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REACTION OF (ARYLHYDRAZONO)-CYANOTHIOACETAMIDES WITH HALO KETONES

I. V. Paramonov, N. P. Belskaia, and V. A. Bakulev

The reaction of (arylhydrazono)cyanothioacetamides with chloro ketones and phenacyl bromides was studied. The products are either thiazoles or 4,5-dihydrothiophenes, depending on the starting thioamides and halo ketones.

Keywords: (arylhydrazono)thioacetamides, halo ketones, thiazoles, thioamide group, thioimidates, thiophenes, cyclocondensation.

Due to the broad range of the chemical properties of these compounds have found common use in synthetic organic chemistry, including heterocyclic synthesis [1-3]. Thus, the reaction of chloroacetone (**1a**) or α-bromoacetophenone with cyanoacetamide or N-cyanothioacetanilide **2** (R^2 = Ph, X = H_2) proceeds through intermediates **3-5** to give thiazole derivatives **6** (X = H_2, R^1 = Me, Ph) or **7** (Y = H, R^1 = Me, Ph) (see reaction scheme below) [1, 4].

In the present work, we studied the reaction of chloroacetone **1a** and phenacyl bromides **1b** and **1c** with various (arylhydrazono)cyanothioacetamides **2a-j** to elucidate the effect of the arylhydrazono fragment, substituent in the thioamide group, and halo ketone structure on the course of this reaction and to synthesize new sulfur heterocyclic compounds (Scheme 1).

The reaction of halo ketones **1** and thioamides **2a** and **2b** with an unsubstituted amide groups (R^2 = H) leads to 4-R^1-2-(arylhydrazono)cyanomethylthiazoles **6a-d**, regardless of the ketone used and nature of the arylhydrazone group. Thin-layer chromatography of the reaction mixture in all cases showed the formation of three products, namely, substituted thiazole **6** as well as proposed intermediates **3** and **4**. Under the reaction conditions, these intermediates are rapidly converted to thiazoles **6**.

The IR spectra of products **6a-d** have a C=N stretching band at 2190-2200 cm^{-1} as well as bands at 3240-3420 cm^{-1} characteristic for NH group stretching vibrations. The ^{13}C NMR spectrum of thiazole **6a** (Table 1) shows signals for the benzene ring carbon ring at 114.6, 116.5, 135.7, and 156.9 ppm characteristic for arylhydrazono derivatives [5]. The finding of an arylhydrazone group in the product eliminates thiadiazepine structures **8** and **9** and supports the formation of a thiazole ring in the reaction studied.

The ^1H NMR spectra of **6a-d** given in Table 1 show double signals (two singlets) for the thiazole ring 5-H proton, hydrazone NH group proton, and 4-Me (**6a** and **6b**) or 4-C_6H_4Me-*p* groups (**6c** and **6d**) in addition to signals of the benzene ring protons (H_{Ar}). The double set of these signals may result from the existence of thiazoles **6** as *E*- and *Z*-isomers (Scheme 2). The *Z*-isomer may be stabilized by intramolecular hydrogen bonding.

Urals State Technical University, Yekaterinburg 620002, Russia; e-mail: belska@htf.ustu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1572-1583, October, 2003. Original article submitted March 19, 2001, submitted after revision March 13, 2002.

