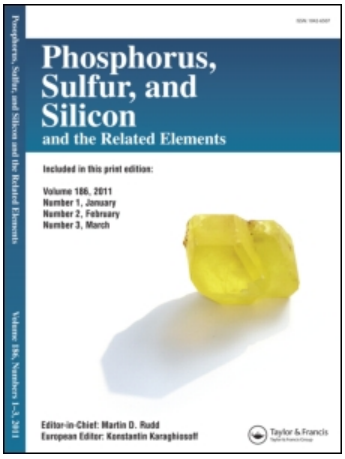

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND REACTIONS OF SEVERAL NEW 2-THIAZOLIN-4-ONYL HYDRAZIDOYL HALIDES

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To cite this Article Ismail, Nabila A. , Fekry, Reda M. , Eldin, Sanaa M. and Abdel-azim, Yassir N.(1993) 'SYNTHESIS AND REACTIONS OF SEVERAL NEW 2-THIAZOLIN-4-ONYL HYDRAZIDOYL HALIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 78: 1, 109 — 118
To link to this Article: DOI: 10.1080/10426509308032427
URL: http://dx.doi.org/10.1080/10426509308032427

Phosphorus, Sulfur, and Silicon, 1993, Vol. 78, pp. 109–118
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SYNTHESIS AND REACTIONS OF SEVERAL NEW 2-THIAZOLIN-4-ONYL HYDRAZIDOYL HALIDES

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(Received September 20, 1992; in final form November 17, 1992)

Several new hydrazidoyl halides containing the 2-thiazolin-4-one moiety were synthesised and reacted with several reagents to yield several additional heterocyclics. Structures were based on both elemental analysis and spectral data.

Key words: Hydrazidoyl halides; 2-thiazolin-4-ones; thiazolinonylpyradiazinones; α-acetyl-α-cyanothioacetamide.

INTRODUCTION

Hydrazidoyl halides are long known to be suitable synthons for different types of heterocycles.[1–6] 2-Thiazolin-4-one and its derivatives are also known to possess diverse biological activities.[7–10] The synthesis of hydrazidoyl halides containing the 2-thiazolinone moiety adds to both the chemistry and biological activities of these derivatives. α-Acetyl-α-cyanothioacetamide[11] seemed to be an excellent starting for the present study to fulfill this objective as a continuation to our effort in this field.[12]

RESULTS AND DISCUSSION

Thus, it has been found that α-acetyl-α-cyanothioacetamide (**1**) reacted with chloroacetic acid to give 2-α-cyanoacetonyl-2-thiazolin-4-one (**2**).[11] Bromination of **2** in glacial acetic acid afforded 2-(α-bromo-α′-cyanoacetonyl)-2-thiazolin-4-one (**3**) whose structure was established using elemental analysis and spectral data (cf. Experimental). Reaction of **3** with dimethyl sulfide yielded the corresponding dimethylsulfonium bromide derivative **4**. Coupling of **4** with a series of diazotized primary aromatic amines led to the formation of the corresponding new hydrazidoyl halides **5a–d** which were taken as the starting components for the present study. The structure assigned for **5a–d** was established using elemental and spectral data. The IR spectra of **5a–d** showed absorption bands related to the presence of NH, sat. CH and CH_2, CN, side chain-CO, ring CO and C=N in each case. The ^{1}H-NMR spectrum of **5a**, as a typical example of the series, revealed signals (δ ppm)

