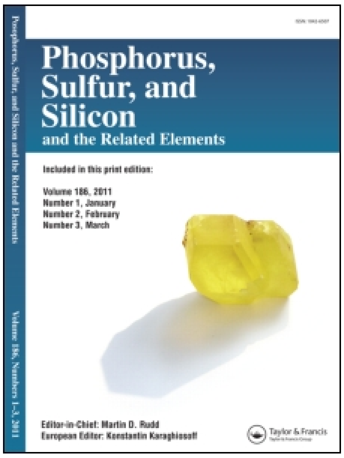

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A NEW SYNTHESIS OF 4H-THIOPYRAN-4-THIONES FROM ACETYLENIC β-DIKETONES

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A NEW SYNTHESIS OF 4H-THIOPYRAN-4-THIONES FROM ACETYLENIC β-DIKETONES

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2,6-Diaryl-4H-thiopyran-4-thiones have been synthesized in excellent yields by the reaction of 1-aryl-5-phenyl-4-pentyne-1,3-diones with phosphorus pentasulfide in dry pyridine at room temperature and were converted into the corresponding hydrazones and oximes. Their oxidation affords the respective. 4H-thiopyran-4-one sulfoxides or sulfones. The structure of the above compounds was confirmed from their spectral characteristics.

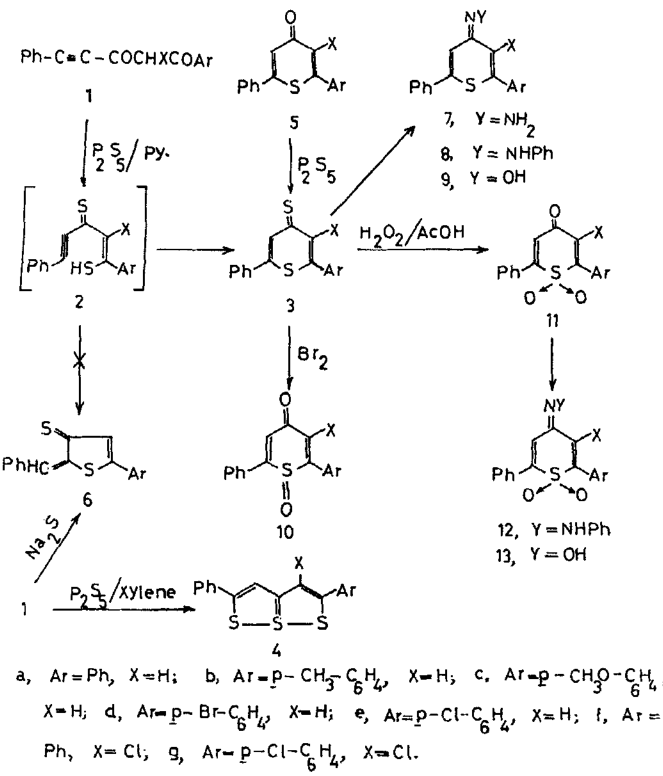
Key words: Acetylenic β-diketones; 4H-thiopyrans; synthesis and structure elucidation.

4H-Thiopyran-4-thiones and their related products are of interest for various potential applications.[1,2] Some of these compounds show fungicidal,[3] pharmacological, medicinal, antibacterial, antiallergic, antihypotensival, sedatival and schistosomicidal properties.[1] They have been extensively investigated for the detection and estimation of heavy metals, and are used in the manufacture of dyes.[1] Certain derivatives of 4H-thiopyran-4-thione form highly conducting "organic metals" with suitable acceptors.[4]

A quantity of work has been carried out on the structure of 4H-thiopyran-4-thiones.[2] The preparation of this ring system has been achieved in only a very limited number of ways, mostly involving the use of either 4H-pyran derivatives[2,5] or dithiolium salts[6] as starting materials. The generality of these methods is impaired by the availability of the starting substrates. In the present study, a new method for the synthesis of 2,6-diaryl-4H-thiopyran-4-thiones from acyclic precursors which do not contain sulfur has been developed.

When dry pyridine solution of the readily available 1,5-diaryl-4-pentyne-1,3-diones[7,8] (**1a–g**) is treated with an excess of phosphorus pentasulfide at room temperature, the corresponding dark brown 2-aryl-6-phenyl-4H-thiopyran-4-thiones (**3a–g**) are obtained in excellent yields. However, the 2-aryl-5-phenyl-6-thiathiophthenes (**4a–g**) are reported[9] to be formed from the reaction of **1a–g** with phosphorus pentasulfide in refluxing dry xylene (Scheme 1).