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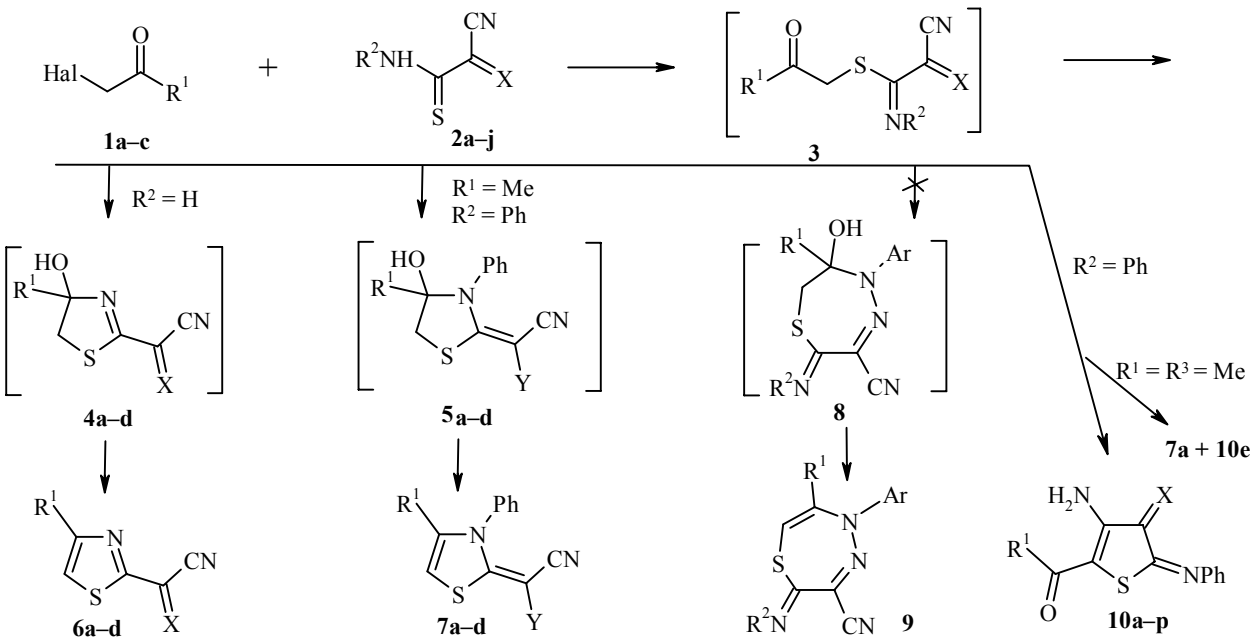
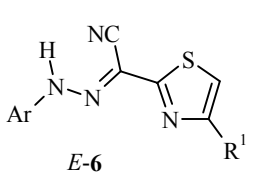
Scheme 1

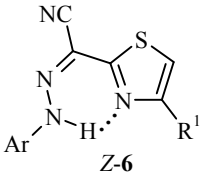


1 a Hal = Cl, **b,c** Hal = Br, **a** R^1 = Me; **b** R^1= C_6H_4Me-*p*, **c** R^1= $C_6H_4NO_2$-*p*, **2**, **4**, **6**, **10** X = N–$NHC_6H_4R^3$-*p*; **2 a**, **b** R^2 = H, **c-j** R^2 = Ph, **a**, **c** R^3 = NO_2, **b**, **h** R^3 = OMe; **d** R^3 = COOEt, **e** R^3= Cl, **f** R^3 = H, **g** R^3 = Me, **i** R^3 = OEt, **j** R^3 = OH; **4**, **6 a**, **b** R^1 = Me, **c**, **d** R^1 = C_6H_4Me-*p*, **a**, **d** R^3 = NO_2; **b**, **c** R^3 = OMe; **5**, **7** Y = –N = $NC_6H_4R^3$-*p*; **7 a-d** R^1 = Ph, **a** R^3 = Me, **b** R^3 = OMe, **c** R^3 = OEt, **d** R^3 = OH, **8, 9** Ar = $C_6H_4R^3$-*p*; **10 a-e** R^1 = Me, **f-m** R^1 = C_6H_4Me-*p*, **n-p** R^1 = $C_6H_4NO_2$-*p,* **a, f, n** R^3 = NO_2; **b**, **g** R^3 = COOEt, **c**, **h** R^3 = Cl, **d**, **i** R^3 = H, **e**, **j**, **o** R^3 = Me; **k** R^3 = OMe, **l** R^3 = OEt, **m** R^3 = OH, **p** R^3 = OEt