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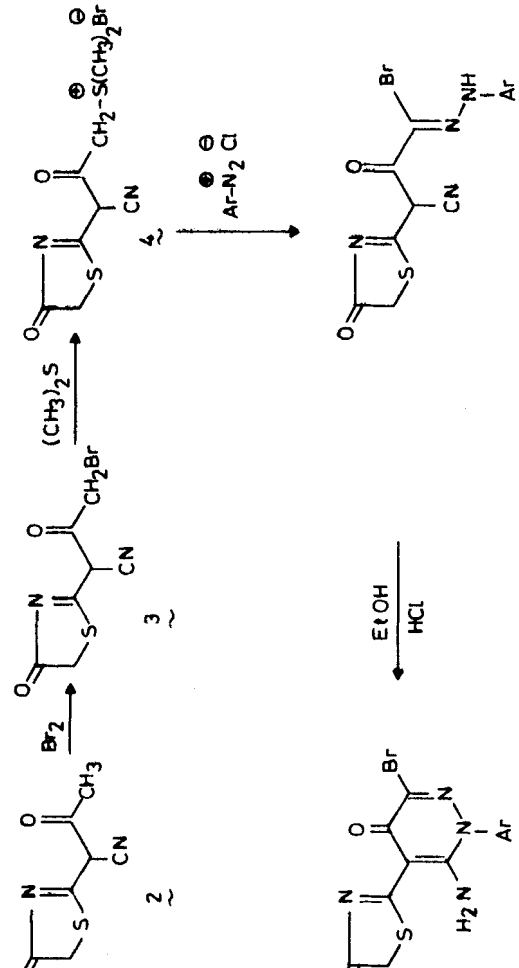
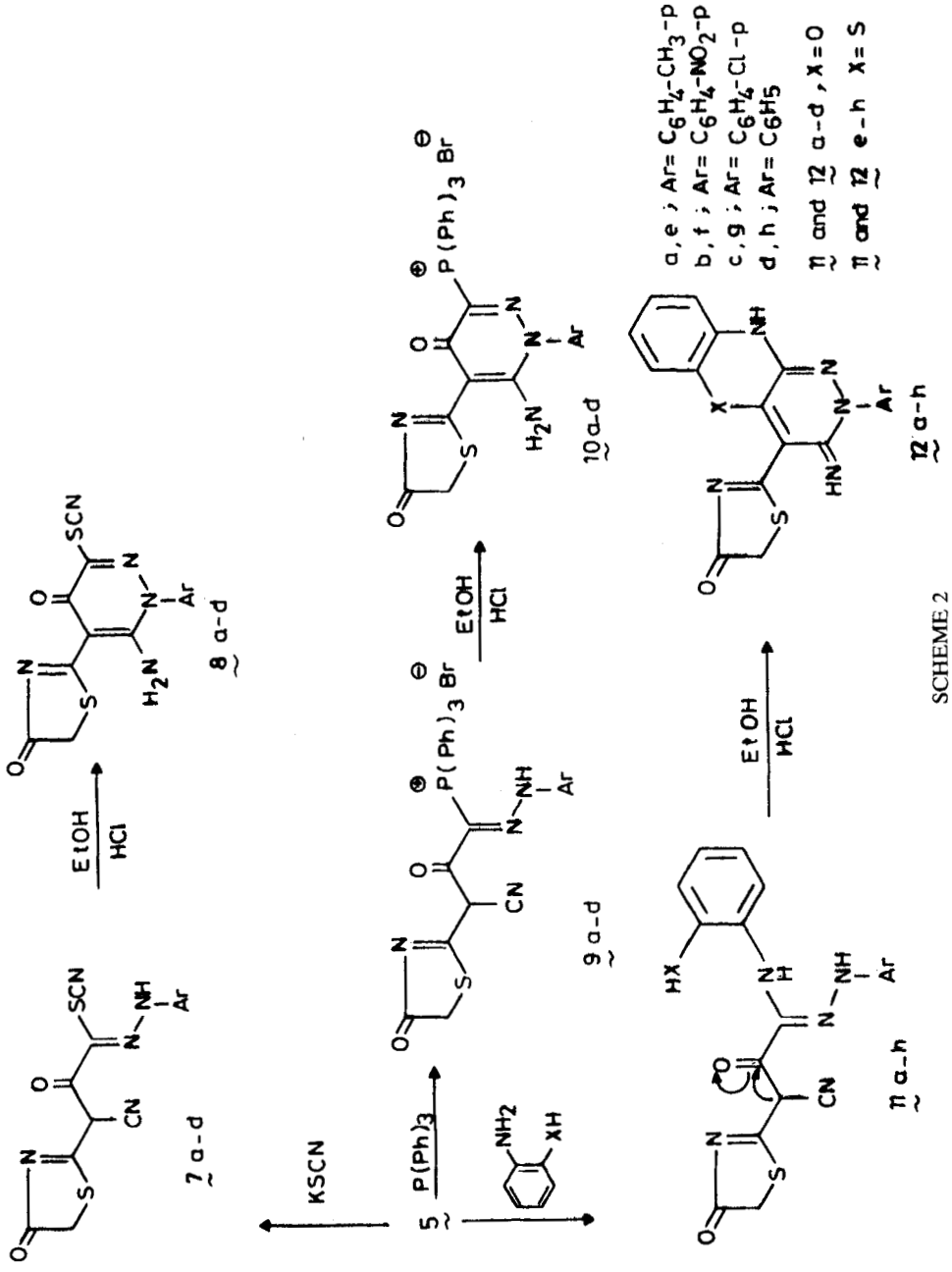


