRESPONDING SELENONES AND THEIR CHARACTERISTICS

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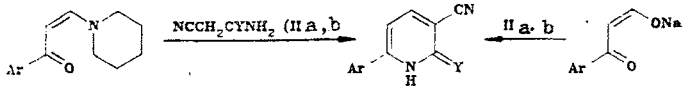
The condensation of cyanothio- and cyanoselenoacetamide with 3-aryl-3-oxo-1-piperidino-1-propene or sodium 3-aryl-3-oxo-1-propen-1-olate takes place regioselectively with the formation of the 6-aryl-3-cyano-2(1H)-pyridinethiones or the corresponding selenones. Thieno[2,3-b]pyridines, thiazolo[3,2-a]pyridinium salts, and other annellated heterocycles were obtained from the 6-aryl-3-cyano-2(1H)-pyridinethiones.

The regioselectivity in the reactions of enamines of the unsymmetrical 1,3-diketone series (benzoylacetone, benzoyltrifluoroacetone, 2-acylcyclopentanone, 2-acylcyclohexanone) with cyanothioacetamide is due to the different electrophilicities of the sp^2-hybridized $C_{(1)}$ and $C_{(3)}$ atoms in the $O{=}C_{(3)}{-}C_{(2)}{=}C_{(1)}{-}N$ pentad of the β-enamino ketones [2-5]. In enamino ketones there is a larger difference in the electrophilic character of the $C_{(1)}$ and $C_{(3)}$ atoms than in 1,3-diketones. As a result of this the reactions of the β-enamines of benzoylacetone with cyanothioacetamide take place with the formation of only 4-methyl-6-phenyl-3-cyano-2(1H)-pyridinethione, whereas the analogous reaction of benzoylacetone leads to the formation of a mixture of 4-methyl-6-phenyl- and 4-phenyl-6-methyl-3-cyano-2(1H)-pyridinethiones [2].

While continuing an investigation into the reactions of β-enaminocarbonyl compounds with derivatives of cyanoacetic acid [2-7], in the present work we studied the reactions of the enamines of β-ketoaldehydes (Ia-f) with cyanothio- and cyanoselenoacetamides (IIa, b) and demonstrated the possibility of using the obtained pyridinethiones for the synthesis of difficultly obtainable annellated heterocycles. The reactions of the β-enamino ketones (Ia-f) with the amides (IIa, b) take place regioselectively with the formation of 6-aryl-3-cyano-2(1H)-pyridinethiones (IIIa-f) or the corresponding selenone (IIIg), respectively. Here the introduction of electron-withdrawing or electron-donating substituents into the benzene ring of the enamino ketones (Ia-e) does not change the direction of the reaction. Regioselectivity of the reaction is also observed in the case of the condensation of 3-(3-pyridyl)-3-oxo-1-piperidino-1-propene (If) with cyanothioacetamide (IIa). The largest yield of (IIIa-g) is obtained when the reaction is carried out in ethanol in the presence of acetic acid as catalyst. We note that the use of bases (sodium ethoxide, piperidine) as catalytic agents leads to resinification of the reaction mixture. Acid catalysis is a distinguishing feature of the reactions of β-enamino ketones (Ia-f), in contrast to the base catalysis of the reactions of the β-enamines of benzoylacetone and acylcyclopentanones and acylcyclohexanones [2-4] with cyanothioacetamide. We also obtained the 6-aryl-3-cyano-2(1H)-pyridinethiones and the corresponding selenone (IIIa-g) from sodium 3-aryl-3-oxo-1-propen-1-olates (IVa-f) and cyanothio(seleno)acetamides (IIa, b). However, their yields were somewhat lower in this method (Table 1).



I a-f III a-g IV a-g

I, IV a Ar=C_6H_5; b Ar=4-ClC_6H_4; c Ar=4-BrC_6H_4; d Ar=4-$CH_3OC_6H_4$; e Ar=3,4-$Cl_2C_6H_3$; f Ar=3-C_5H_4N; II a Y=S; b Y=Se; III a Ar=C_6H_5, Y=S; b Ar=4-ClC_6H_4, Y=S; c Ar=4-BrC_6H_4, Y=S; d Ar=4-$CH_3OC_6H_4$, Y=S; e Ar=3,4-$Cl_2C_6H_3$, Y=S; f Ar=3-C_5H_4N, Y=S; g Ar=C_6H_5, Y=Se

*For Communication 28, see [1].

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