Scheme 2



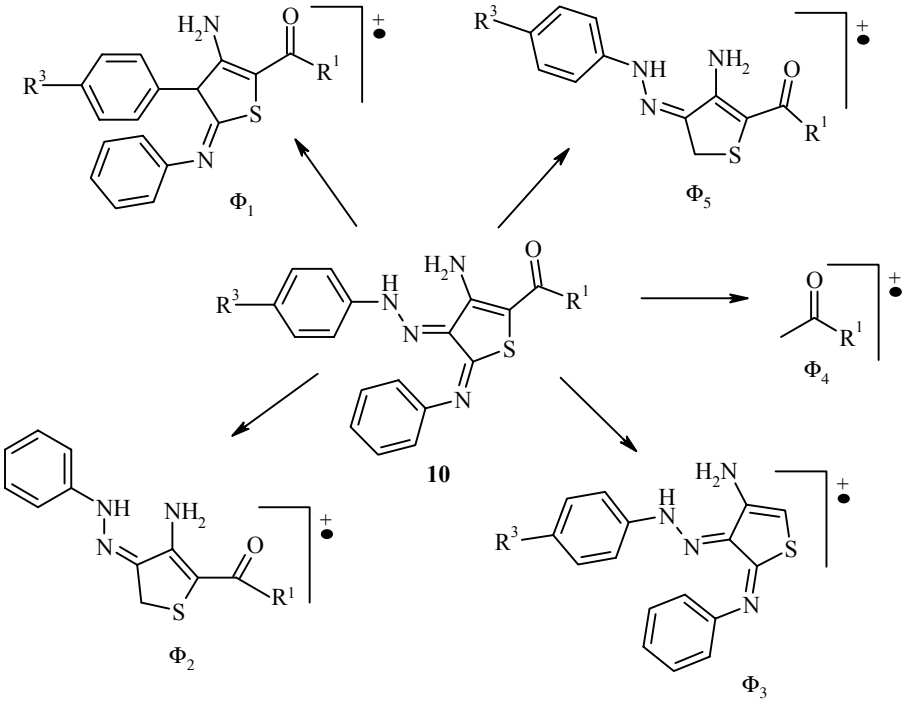
E-**6**



Z-**6**

Thus, the reactions of halo ketones **1a** and **1b** with thioamides **2a** and **2b** proceed exclusively through the unsubstituted thioamide group and lead to thiazoles **6**.

A study of the reaction of halo ketones **1a-c** with N-phenylthiocarbamoyl derivatives **2c-j** showed that the introduction of a phenyl substituent into the thioamide group of the arylhydrazone molecule leads to significant changes in the direction of cyclization of thioimidate **3** formed in the first reaction step.



Thus, 2-acetyl-3-amino-4-(arylhydrazono)-5-phenylimino-4,5-dihydrothiophenes **10a-d** were obtained in 88-97% yield in the reaction of chloroacetone **1a** with (arylhydrazono)cyanothioacetamides **2c-f** containing an electron-withdrawing group or hydrogen at $C_{(4)}$ of the aromatic ring. The ^{1}H NMR spectra of these products given in Table 2 show signals for an AA'BB' system of aromatic ring protons, a three-proton singlet corresponding to acetyl group protons, one-proton singlet for the NH group, and two-proton singlet for the NH_2 group. The IR spectra of **10** characteristically show a strong band at 1610-1640 cm^{-1} presumably assigned to the C=O group linked by a strong hydrogen bond to the NH_2 group and amino group stretching vibrations at 3280-3480 cm^{-1} but lack C=N stretching bands at 2210-2220 cm^{-1}, which was found in the spectra of thiazoles **6** and **7**.

Mass spectrometry provided additional evidence for the structure of products **10a-d**. Thus, the mass spectra of these compounds contain peaks for molecular and fragment ions corresponding to decomposition with loss of substituents in the side-chain (see Table 3).

TABLE 1. ^{1}H NMR Spectra of Thiazoles **6a-d**

Compound	Chemical shifts (DMSO-d_6), δ, ppm (SSCC, *J*, Hz)					
	NH (1H, two br. s	5-H (1H, two s)	4-C_6H_4Me-*p* (3H, two s)	4-Me (3H, two s)	R^3 (3H, two s, OMe)	H_{Ar}
6a	12.22 and 14.03	7.39 and 7.71	—	2.42 and 2.58		7.57 and 8.25 (4H, AA'BB', *J* = 9.2)
6b*	11.70 and 13.97	7.23 and 7.56	—	2.50 and 2.54	3.75 and 3.77	6.96, 6.99, 7.37 and 7.57 (4H, AA′BB′+AA'BB', *J* = 9.1)
6c	11.82 and 14.02	7.99 and 8.29	2.35 and 2.38	—	3.76 and 3.78	6.96-7.05 (2H, m); 7.25-7.40 (2H, m); 7.84-7.94 (4H, m)
6d	12.02 and 13.95	7.97 and 8.30	2.34 and 2.37	—	—	7.02, 7.06, 7.51 and 7.54 (4H, AA'BB' + AA'BB', *J* = 8.6); 7.87, 7.94 and 8.24 (4H, AA'BB' + AA'BB', *J* = 8.6)

* ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 17.04 (CH_3), 55.56 (OCH_3), 106.4 (C–CN), 113.9 (CH_{thiaz}), 114.8, 116.5, 156.9 (C_{Ar}), 117.0 (CN), 153.5 (CCH_3), 160.0 (C_{thiaz}).