SCHEME 1



SCHEME 2

of Ar-CH_3 (s, 2.4); thiazolinone-CH_2 (s, 5.6); CH (s, 6.2); aromatic protons (m, 7.1–7.8) in addition to NH (s, br, 9.8; lost after D_2O exchange).

Compounds **5a–d** reacted with ethanolic hydrochloric acid to undergo a cyclization reaction which led to the formation of the corresponding 1-aryl-3-bromo-5-(2-thiazolin-4-on-2-yl)-6-aminopyridazin-4-one derivatives **6a–d**, respectively. The IR spectra of each of **6a–d** were found entirely free of the absorption bands of the nitrile function in each case thus proving the involvement of this group in the cyclization step. The ^{1}H-NMR spectra of **6a–d** were in good agreement with the assigned structure and revealed no signals for each of the —CHCN or NH protons (cf. Experimental).

Compounds **5a–d** reacted with potassium thiocyanate to yield the corresponding substitution reaction products **7a–d**. The absorption bands related to the presence of the CN and SCN groups were clearly shown in the IR spectra of each of **7a–d**. Cyclization of the thiocyanato derivatives **7a–d** using ethanolic hydrochloric acid yielded the corresponding thiocyanato pyridazinone derivatives **8a–d**. The IR spectra of **8a–d** showed no absorption bands of CN groups and those of the SCN groups were clearly detected. No signals of NH or —CHCN protons were revealed in the ^{1}H-NMR spectra of **8a–d** (cf. Experimental).

Similar to their behaviour towards KSCN, compounds **5a–d** reacted with triphenylphosphine to give the corresponding triphenyl phosphonium bromide derivatives **9a–d**; cyclization of **9a–d** gave also the corresponding pyridazinone derivatives **10a–d**. Structures of **9a–d** and **10a–d** were established by elemental analysis and spectral data. The ^{1}H-NMR spectra of **10a–d** were found entirely free of the signals corresponding to the presence of either NH or —CHCN protons (cf. Experimental).

Compounds **5a–d** reacted with each of o-aminophenol and o-aminothiophenol to yield the corresponding substitution reaction products **11a–h**. Cyclization of **11a–h** led, in turn, to the formation of reaction products showing no nitrile function and one ring carbonyl group in each case. These cyclization products could be formulated as the thiazolinonyl benz[1,4]oxazino- and thiazolinonyl-benz[1,4]thiazino[3,2-c]pyridazine derivatives **12a–h** on the basis of elemental analysis and spectral data. The ^{1}H-NMR spectra of **12a–h** revealed patterns which could be interpreted in terms of structure **12a–h** only and revealed the absence of any signals of the —CHCN group in each case (cf. Experimental).

EXPERIMENTAL

All melting points are uncorrected. IR (KBr) were recorded on a Pye Unicam SP. 1100 spectrometer. ^{1}H-NMR spectra were recorded in DMSO-d_6 on a Varian EM 390 90 MHz spectrometer using TMS as an internal standard. Chemical shifts are expressed as δ ppm units. The microanalyses were performed at the Microanalytical Center of Cairo University using a Perkin-Elmer 2400 C H N Analyzer.

Preparation of 2-(α-bromo-α'-cyano-actonyl)-2-thiazolin-4-one (**3**). A solution of (**2**) (0.01 mole), in acetic acid (30 ml) reacted with bromine (0.01 mole). The reaction mixture was heated under reflux for 1.5 h. The solid product obtained after cooling was filtered and crystallized from the proper solvent to give **3** (Tables I and II).