The formation of the 1,4-dithiopyrones **3** presumably proceeds through the initial formation of the 1,5-diaryl-4-pentyne-1,3-dithiones (**2**) and subsequent cyclization (Michael type addition). In accordance with Baldwin rules for ring closure,[10] this type of cyclization, 6-endo-digonal for the 4H-thiopyran-4-thiones **3** is more favorable due to inductive effects. This mechanism is supported by the fact that the 4H-thiopyran-4-thiones **3a,f** are reported[11] to be formed from the reaction of the respective 4H-thiopyran-4-ones **5** and phosphorus pentasulfide. Also, similar Michael mechanisms were suggested for the formation of 4H-chalcogenapyran-4-ones from pentadiyn-3-ones[12] or acetylenic ketones[13] and also for 4-pyridones[14] from the amine adducts of pentadiyn-3-ones. The absence of 5-aryl-2-benzylidene-3(2H)-



SCHEME 1

thiophenethiones (**6**) in the above reaction may be due to the basic conditions which would minimize the concentration of the species containing chalcogen-hydrogen bonds, which are believed to be necessary for the anti-Michael addition.[12,15] Compounds **6a–e** are obtained by the reaction of **1a–e** with sodium sulfide.[16]

Evidently, the above reaction provides a convenient and apparently general method and is among the best routes for the preparation of 4H-thiopyran-4-thiones carrying aryl substituents of which only a few examples are reported in the literature.[2,17]

The structure of the 4H-thiopyran-4-thiones was confirmed by their spectral and analytical data (Tables I and II). Their IR spectra showed the thiocarbonyl absorption at 1059–1138 cm^{-1} in almost the same region reported for 2,6-diaryl-4H-thiopyran-4-thiones.[17] Also, the NMR spectra of **3a–g** exhibited a singlet at δ 7.91–8.30 for H-3 and H-5 ring protons. Further support of the structure of the 4H-thiopyran-4-thiones was obtained from their mass spectra. The dithiopyrones **3a–c,e,f** gave a relatively intense molecular ion peaks which gave rise to a series of fragments characteristic of 4H-thiopyran-4-thiones (cf. Experimental).

The 4H-thiopyran-4-thiones **3**, bearing a thiocarbonyl group, appeared to be attractive intermediates for the synthesis of 4H-thiopyrans having reactive functional groups in position **4**. In the present study, the reaction of **3a–g** with hydrazine hydrate, phenylhydrazine or hydroxylamine led to the formation of the corresponding hydrazones **7a–g**, phenylhydrazones **8a–c,f,g** or oximes **9a–c,e–g**, respectively. Moreover, **3a–g** could be oxidized to the corresponding 4H-thiopyran-4-one sulfoxides (**10b–e,g**) or 4H-thiopyran-4-one sulfones (**11a–g**) on reaction with bromine in wet ether or with hydrogen peroxide in glacial acetic acid. The latter sulfones **11a–c,f,g** afforded with phenylhydrazine and hydroxylamine the sulfone phenylhydrazones **12a–c,f,g** and sulfone oximes **13a–c,f,g**, respectively (Scheme I). The structures of all the compounds were confirmed by their spectral and analytical data (Tables I and II) and supported by the reported data for similar systems.[17–20] These 4H-thiopyran-4-thiones **3** are useful starting materials for the preparation of some 4H-thiopyran derivatives of which only a few examples are reported in the literature.[1,17]

EXPERIMENTAL

Microanalyses were performed by the Microanalysis Unit, Cairo University, Cairo. IR spectra were measured with a Unicam SP 1025 spectrophotometer for potassium bromide pellets. The NMR spectra were recorded in $CDCl_3$ solution on a Varian EM-390 90 MHz spectrometer with TMS as internal standard. Mass spectra were recorded on an AEI MS 30 spectrometer. For TLC, Merck Kieselgel 60-F 254 precoated plastic plates were used.