TABLE 2. Spectral Data of Thiazolidines **7** and 3-Aminothiophenes **10**

Com-pound	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum (DMSO-d_6), δ, ppm (SSCC, *J*, Hz)					
	NH	C≡N	C=O	NH (1H, br. s)	NH_2 (2H, br. s)	4-Me or 2-COMe (3H, s)	5-H (1H, s)	R^3	H_{Ar}
7b	—	2190	—	—	—	1.93	7.03	3.78 (3H, s, OMe)	6.95 and 7.42 (4H, AA'BB', *J* = 8.9, H_{Ar}); 7.58-7.64 (5H, m, H_{Ph})
7c	—	2190	—	—	—	1.92	6.81	1.36 (3H, t, *J* = 6.71, $OCH_2\underline{CH_3}$); 4.02 (2H, q, *J* = 6.71, $OCH_2\underline{CH_3}$)	6.84-6.87 (2H, m, H_{Ar}); 7.30-7.53 (4H, m, H_{Ph}+H_{Ar}); 7.53-7.70 (3H, m, H_{Ph})
7d	—	2200	—	—	—	1.91	6.85	9.39 (1H, br. s, OH)	6.73 and 7.31(4H, AA'BB', *J* = 8.45, H_{Ar}), 7.47-7.49 (2H, m, H_{Ph}), 7.58-7.60 (3H, m, H_{Ph})
7a + **10e**	—	—	—	13.15	7.6	2.10 and 1.93	— 6.85	2.32 and 2.37 (6H, two s, $2CH_3$)	7.11-7.14 (3H, m, H_{Ph}+H_{Ar}); 7.21-7.24 (3H, m, H_{Ph}); 7.35-7.49 (8H, m, H_{Ph}+H_{Ar}); 7.53-7.70 (4H, m, H_{Ph}+H_{Ar})
10a	3480, 3330	—	1640	13.93	7.82	2.12	—	—	7.28-7.34 (1H, m, H_{Ph}); 7.38-7.41 (2H, m, H_{Ph}); 7.49-7.55 (2H, m, H_{Ph}); 7.97 and 8.26 (4H, AA'BB', *J* = 9.16, H_{Ar})
10b	3430, 3300	—	1710 1610	13.75	7.87	2.11	—	1.34 (3H, s, *J* = 7.1, $CH_2\underline{CH_3}$); 4.32 (2H, s, *J* = 7.1, $\underline{CH_2}CH_3$)	7.26-7.32 (1H, m, H_{Ph}); 7.38-7.42 (2H, m, H_{Ph}); 7.48-7.54 (2H, m, H_{Ph}); 7.87 and 8.26 (4H, AA'BB', *J* = 8.85, H_{Ar})
10c	3390, 3280	—	1630	12.81	7.87	2.12	—	—	7.25-7.30 (1H, m, H_{Ph}); 7.45-7.61 (6H, m, H_{Ph}+H_{Ar}); 7.88-7.95 (2H, m, H_{Ar})
10d	3390, 3260	—	1620	13.42	7.73	2.10	—	—	7.28-7.34 (2H, m, H_{Ph}); 7.34-7.51 (2H, m, H_{Ph}); 7.76-7.79 (2H, m, H_{Ph})

* See H_{Ar}.