Reaction of (**3**) *with dimethyl sulfide.* A solution of (**3**) (0.01 mole), in ethanol (30 ml) was treated with dimethyl sulfide (0.01 mole), and the reaction mixture was then refluxed for 2 h. The reaction mixture was cooled and ether was added then (**4**) precipitated which was filtered, washed with a little ether, and crystallized from the proper-solvent (Tables I and II).

TABLE I

Characterization data of the newly synthesized derivatives

Comp.	Colour (Solvent)	M.P.	Yield	Mol. Formula	% Analysis Calcd./Found				
					C	H	N	S	Hal.
3	Buff (ethanol)	195	75	$C_7H_5N_2SO_2Br$	32.2 32.0	1.9 1.8	10.7 10.5	12.3 12.1	30.6 30.5
4	Buff (ethanol)	217	80	$C_9H_{11}N_2S_2O_2Br$	33.4 33.2	3.4 3.3	8.7 8.5	19.8 19.7	24.7 24.5
5a	Brown (ethanol)	185	75	$C_{14}H_{11}N_4SO_2Br$	44.3 44.2	3.7 3.6	14.8 14.8	8.5 8.5	21.1 21.0
5b	Brown (ethanol)	205	70	$C_{13}H_8N_5SO_4Br$	38.1 38.0	1.8 1.6	17.1 17.0	7.8 7.6	19.5 19.4
5c	Break red (ethanol)	235	75	$C_{13}H_8N_4SO_2BrCl$	39.1 39.0	2.0 1.8	14.0 13.9	8.0 8.0	28.9 28.7
5d	Orange (ethanol)	295	75	$C_{13}H_9N_4SO_2Br$	42.8 42.6	2.5 2.3	15.3 15.2	8.8 8.6	21.9 21.7
6a	Brown (ethanol)	215	70	$C_{14}H_{11}N_4SO_2Br$	44.3 44.1	3.7 3.5	14.8 14.7	8.5 8.3	21.1 21.0
6b	Brown (ethanol)	230	65	$C_{13}H_8N_5SO_4Br$	38.1 37.9	1.8 1.7	17.1 17.0	7.8 7.6	19.5 19.3
6c	Brown (ethanol)	270	65	$C_{13}H_8N_4SO_2BrCl$	39.1 39.0	2.0 1.8	14.0 13.8	8.0 7.9	28.9 28.7
6d	Brown (ethanol)	330	70	$C_{13}H_9N_4SO_2Br$	42.8 42.6	2.5 2.3	15.3 15.1	8.8 8.6	21.9 21.7
7a	Brown (ethanol)	160	65	$C_{15}H_{11}N_5S_2O_2$	50.4 50.1	3.1 3.0	19.6 19.4	17.9 17.7	
7b	Brown (ethanol)	180	60	$C_{14}H_8N_6S_2O_4$	43.3 43.1	2.1 2.0	21.6 21.4	16.5 16.3	
7c	Brown (ethanol)	210	70	$C_{14}H_8N_5S_2O_2Cl$	44.5 44.3	2.1 2.0	18.5 18.3	17.0 16.8	9.4 9.2
7d	Brown (ethanol)	220	70	$C_{14}H_9N_5S_2O_2$	49.0 48.8	2.6 2.4	20.4 20.2	18.7 18.5	
8a	Brown (ethanol)	210	70	$C_{15}H_{11}N_5S_2O_2$	50.4 50.2	3.1 2.9	19.6 19.4	17.9 17.8	
8b	Brown (ethanol)	230	65	$C_{14}H_8N_6S_2O_4$	43.3 43.2	2.1 1.9	21.6 21.4	16.5 16.3	
8c	Brown (ethanol)	270	65	$C_{14}H_8N_5S_2O_2Cl$	44.5 44.3	2.1 2.0	18.5 18.3	17.0 16.8	9.4 9.2
8d	Brown (ethanol)	>300	70	$C_{15}H_9N_5S_2O_2$	49.0 48.8	2.6 2.5	20.4 20.2	18.7 18.5	
9a	Brown (toluene)	135	70	$C_{32}H_{26}N_4SO_2Br$-p	59.9 59.7	4.1 4.0	8.7 8.6	5.0 4.8	12.5 12.3
9b	Brown (toluene)	180	70	$C_{31}H_{23}N_5SO_4Br$-p	55.4 55.2	3.5 3.3	10.4 10.1	4.8 4.6	11.9 11.8
9c	Break red (toluene)	215	70	$C_{31}H_{23}N_4SO_2BrCl$-p	56.2 56.0	3.5 3.3	8.5 8.2	4.9 4.9	17.5 17.3
9d	Brown (toluene)	255	70	$C_{31}H_{24}N_4SO_2Br$-p	56.6 56.5	3.7 3.5	8.5 8.3	4.9 4.7	12.2 12.0