2-Aryl-6-phenyl-(**3a–e**)*- and 2-Aryl-3-chloro-6-phenyl-*(**3f,g**)*-4H-thiopyran-4-thiones (Tables I and II).* A solution of **1a–g** (0.8 g; 0.0032 mol) in dry pyridine (15 mL) was stirred with phosphorus pentasulfide (2.0 g; 0.0089 mol) for 3–5 h at room temperature. The pyridine solution was decanted and the residue was boiled with benzene. The combined pyridine and benzene solutions were washed with ammonium sulfide, water, and dried (Na_2SO_4). After removal of most of the solvents under reduced pressure, the separated dithiopyrones **3a–g** were crystallized from benzene as dark brown needles. The 4H-thiopyran-4-thiones **3a,f** were found to be completely identical (m.p. mixed m.p., IR and NMR spectra) with authentic samples prepared from the reaction of 2,6-diaryl-4H-thiopyran-4-ones (**5a,f**) with phosphorus pentasulfide.[11] MS, m/z for **3a**: 280 (M^+), 236 (M^+—CS), 121 (PhCS), 115 (C_9H_7), 102 (Ph—C≡CH), 77 (Ph); **3b**: 294 (M^+), 250 (M^+—CS), 135 (*p*—CH_3—C_6H_4CS), 129 ($C_{10}H_9$), 121 (PhCS), 116 (*p*—CH_3—C_6H_4—C≡CH), 115 (C_9H_7), 102 (PhC≡CH), 91 (*p*—CH_3—C_6H_4), 77 (Ph); **3c**: 310 (M^+), 266 (M^+—CS), 151 (*p*—CH_3O—C_6H_4CS), 145 ($C_{10}H_9O$), 132 (*p*—CH_3O—C_6H_4—C≡CH), 121 (PhCS), 115 (C_9H_7), 107 (*p*—CH_3O—C_6H_4), 102 (Ph—C≡CH), 77 (Ph); **3e**: 314 (M^+), 270 (M^+—CS), 155 (*p*—Cl—C_6H_4CS), 149 (C_9H_6Cl), 136 (*p*—Cl—C_6H_4—C≡CH), 121 (PhCS), 115 (C_9H_7), 111 (*p*—Cl—C_6H_4), 102 (Ph—C≡CH), 77 (Ph); **3f**: 279 (M^+—Cl), 235 (M^+—Cl—CS), 121 (PhCS), 114 (C_9H_6), 101 (Ph—C≡CH), 77 (Ph).

2-Aryl-6-phenyl-(**7a–e**)*- and 2-Aryl-3-chloro-6-phenyl-*(**7f,g**)*-4H-thiopyran-4-one Hydrazones and Phenylhydrazones* (**8a–c,f,g**) *(Tables I and II).* A suspension of **3a–g** (0.4 g; 0.0001 mol) in ethanol (10 mL) was heated under reflux with 99% hydrazine hydrate (2 mL; 0.0398 mol) or phenylhydrazine (0.3 mL; 0.0004 mol) for 30–60 min, during which time the starting material dissolved and the dark colored mixture became yellow-orange with evolution of hydrogen sulfide. Dilution with water gave the hydrazones **7a–g** or phenylhydrazones **8a–c,f,g** which were crystallized from methanol-water or benzene-petroleum ether (b.p. 40–60°C) as orange needles.

2-Aryl-6-phenyl-(**9a–c,e**)*- and 2-Aryl-3-chloro-6-phenyl-*(**9f,g**)*-4H-thiopyran-4-one Oximes (Tables I and II).* A suspension of **3a–c,e–g** (0.4 g; 0.0001 mol) in ethanol (30 mL) was heated under reflux with hydroxylamine hydrochloride (0.8 g; 0.0115 mol) and fused sodium acetate (0.8 g; 0.0096 mol) in water (2 mL) for 3–5 h. After concentration and dilution with water, the separated oximes **9a–c,e–g** were crystallized from benzene as yellow needles.

2-Aryl-6-phenyl-(**10b–e**)*- and 2-Aryl-3-chloro-6-phenyl-(10g)-4H-thiopyran-4-one Sulfoxides (Tables I and II).* A solution of **3b–e,g** (0.4 g; 0.0001 mol) in ether (15 mL) was shaked well with bromine water (20 mL; 0.62 g; 0.0039 mol). The ethereal solution after washing with water for three times, drying (Na_2SO_4) and evaporation gave **10b–e,g** which crystallized from methanol as pale yellow needles.

2-Aryl-6-phenyl-(**11a–e**)*- and 2-Aryl-3-chloro-6-phenyl-*(**11f,g**)*-4H-thiopyran-4-one Sulfones (Tables I and II).* A solution of **3a–g** (0.4 g; 0.0001 mol) in glacial acetic acid (10 mL) was heated on a boiling water bath with 30% hydrogen peroxide (9 mL) for 2–3 h. The sulfones **11a–g** which separated were crystallized from methanol as yellow needles.