TABLE 3. Mass Spectra of 3-Aminothiophenes **10a-p**

Compound	*m/z* (*I*, %)					
	$[M]^{+\bullet}$	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5
10a	381 (100)	352 (18.48)	244 (63.35)	338 (6.36)	—	—
10b	408 (100)	379 (32.30)	244 (57.56)	365 (7.11)	—	316 (1.50)
10c	370 (100)	341 (27.37)	244 (37.99)	327 (5.78)	—	278 (1.56)
10d	336 (41.42)	307 (10.40)	244 (14.87)	293 (3.64)	—	244 (14.87)
10e	350 (72.53)	303 (4.03)	244 (20.09)	289 (1.08)	—	258 (2.07)
10f	458 (51.94)	428 (12.51)	320 (11.83)	—	119 (100)	365 (0.29)
10g	484 (100)	455 (19.87)	320 (16.31)	365 (1.48)	119 (88.77)	392 (1.07)
10h	447 (33.80)	418 (9.15)	—	—	—	355 (100)
10i	412 (100)	383 (14.70)	320 (15.53)	293 (2.18)	119 (74.79)	320 (15.53)
10j	426 (100)	397 (95.68)	320 (13.65)	307 (5.40)	119 (100)	334 (1.25)
10k	442 (89.49)	413 (32.45)	320 (10.46)	323 (2.40)	119(100)	350 (1.44)
10l*	457 (23.03)	427 (10.02)	320 (3.62)	—	119 (57.22)	—
10m	428 (92.48)	399 (32.05)	320 (17.05)	309 (3.36)	119 (100)	336 (1.74)
10n	488 (12.28)	459 (5.53)	351 (7.68)	338 (2.18)	150 (46.87)	—
10o	457 (100)	428 (37.74)	351 (17.24)	307 (4.94)	150 (24.65)	365 (2.54)
10p	487 (100)	458 (5.70)	351 (13.62)	337 (3.85)	150 (30.05)	395 (2.29)

* $[M]^+ + 1$ ion recorded for compound **10 l**.

TABLE 4. Spectral Data for 3-Aminothiophenes **10f-p**

Compound	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum (DMSO-d_6), δ, ppm (SSCC, *J*, Hz)				
	NH	CH	C=O	NH (1H, br. s)	NH_2 (2H, br. s)	R^3	$C_6H_4\underline{Me}$ (3H, s) (R^1)	H_{Ar}
10f	3450 3320	2980 2930	1600	13.67	8.34	—	2.34	7.26 and 7.50 (4H, AA'BB', *J* = 8.5, H_{Ar}); 7.28 (1H, d, *J* = 8.2, H_{Ph}); 7.37 (2H, d, *J* = 7.3, H_{Ph}); 7.49 (2H, d, *J* = 8.2, H_{Ph}); 8.04 and 8.28 (4H, AA'BB', *J* = 9.2, H_{Ar})
10g	3400 3300	2970	1710 1610	13.49	8.31	1.34 (3H, t, *J* = 7.02, $CH_2\underline{CH_3}$); 4.32 (2H, q, *J* = 7.02, $\underline{CH_2}CH_3$)	2.34	7.25 and 7.49 (4H, AA'BB', *J* = 7.9, H_{Ar}); 7.27 (1H, t, *J* = 7.35, H_{Ph}); 7.37 (2H, d, *J* = 7.35, H_{Ph}); 7.47 (2H, t, *J* = 7.35, H_{Ph}); 7.94 and 8.02 (4H, AA'BB', *J* = 8.8, H_{Ar})
10h	3450 3310	2970 2920	1600	12.50	8.36	—	2.35	7.23 (2H, d, *J* = 8.2, H_{Ar}); 7.21–7.30 (1H, m, H_{Ph}); 7.40-7.55 (8H, m, H_{Ph}+H_{Ar}); 8.00 (2H, d, *J* = 8.8, H_{Ar})
10i	—	—	—	12.11	8.15	—*	2.38	7.04-7.52 (11H, m, H_{Ph}+H_{Ar}); 7.83 (2H, d, J = 7.7, H_{Ar})
10j	3460 3330	—	1600	12.89	8.17	2.38 (3H, s, Me)	2.38	7.15-7.26 (5H, m, H_{Ph}+H_{Ar}); 7.32–7.45 (4H, m, H_{Ph}+H_{Ar}); 7.49-7.56 (2H, m, H_{Ph}); 7.75 (2H, d, *J* = 8.2, H_{Ar})
10k	3450 3300	2920	1600	11.93	8.33	3.84 (3H, s, OMe)	2.35	7.06 and 8.00 (4H, AA'BB', *J* = 9.2, H_{Ar}); 7.26 and 7.52 (4H, AA'BB', *J* = 7.9, H_{Ar}); 7.18-7.33 (1H, m, H_{Ph}); 7.40-7.49 (4H, m, H_{Ph})
10l	3470	2980 2930	1600	12.45	8.25	1.40 (3H, t, *J* = 7.0, $OCH_2\underline{CH_3}$); 4.09 (2H, q, *J* = 7.0, $O\underline{CH_2}CH_3$)	2.38	6.98 and 7.88 (4H, AA'BB', *J* = 8.8, H_{Ar}); 7.17 and 7.52 (4H, AA'BB', *J* = 7.6, H_{Ar}); 7.18-7.25 (1H, m, H_{Ph}); 7.30-7.45 (4H, m, H_{Ph})
10m	3480 3340	—	1600	12.12	8.18	9.74 (1H, br. s, OH)	2.38	6.86 and 7.81 (4H, AA'BB', *J* = 8.8, H_{Ar}); 7.16 (1H, m, H_{Ph}); 7.23 and 7.53 (4H, AA'BB', *J* = 7.9, H_{Ar}); 7.36-7.41 (4H, m, H_{Ph})
10n	3440 3300	2970	1600	13.79	8.49	—	—	7.25-7.47 (4H, m, H_{Ar}); 7.57–7.74 (1H, m, H_{Ph}); 7.80 and 8.02 (4H, AA'BB', *J* = 9.2, H_{Ar}) 8.24-8.29 (4H, m, H_{Ph})
10o	3450 3320	2970	1600	12.81	8.35	2.40 (3H, s, Me)	—	7.17-7.44 (7H, m, H_{Ph}+H_{Ar}); 7.67–7.84 (4H, m, H_{Ph}+H_{Ar}); 8.27 (2H, d, *J* = 8.5, H_{Ar})
10p	3450 3300	2950	1600	11.92	8.48	1.31 (3H, t, $OCH_2\underline{CH_3}$); 4.10 (2H, q, $O\underline{CH_2}CH_3$)	—	7.04 (2H, d, *J* = 8.5, H_{Ar}); 7.24 (1H, br. s, H_{Ph}); 7.43 (4H, br. s, H_{Ph}+H_{Ar}); 7.85 and 8.28 (4H, AA'BB', *J* = 7.9, H_{Ar}); 8.00 (2H, d, *J* = 7.7, H_{Ph})