TABLE I (*Continued*)

Comp.	Colour (Solvent)	M.P.	Yield	Mol. Formula	% Analysis Calcd./Found				
					C	H	N	S	Hal.
10a	Brown (toluene)	230	60	$C_{31}H_{24}N_4SO_2Br$-p	59.9 59.6	4.1 4.0	8.7 8.5	5.0 4.8	12.5 12.3
10b	Brown (toluene)	290	60	$C_{31}H_{23}NSO_4Br$-p	55.4 55.2	3.5 3.4	10.4 10.2	4.8 4.6	11.9 11.8
10c	Brown (toluene)	>330	60	$C_{31}H_{23}N_4SO_2BrCl$-p	56.2 56.0	3.5 3.3	8.5 8.3	4.9 4.7	17.5 17.3
10d	Brown (toluene)	>330	60	$C_{31}H_{24}N_4SO_2Br$-p	56.6 56.4	3.7 3.5	8.5 8.3	4.9 4.7	12.2 12.0
11a	Brown (benzene)	155	70	$C_{20}H_{17}N_5SO_3$	59.0 58.8	4.2 4.0	17.2 17.0	7.9 7.7	
11b	Brown (benzene)	170	60	$C_{19}H_{14}N_6SO_5$	52.1 52.0	3.2 3.0	19.2 19.0	7.3 7.1	
11c	Brown (benzene)	190	70	$C_{19}H_{14}N_5SO_3Cl$	53.3 53.1	3.3 3.1	16.4 16.3	7.5 7.4	8.3 8.1
11d	Brown (benzene)	135	65	$C_{19}H_{15}N_5SO_3$	58.0 57.8	3.8 3.6	17.8 17.6	8.2 8.0	
12a	Brown (benzene)	180	60	$C_{20}H_{17}N_5SO_3$	59.0 58.8	4.2 4.0	17.2 17.0	7.9 7.7	
12b	Brown (benzene)	210	60	$C_{19}H_{14}N_6SO_5$	52.1 52.0	3.2 3.0	19.2 19.0	7.3 7.2	
12c	Brown (benzene)	250	60	$C_{19}H_{14}N_5SO_3Cl$	53.2 53.0	3.3 3.1	16.4 16.2	7.5 7.3	8.3 8.1
12d	Brown	185	60	$C_{19}H_{15}N_5SO_3$	58.0 57.9	3.8 3.6	17.8 17.7	8.2 8.0	
11e	Brown (ethanol)	120	60	$C_{20}H_{17}N_5S_2O_2$	56.7 56.5	4.0 3.8	16.5 16.3	15.1 15.0	
11f	Brown (ethanol)	100	60	$C_{19}H_{14}N_6S_2O_4$	50.2 50.0	3.1 3.0	18.5 18.3	14.1 14.0	
11g	Brown (ethanol)	85	60	$C_{19}H_{14}N_5S_2O_2Cl$	51.4 51.2	3.2 3.0	15.8 15.6	14.4 14.1	8.0 7.8
11h	Orange	72	60	$C_{19}H_{15}N_5S_2O_2$	55.7 55.5	3.7 3.5	17.1 17.0	15.6 15.4	
12e	Brown (ethanol)	170	60	$C_{20}H_{17}N_5S_2O_2$	56.7 56.4	4.0 3.8	16.5 16.3	15.1 15.0	
12f	Brown (ethanol)	150	60	$C_{19}H_{14}N_6S_2O_4$	50.2 50.0	3.1 3.0	18.5 18.4	14.1 14.0	
12g	Brown (ethanol)	130	60	$C_{19}H_{14}N_5S_2O_2Cl$	51.4 51.2	3.2 3.1	15.8 15.6	14.4 14.2	8.0 7.9
12h	Brown (ethanol)	120	60	$C_{19}H_{15}N_5S_2O_2$	55.7 55.4	3.7 3.5	17.1 17.0	15.6 15.4	