TABLE I

Characterization data of the 4H-thiopyran-4-thione derivatives

	IR (cm^{-1})								NMR (δ/ppm)[a]		
Compd.	C=S	C=N	NH_2	NH	OH	C=O	SO	SO_2	H-3 & H-4(a) (s)	Ar-H (m)	Others[b] (s)
3a	1059								8.10	7.50	
3b	1122								7.95	7.31	2.26 (CH_3)
3c	1130								7.91	7.53	3.90 (OCH_3)
3d	1135								8.01	7.42	
3e	1138								8.15	7.60	
3f	1126								8.30	7.45	
3g	1128								8.03	7.40	
7a		1618	3345,3196						7.13	7.55	6.51 (NH_2)
7b		1610	3420,3180						7.23	7.62	2.22 (CH_3), 6.40 (NH_2)
7c		1603	3427,3051						7.12	7.78	3.87 (OCH_3), 6.55 (NH_2)
7d		1610	3365,3200						7.15	7.89	6.55 (NH_2)
7e		1619	3367,3187						7.10	7.19	6.74 (NH_2)
7f		1630	3340,3190						7.11	7.23	6.56 (NH_2)
7g		1632	3345,3183						7.01	7.69	6.48 (NH_2)
8a		1615		3195					7.13	7.52	11.13 (NH)
8b		1610		3210					7.03	7.67	2.28 (CH_3), 11.17 (NH)
8c		1606		3215					7.10	7.70	3.91 (OCH_3), 10.98 (NH)
8f		1600		3230					7.15	7.18	11.15 (NH)
8g		1602		3185					7.08	6.98	12.00 (NH)
9a		1617			3152				6.83,7.16	7.50	8.25 (OH)
9b		1624			3163				6.32,6.50	7.57	2.20 (CH_3), 8.50 (OH)
9c		1620			3190				6.30,6.40	7.25	3.77 (OCH_3), 8.30 (OH)
9e		1618			3142				6.70,6.90	7.37	8.30 (OH)
9f		1612			3150				7.20	7.48	9.56 (OH)
9g		1610			3155				7.22	7.52	9.50 (OH)
10b						1625	1036		6.78	7.53	2.40 (CH_3)
10c						1630	1053		6.70	7.59	3.72 (OCH_3)
10d						1635	1060		6.66	7.70	
10e						1640	1042		6.62	7.69	
10g						1645	1045		6.76	7.15	

11a				1645	1138,1310,1340	6.60	7.65	
11b				1650	1140,1312,1320	6.70	7.55	2.43 (CH_3)
11c				1655	1141,1310,1330	6.65	7.60	3.70 (OCH_3)
11d				1632	1145,1315,1335	6.72	7.69	
11e				1640	1136,1319,1325	6.78	7.75	
11f				1663	1140,1320,1328	6.83	7.65	
11g				1665	1142,1322,1338	6.89	7.70	
12a	1602	3200			1131,1308,1328	7.13	7.55	11.53 (NH)
12b	1605	3196			1133,1310,1326	7.01	7.53	2.23 (CH_3), 11.45 (NH)
12c	1600	3210			1138,1312,1329	7.10	7.52	3.78 (OCH_3), 11.12 (NH)
12f	1610	3119			1132,1311,1330	(b)	6.93	11.68 (NH)
12g	1615	3203			1137,1307,1332	(b)	6.98	11.55 (NH)
13a	1634		3210		1138,1305,1332	6.86,6.92	7.60	
13b	1622		3220		1140,1306,1330	6.66,6.90	7.55	2.12 (CH_3), 9.15 (OH)
13c	1624		3200		1140,1300,1330	6.73,6.87	7.65	3.67 (OCH_3), 9.50 (OH)
13f	1630		3215		1132,1310,1329	6.81	7.45	
13g	1635		3225		1137,1305,1328	6.75	7.48	10.25 (OH)

[a] s: Singlet. m: Multiplet. The solvent for NMR spectra was DMSO-d_6 for **10,12**.

[b] All NH_2, NH and OH protons are exchanged with deuterium oxide. (a) The H-3 and H-5 protons are doublet for **9a–c,e** (J = 2 Hz), **13a–c** (J = 0.07 Hz). (b) The H-5 protons are overlapped by the aromatic protons multiplet.