* See H_{Ar}.

The formation of substituted thiophenes **10** probably occurs as the result of an intramolecular reaction of the CH_2 and CN groups in intermediate thioimidate **3**.

The reaction of (*p*-tolylhydrazono)cyano-N-phenylthioacetamide **2g** with chloroacetone **1a** gives a mixture of 4-methyl-3-phenyl-2-(*p*-tolylazocyanomethylene)thiazole (**7a**) and 2-acetyl-3-amino-5-phenylimino-4-(*p*-tolylhydrazono)-4,5-dihydrothiophene (**10e**).

It is interesting to note that the reactions of N-phenylthioacetamides **2h-j**, containing alkoxy and hydroxy groups in the arylhydrazone moiety, with ketone **1a** lead to single 2-(arylazocyanomethylene)-4-methyl-3-phenylthioazoles **7b-d**.

Thus, the direction of the reaction of N-phenylthioamides **2c-j** with chloroacetone is a function of the substituent in the aromatic fragment of the hydrazone molecule.

Regardless of the electronic effect of the substituent at $C_{(4)}$ in the aromatic ring of arylhydrazonothioacetamides **2**, the reaction of thioamides **2c-j** gives single 3-amino-2-aroyl-4-(arylhydrazono)-5-phenylimino-4,5-dihydrothiophenes **10f-p** in 78-92% yield. The structures of **10f-p** were supported by the spectral data given in Tables 3 and 4 and the elemental analysis results (Table 5).