TABLE II
IR and ^{1}H-NMR data

Comp.	IR, KBr, cm^{-1}	^{1}H-NMR (DMSO-d_6), δ ppm
3	2970 (sat. CH and CH_2); 2210 (CN); 1710 (CO); 1680 (ring CO) and 1630 (C=N).	4.2 (s, 2H, $COCH_2Br$); 5.6 (s, 2H, thiazoline -CH_2) and 6.2 (s, 1H, CHCN).
4	2970 (sat. CH and CH_2); 2200 (CN); 1710 (CO); 1680 (ring CO) and 1630 (C=N).	2.1 (s, 6H, two CH_3); 4.2 (s, 2H, $COCH_2$); 5.6 (s, 2H, thiazoline-CH_2) and 6.2 (s, 1H, CHCN).
5a	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 1715 (CO); 1680 (ring CO) and 1620 (C=N)	2.4 (s, 3H, Ar-CH_3); 5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 4H, Ar'Hs); and 9.6 (s, br, 1H,NH)
5b	3300 (NH); 2980 (sat. CH and CH_2); 2200 (CN); 1720 (CO); 1690 (ring CO) and 1630 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 4H, Ar'Hs); and 9.6 (s, br, 1H, NH).
5d	3310 (NH), 2970 (sat. CH and CH_2); 2200 (CN); 1710 (CO); 1680 (ring CO) and 1620 (C=N)	5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 5H, Ar'Hs); and 9.6 (s, br, 1H, NH).
6a	3350, 3300 (NH_2); 2970 (sat. CH_2); 1720 (CO); 1680 (ring CO) and 1635 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.6 (s, 2H, thiazoline-CH_2); 7.1-7.8 (m, 4H, Ar'Hs); and 9.6 (s, br, 2H, NH_2).
6c	3350, 3300 (NH_2); 2970 (sat. CH_2); 1710 (CO); 1680 (ring CO); and 1630 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 7.1-7.8 (m, 4H, Ar'Hs) and 9.7 (s, br, 2H, NH_2).
6d	3350, 3300 (NH_2); 2970 (sat. CH_2); 1710 (CO); 1680 (ring CO) and 1635 (C=N).	5.6 (s, 2H thiazoline-CH_2); 7.1-7.8 (m, 5H, Ar'Hs) and 9.9 (s, br, 2H, NH_2).
7a	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 2160 (SCN); 1720 (CO); 1680 (ring CO) and 1650 (C=N).	2.4 (s, 3HAr-CH_3); 5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 4H, Ar'Hs); and 9.6 (s, br, 1H, NH).
7b	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 2160 (SCN) 1710 (CO); 1680 (ring CO) and 1635 (C=N).	5.6 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 4H, Ar'Hs and 9.6 (s, br, 1H, NH).
7d	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 2160 (SCN); 1710 (CO); 1680 (ring CO); and 1640 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 5H, Ar'Hs); and 9.6 (s, br, 1H, NH).
8a	3350, 3300 (NH_2); 2970 (sat. CH_2); 2160 (SCN); 1720 (CO); 1680 (ring CO) and 1630 (C=N)	2.4 (s, 3H, Ar-CH_3); 5.6 (s, 2H, thiazoline-CH_2); 7.1-7.8 (m, 4H, Ar'Hs) and 9.7 (s, br, 2H, NH_2).