TABLE II
Analytical data of the 4H-thiopyran-4-thione derivatives

Compd.	m.p. (°C)	Yield (%)	Molecular Formula	% Found/Required C	H	N	S	X
3a	129–130	90	$C_{17}H_{12}S_2$	73.1	4.2		22.6	
				(72.9	4.3		22.9	)
3b	143–144	86	$C_{18}H_{14}S_2$	73.8	4.5		22.1	
				(73.5	4.7		21.8	)
3c	128–130	78	$C_{18}H_{14}OS_2$	69.9	4.6		20.4	
				(69.7	4.5		20.7	)
3d	143–145	81	$C_{17}H_{11}BrS_2$	56.6	3.0		17.9	22.0
				(56.9	3.1		17.8	22.3)
3e	132–133	85	$C_{17}H_{11}ClS_2$	65.2	3.7		20.1	11.7
				(64.9	3.5		20.4	11.3)
3f	153–155	87	$C_{17}H_{11}ClS_2$	65.1	3.4		20.7	11.0
				(64.9	3.5		20.4	11.3)
3g	163–164	83	$C_{17}H_{10}Cl_2S_2$	58.8	3.1		18.6	20.0
				(58.5	2.9		18.3	20.3)
7a	103–104	81	$C_{17}H_{14}N_2S$	73.5	5.3	10.2	11.2	
				(73.4	5.0	10.1	11.5	)
7b	85–86	50	$C_{18}H_{16}N_2S$	74.3	5.3	9.9	11.3	
				(74.0	5.5	9.6	11.0	)
7c	125–127	60	$C_{18}H_{16}N_2OS$	70.4	5.0	8.9	10.7	
				(70.1	5.2	9.1	10.4	)
7d	102–105	72	$C_{17}H_{13}BrN_2S$	56.9	3.8	8.0	9.3	22.0
				(57.1	3.6	7.8	9.0	22.4)
7e	115–118	66	$C_{17}H_{13}ClN_2S$	65.6	4.0	9.3	10.0	11.9
				(65.3	4.2	9.0	10.2	11.4)
7f	163–165	77	$C_{17}H_{13}ClN_2S$	65.1	4.0	9.3	10.4	11.0
				(65.3	4.2	9.0	10.2	11.4)
7g	176–178	62	$C_{17}H_{12}Cl_2N_2S$	58.5	3.8	8.3	9.0	20.9
				(58.8	3.6	8.1	9.2	20.5)
8a	132–133	45	$C_{23}H_{18}N_2S$	78.3	5.0	7.6	9.3	
				(78.0	5.1	7.9	9.0	)
8b	142–145	53	$C_{24}H_{20}N_2S$	78.6	5.2	7.9	8.9	
				(78.3	5.4	7.6	8.7	)
8c	122–123	60	$C_{24}H_{20}N_2OS$	74.8	5.0	7.0	8.6	
				(75.0	5.2	7.3	8.3	)

8f	145–147	70	$C_{23}H_{17}ClN_2S$	71.3	4.6	7.0	8.4	9.5
				(71.0	4.4	7.2	8.2	9.1)
8g	174–176	55	$C_{23}H_{16}Cl_2N_2S$	65.0	3.6	6.8	7.9	16.3
				(65.3	3.8	6.6	7.6	16.8)
9a	203–205	85	$C_{17}H_{13}NOS$	73.0	4.8	4.8	11.3	
				(73.1	4.7	5.0	11.5	)
9b	192–193	75	$C_{18}H_{15}NOS$	73.5	5.0	4.6	10.7	
				(73.7	5.1	4.8	10.9	)
9c	228–230	82	$C_{18}H_{15}NO_2S$	70.1	5.0	4.8	10.7	
				(69.9	4.9	4.5	10.4	)
9e	235–237	78	$C_{17}H_{12}ClNOS$	64.8	4.0	4.8	10.0	11.7
				(65.1	3.8	4.5	10.2	11.3)
9f	230–232	86	$C_{17}H_{12}ClNOS$	65.3	4.0	4.8	10.3	11.6
				(65.1	3.8	4.5	10.2	11.3)
9g	240–242	80	$C_{17}H_{11}Cl_2NOS$	58.9	3.2	4.3	9.4	20.0
				(58.6	3.2	4.6	9.2	20.4)
10b	188–190	65	$C_{18}H_{14}O_2S$	73.8	4.6		11.1	
				(73.5	4.8		10.9	)
10c	210–212	68	$C_{18}H_{14}O_3S$	69.9	4.4		10.0	
				(69.7	4.5		10.3	)
10d	197–198	70	$C_{17}H_{11}BrO_2S$	57.0	3.3		9.2	22.0
				(56.8	3.1		8.9	22.3)
10e	200–202	56	$C_{17}H_{11}ClO_2S$	65.2	3.7		9.9	11.7
				(64.9	3.5		10.2	11.3)
10g	175–176	62	$C_{17}H_{10}Cl_2O_2S$	58.3	3.1		9.5	19.8
				(58.5	2.9		9.2	20.3)
11a	146–148	45	$C_{17}H_{12}O_3S$	68.6	4.3		11.1	
				(68.9	4.1		10.8	)
11b	143–145	59	$C_{18}H_{14}O_3S$	69.5	4.2		10.0	
				(69.7	4.5		10.3	)
11c	153–155	53	$C_{18}H_{14}O_4S$	66.0	4.5		10.1	
				(66.3	4.3		9.8	)
11d	167–168	62	$C_{17}H_{11}BrO_3S$	54.7	3.1		8.8	21.7
				(54.4	2.9		8.5	21.3)
11e	148–150	58	$C_{17}H_{11}ClO_3S$	61.4	3.5		9.9	10.3
				(61.7	3.3		9.7	10.7)
11f	163–164	70	$C_{17}H_{11}ClO_3S$	61.5	3.3		10.0	10.3
				(61.7	3.3		9.7	10.7)