TABLE 5. Characteristics of Compounds **2, 6, 7,** and **10**

Compound	Reaction time, h	Empirical formula	Found, % / Calculated, %		mp, °C	Yield, %
			N	S		
1	2	3	4	5	6	7
2a	2.0	$C_9H_7N_5O_2S$	28.00 / 28.11	12.90 / 12.85	>290	93
2b	3.0	$C_{10}H_{10}N_4OS$	23.87 / 23.93	13.75 / 13.67	211-213	92
2c	3.5	$C_{15}H_{11}N_5O_2S$	21.60 / 21.54	9.90 / 9.85	245-247	95
2d	3.0	$C_{18}H_{16}N_4O_2S$	16.02 / 15.91	9.12 / 9.09	195-196	96
2e	3.0	$C_{15}H_{11}ClN_4S$	18.00 / 17.81	10.25 / 10.17	223-225	96
2f	2.5	$C_{15}H_{12}N_4S$	19.95 / 20.00	11.60 / 11.43	195-197	85
2g	3.0	$C_{16}H_{14}N_4S$	19.00 / 19.05	11.02 / 10.88	240-242	82
2h	3.5	$C_{16}H_{14}N_4OS$	18.03 / 18.06	10.40 / 10.32	210-212	82
2i	4.0	$C_{17}H_{16}N_4OS$	17.19 / 17.28	9.95 / 9.87	235-237	72
2j	4.0	$C_{15}H_{12}N_4OS$	19.05 / 18.92	10.70 / 10.81	225-226	58
6a	5.0	$C_{12}H_9N_5O_2S$	24.60 / 24.35	11.02 / 11.15	264-265	85
6b	6.0	$C_{13}H_{12}N_4OS$	20.60 / 20.59	11.70 / 11.76	115-116	93
6c	5.0	$C_{19}H_{16}N_4OS$	16.05 / 16.09	9.25 / 9.20	>250	75
6d	7.0	$C_{18}H_{13}N_5O_2S$	19.15 / 19.28	8.90 / 8.82	138-139	59
7b	26.0	$C_{19}H_{16}N_4OS$	15.50 / 16.09	8.53 / 9.20	215-217	85
7c	27.0	$C_{20}H_{18}N_4OS$	16.16 / 15.47	8.80 / 8.84	158-160	82
7d	26.0	$C_{18}H_{14}N_4OS$	16.33 / 16.77	9.80 / 9.58	233-235	92
10a	25.0	$C_{18}H_{15}N_5O_3S$	14.73 / 15.26	8.91 / 8.72	255-257	97
10b	22.0	$C_{21}H_{20}N_4O_3S$	13.60 / 13.21	8.18 / 7.54	202-203	90

TABLE 5 (continued)

1	2	3	4	5	6	7
10c	23.0	$C_{18}H_{15}ClN_4OS$	15.02 / 15.11	8.45 / 8.64	185-187	89
10d	26.0	$C_{18}H_{16}N_4OS$	16.43 / 16.67	9.58 / 9.52	160-162	88
10f	32.0	$C_{24}H_{19}N_5O_3S$	15.14 / 15.32	7.31 / 7.00	270-272	79
10g	34.0	$C_{21}H_{20}N_4O_3S$	11.07 / 11.57	7.25 / 6.61	220-222	92
10h	35.0	$C_{24}H_{19}ClN_4OS$	13.00 / 12.54	7.48 / 7.17	194-195	95
10i	34.0	$C_{24}H_{20}N_4OS$	13.55 / 13.59	8.49 / 7.77	150-152	94
10j	33.0	$C_{25}H_{22}N_4OS$	12.87 / 13.15	7.65 / 7.51	110-112	84
10k	36.0	$C_{25}H_{22}N_4O_2S$	12.46 / 12.67	7.25 / 7.24	183-185	86
10l	36.0	$C_{26}H_{24}N_4O_2S$	12.38 / 12.28	7.28 / 7.02	160-161	94
10m	35.0	$C_{24}H_{20}N_4O_2S$	12.36 / 13.08	7.56 / 7.48	235-237	79
10n	35.0	$C_{23}H_{16}N_6O_5S$	17.86 / 17.21	6.70 / 6.56	>245	83
10o	34.0	$C_{24}H_{19}N_5O_3S$	15.40 / 15.32	7.14 / 7.00	220-222	78
10p	36.0	$C_{25}H_{21}N_5O_4S$	13.83 / 14.37	7.44 / 6.57	231-233	89

The formation of the thiophene ring in the reaction of N-phenylthioacetamides **2** with halo ketones may be explained by the diminution of the nucleophilicity of the thioamide nitrogen atom upon introducing a phenyl substituent and the concurrent appearance of the electronic effects of the substituent in the aromatic ring of the arylhydrazone group, which is quite distant from the reaction sites, but nevertheless activates the cyano group and thereby enables its involvement in cyclization to give product **10**.

Comparison of the results of the reaction of 2-arylhydrazono-2-cyanothioacetamides with chloroacetone and phenacyl bromides showed that the structure of the products depends on the structure of the starting hydrazones and halo ketones used. While the reaction of thioacetamide and thioacetanilide with halocarbonyl compounds leads to cyclization only to the corresponding thiazoles **6** (X = H_2) and **7** (Y = H), the introduction of a hydrazone fragment into these molecules permits the formation of both thiazoles **6** (X = NNHAr) or **7** (Y = N=NHAr) and thiophenes **10** (X = NNHAr). Thus, the arylhydrazone group, which does not participate directly in the reaction, may affect the direction of cyclization since it is a "fine" transmitter of electronic effects from rather distant parts of the molecule to the reaction site.