TABLE II (*Continued*)

Comp.	IR, KBr, cm^{-1}	^{1}H-NMR (DMSO-d_6) δ ppm
8c	3350, 3300 (NH_2); 2970 (sat. CH_2); 2160 (SCN); 1715 (CO); 1680 (ring CO) and 1640 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 7.1-7.8 (m, 4H, Ar'Hs) and 9.7 (s, br, 2H, NH_2).
8d	3350, 3300 (NH_2); 2970 (sat. CH_2); 2160 (SCN); 1710 (CO); 1680 (ring CO) and 1620 (C=N).	5.6 (s, 2H, thiazoline CH_2); 7.1-7.8 (m, 5H, Ar'Hs) and 9.7 (s, br, 2H, NH_2).
9a	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 1720 (CO); 1680 (ring CO) and 1630 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.6 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.1-7.8 (m, 19H, ArH's) and 9.6 (s, br, 1H, NH).
9b	3300 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 1710 (CO); 1680 (ring CO) and 1635 (C=N).	5.6 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.2-7.9 (m, 19H, Ar'Hs); and 9.6 (s, br, 1H, NH).
9d	3310 (NH); 2970 (sat. CH and CH_2); 2200 (CN); 1710 (CO); 1680 (ring CO) and 1620 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.2-7.9 (m, 20 H, Ar'Hs) and 9.6 (s, br, 1H, NH).
10a	3350, 3300 (NH_2); 2970 (sat. CH_2); 1720 (CO); 1680 (ring CO) and 1630 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.6 (s, 2H thiazoline-CH_2); 7.1-7.8 (m, 19H, ArH's) and 9.9 (s, br, 2H, NH_2).
10c	3350, 3300 (NH_2); 2970 (sat. CH_2); 1720 (CO); 1680 (ring CO); and 1630 (C=N).	5.6 (s, 2H thiazoline-CH_2); 7.1-7.8 (m, 19H, Ar'Hs), and 9.6 (s, br, 2H, NH_2).
10d	3350, 3300 (NH_2); 2970 (sat. CH_2); 1710 (CO); 1670 (ring CO); and 1620 (C=N).	5.6 (s, 2H, thiazoline-CH_2); 7.1-7.8 (m, 20 H, Ar'Hs) and 9.7 (s, br, 2H, NH_2).
11a	3450 (OH); 3350 (NH); 3310 (NH); 3200 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1720 (CO); 1680 (ring CO); 1630 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.8 (s, 2H, thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 8H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.2 (s, 1H, OH).
11b	3450 (OH); 3350 (NH); 3300 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1720 (CO); 1680 (ring CO) and 1640 (C=N).	5.8 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 8H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.2 (s, 1H, OH).
11d	3450 (OH); 3250 (NH); 3210 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1725 (CO); 1680 (ring CO) and 1630 (C=N).	5.8 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 9H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.2 (s, 1H, OH).
12a	3350 (NH); 3300 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1620 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.8 (s, 2H, thiazoline-CH_2); 7.3-8.0 (m, 8H, Ar'Hs) and 9.3 (s, br, 1H, NH).

TABLE II (*Continued*)

Comp.	IR, KBr, cm^{-1}	^{1}H-NMR (DMSO-d_6) δ ppm
12b	3350 (NH); 3300 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1630 (C=N).	5.8 (s, 2H, thiazoline-CH_2); 7.3-8.0 (m, 8H, Ar'Hs) and 9.3 (s, br, 1H, NH).
12d	3350 (NH); 3300 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1625 (C=N).	5.8 (s, 2H, thiazoline-CH_2); 7.3-8.0 (m, 9H, Ar'Hs) and 9.3 (s, br, 1H, NH).
11e	3460 (SH), 3250 (NH); 3210 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1720 (CO); 1680 (ring CO) and 1620 (C=N).	2.4 (s, 3H, Ar-CH_3); 5.8 (s, 2H, thiazoline CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 8H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.5 (s, 1H, SH).
11f	3460 (SH); 3250 (NH); 3210 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1720 (CO); 1680 (ring CO) and 1640 (C=N).	5.8 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 8H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.5 (s, 1H, SH).
11h	3460 (SH); 3250 (NH); 3210 (NH); 2980 (sat. CH and CH_2); 2220 (CN); 1710 (CO); 1680 (ring CO) and 1630 (C=N).	5.8 (s, 2H thiazoline-CH_2); 6.2 (s, 1H, CHCN); 7.3-8.0 (m, 9H, Ar'Hs); 9.3 (s, br, 1H, NH) and 10.5 (s, 1H, SH).
12e	3350 (NH); 3200 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1620 (C=N).	2.5 (s, 3H, Ar-CH_3); 5.8 (s, 2H thiazoline-CH_3); 7.3-8.0 (m, 8H, Ar'Hs) and 9.3 (s, br, 1H, NH).
12f	3350 (NH); 3300 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1630 (C=N).	5.8 (s, 2H, thiazoline-CH_2); 7.3-8.0 (m, 9H, Ar'Hs); and 9.3 (s, br, 1H, NH).
12h	3350 (NH); 3300 (NH); 2980 (sat. CH_2); 1680 (ring CO) and 1625 (C=N).	5.8 (s, 2H, thiazoline-CH_2); 7.3-8.0 (m, 9H, Ar'Hs) and 9.3 (s, br, 1H, NH).