TABLE II (*Continued*)

Compd.	m.p. (°C)	Yield (%)	Molecular Formula	% Found/Required				
				C	H	N	S	X
11g	175–177	63	$C_{17}H_{10}Cl_2O_2S$	56.1	3.0		9.0	19.0
				(55.9	2.9		8.8	19.5)
12a	240–241	66	$C_{23}H_{18}N_2O_2S$	71.8	4.5	7.5	8.0	
				(71.5	4.7	7.3	8.3	)
12b	253–255	73	$C_{24}H_{20}N_2O_2S$	72.3	5.2	7.3	7.8	
				(72.0	5.0	7.0	8.0	)
12c	269–270	70	$C_{24}H_{20}N_2O_3S$	69.5	5.0	6.4	7.9	
				(69.2	4.8	6.7	7.7	)
12f	205–207	53	$C_{23}H_{17}ClN_2O_2S$	65.3	4.2	6.9	7.3	8.0
				(65.6	4.0	6.7	7.6	8.4)
12g	215–217	78	$C_{23}H_{16}Cl_2N_2O_2S$	60.9	3.7	6.0	7.3	15.9
				(60.7	3.5	6.2	7.0	15.6)
13a	193–195	58	$C_{17}H_{13}NO_3S$	65.9	4.0	4.3	10.7	
				(65.6	4.2	4.5	10.3	)
13b	209–210	68	$C_{18}H_{15}NO_3S$	66.3	4.8	4.0	10.1	
				(66.5	4.6	4.3	9.9	)
13c	212–215	56	$C_{18}H_{15}NO_4S$	63.5	4.2	4.3	9.7	
				(63.3	4.4	4.1	9.4	)
13f	211–213	70	$C_{17}H_{12}ClNO_3S$	59.3	3.8	4.3	9.6	10.8
				(59.1	3.5	4.1	9.3	10.3)
13g	232–233	68	$C_{17}H_{11}Cl_2NO_3S$	53.9	3.0	3.9	8.1	18.3
				(53.7	2.9	3.7	8.4	18.7)

2-Aryl-6-phenyl-(**12a–c**)*- and 2-Aryl-3-chloro-6-phenyl-*(**12f,g**)*-4H-thiopyran-4-one Sulfone Phenylhydrazones (Tables I and II).* A solution of **11a–c,f,g** (0.4 g; 0.0014 mol) in ethanol (10 mL) was stirred with phenylhydrazine (0.3 mL; 0.0004 mol) for 2–3 h at room temperature. The reaction mixture was then poured into cold water and the separated **12a–c,f,g** were crystallized from methanol as red needles.

2-Aryl-6-phenyl-(**13a–c**)*- and 2-Aryl-3-chloro-6-phenyl-*(**13f,g**)*-4H-thiopyran-4-one Sulfone Oximes (Tables I and II).* A solution of **11a–c,f,g** (0.4 g; 0.0014 mol) in ethanol (10 mL) was heated under reflux with a mixture of hydroxylamine hydrochloride (0.8 g; 0.0115 mol) and fused sodium acetate (0.8 g; 0.0096 mol) in water (2 mL) for 5–15 min. The reaction mixture was then diluted with cold water and the sulfone oximes **13a–c,f,g** which separated were filtered and crystallized from methanol as yellow needles.

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