EXPERIMENTAL

The reaction and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates using 6:1, 10:1, and 15:1 chloroform–ethanol and 2:1 and 1:1 hexane–ethyl acetate as the eluents. The IR spectra were taken on a UR-20 spectrometer for KBr pellets. The ^{1}H NMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz and Bruker spectrometer at 300 MHz with TMS as the internal standard. The mass spectra were taken on a Varian MAT-311A spectrometer with 70 eV ionizing radiation and direct sample inlet into the source.

TABLE 6. Spectral Data for 2-Arylhydrazono-2-cyanothioacetamides **2a-j**

Com-pound	IR spectrums, ν, cm^{-1}		^{1}H NMR spectrum (DMSO-d_6), δ, ppm (SSCC, *J*, Hz)						
	NH	C≡N	N–NH (1H, s)	R^2NH	R^3	H_{Ph} (*J*)			H_{Ar}(4H,AA'BB')
						1H, t, *p*-H	2H, t, 2 *m*-H	2H, d, 2 *o*-H	
2a	3360, 3240	2210	11.78	9.38 (1H, s), 9.70 (1H, s)	—	—	—	—	7.89 and 8.14 (*J* = 9.1)
2b	3420, 3260	2220	11.43	9.47 (1H, s), 9.18 (1H, s)	3.75 (3H, s, OMe)	—	—	—	6.91 and 7.66 (*J* = 9.3)
2c	3320, 3220	2210	11.61	12.02 (1H, br. s)	—	7.32 (7.3)	7.47 (7.3)	7.67 (7.6)	7.94 and 8.24 (*J* = 9.5)
2d	3350, 3230	2210	11.50	11.83 (1H, br. s)	1.32 (3H, t, *J* = 7.0, $CH_2\underline{CH_3}$); 4.30 (2H, q, *J* = 7.0, $\underline{CH_2}CH_3$)	7.31 (7.9)	7.46 (7.9)	7.66 (7.6)	7.85 and 7.95 (*J* = 8.9)
2e	3320, 3220	2220	11.41	11.68 (1H, br. s)	—	7.30 (7.3)	7.45 (7.3)	7.65 (7.6)	7.42 and 7.78 (*J* = 8.8)
2f	3320, 3220	2210	11.20	11.48 (1H, br. s)	—*	7.08 (7.3)	7.22-7.43 (5H, m); 7.67-7.75 (4H, m)		
2g	3320, 3230	2220	11.14	11.42 (1H, br. s)	2.31 (3H, s, Me)	7.24 (7.3)	7.39 (7.3)	7.62 (8.0)	7.12 and 7.62 (*J* = 8.2)
2h	3320, 3220	2210	11.25	11.58 (1H, br. s)	3.76 (3H, s, OMe)	7.28 (7.3)	7.43 (7.3)	7.65 (7.6)	6.96 and 7.72 (*J* = 9.0)
2i	3450, 3320	2220	11.07	11.43 (1H, br. s)	1.36 (3H, t, *J* = 7.0, $CH_2\underline{CH_3}$); 4.01 (2H, q, *J* = 7.0, $\underline{CH_2}CH_3$)	7.24 (7.3)	7.39 (7.3)	7.68 (7.6)	6.85 and 7.66 (*J* = 8.9)
2j	3370, 3230	2220	11.01	11.39 (1H, br. s)	—	7.23 (7.3)	7.38 (7.3)	7.69 (7.6)	6.72 and 7.55 (*J* = 8.9)

* See H_{Ph}, H_{Ar}.

Starting arylhydrazonocyanothioacetamides **2a-j** were obtained from the corresponding aryldiazonium chlorides and cyanothioacetamide or cyanothioacetanilide according to Dubenko [4] and Belskaya [5]. The indices for these compounds are given in Tables 5 and 6.

General Method for the Reaction of (Arylhydrazono)cyanothioacetamide 2a-j with Chloroacetone 1a and Phenacyl Bromides 1b and 1c. A sample of corresponding halo ketone **1a-c** (10 mmol) and triethylamine (10 mmol) were added to a solution of **2a-j** (10 mmol) in DMF. The reaction mixture was maintained at 80°C until the starting compounds disappeared as indicated by thin-layer chromatography and, then, poured into water. The precipitated product was filtered off and crystallized from ethanol.

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