Formation of (**5a–d**). A cold solution of (**4**) (0.01 mole), in acetic acid (30 ml) containing sodium acetate (1 g) was treated with a cold solution of diazotised *p*-toluidine, *p*-nitroaniline, *p*-chloroaniline or aniline (0.02 mole) dropwise with stirring while the temperature was kept below 5°C. After complete addition (30 min.) the reaction mixture was kept in the ice-chest for 2 h. The solid, thus formed was filtered, washed with water, then crystallized from the proper solvent to give **5a–d** (Tables I and II).

Reactions of **5a–d** *with KSCN.* A solution of the appropriate **5a–d** (0.01 mole), in ethanol (30 ml) was treated with a solution of KSCN (0.01 mole) in water (10 ml) and the reaction mixture was stirred for 4 h at room temperature. The crude solid products thus obtained were filtered off, washed with water, then crystallized from the proper solvent to give **7a–d** (Tables I and II).

Reactions of **5a–d** *with triphenylphosphine, o-aminophenyl and o-aminothiophenol.* General Procedure: A solution of **5a–d** (0.01 mole), in ethanol (30 ml) was treated with (0.01 mole) of each of triphenylphosphine, *o*-aminophenol or *o*-aminothiophenol and the reaction mixture was heated under reflux for 2–3 h. The solid products obtained while the reaction mixture was still boiling or after cooling were collected by filtration, and then crystallized from the proper solvents to give **5a–d, 11a–d** and **11e–h** (Tables I and II).

General procedure for the cyclization of each of **5a–d, 7a–d, 9a–d, 11a–d**, *and* **11e–h.** A solution of each solid compound (1.0 g) and conc. hydrochloric acid (2.6 ml) in ethanol (20 ml) was heated under reflux for 3–4 h and then poured onto ice water. The solid product obtained after cooling was filtered off and crystallized from the proper solvent to give **6a–d, 8a–d, 10a–d, 12a–d** and **12e–h** (Tables I and II).

REFERENCES

1. W. Fliege, R. Grashy and R. Huisgen, *Chem. Ber.*, **117,** 1197 (1984).
2. T. Sasaki and T. Yoshioka, *Chem. Soc. Jpn.*, **49,** 321 (1976).
3. K. H. Pfortner and J. Foricher, *Helv. Chem. Acta*, **63,** 654 (1980).
4. A. O. Abdelhamid and S. E. Abdou, *Sulfur Lett.*, **6,** 41 (1987).
5. N. A. Ismail, F. A. Khalifa and A. A. Magd El-Din, *Heterocycles* Vol. **32,** No. 6, 1101 (1991).
6. A. O. Abdelhamid and F. A. Attaby, *Sulfur Lett.*, **7,** 239 (1988).
7. L. Szekeres, *Gazz. Chim. Ital.*, **78,** 681 (1948); *Chem. Abstr.*, **43,** 2967 (1949).
8. J. G. Fischer, "Encyclopedia of Chemical Technology" (Kirk Othmer), 2nd ed., Interscience New York, **20,** 191 (1969).
9. H. Taniyoma, B. Yasui and F. Inoue, *J. Pharm. Soc. Japan*, **173**, 276 (1953).
10. I. Hyakowa, Y. Tanaka and Y. Nagata, Japan Patent, 77, 83, 588 (1976); *Chem. Abstr.*, **88,** 37785 c (1978).
11. H. Schafer, K. Gewald, *J. Prakt. Chem.*, **317,** 717 (1975).
12. N. A. Ismail, F. A. Khalifa, R. M. Fekry and Y. N. Abdel Azim, *Phosphorous, Sulfur and Silicon*, **66,** 29 (1992).