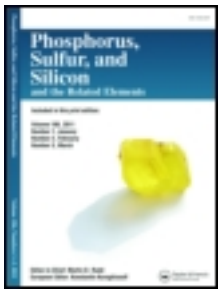


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

SYNTHESIS, REACTIONS AND SPECTRAL PROPERTIES OF 3-CHLORO-2,6DIARYL-4H-THIOPYRAN-4-ONES. SYNTHESIS OF SOME NEW 3-CHLORO-SPIROTHIOPYRAN DERIVATIVES

Abdel Moneim El-Ghanam [a]

[a] Alexandria University, Alexandria, Egypt

Version of record first published: 16 Aug 2010.

To cite this article: Abdel Moneim El-Ghanam (2004): SYNTHESIS, REACTIONS AND SPECTRAL PROPERTIES OF 3-CHLORO-2,6DIARYL-4H-THIOPYRAN-4-ONES. SYNTHESIS OF SOME NEW 3-CHLORO-SPIROTHIOPYRAN DERIVATIVES, Phosphorus, Sulfur, and Silicon and the Related Elements, 179:6, 1075-1083

To link to this article: http://dx.doi.org/10.1080/10426500490459696

Phosphorus, Sulfur, and Silicon, 179:1075–1083, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490459696

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, REACTIONS AND SPECTRAL PROPERTIES OF 3-CHLORO-2,6-DIARYL-4H-THIOPYRAN-4-ONES. SYNTHESIS OF SOME NEW 3-CHLORO-SPIROTHIOPYRAN DERIVATIVES

Abdel Moneim El-Ghanam
Alexandria University, Alexandria, Egypt

(Received August 16, 2003; accepted October 9, 2003)

3-Chloro-2-phenyl-6-p-tolyl and 3-chloro-2,6-di-p-tolyl-4H-thiopyran-4-ones have been synthesized in moderate yieldes from the reaction of 3-chloro-tetrahydrothiopyran-4-ones with phosphorus pentachloride. Their thiones, oximes, and hydrazones have been also prepared. Treatment of thiones with malononitrile gave the corresponding 3-chloro-4-thiopyrylidenemalononitriles which gave 3-chloro-spirothiopyran derivatives of pyrazole, isoxazole, 1,3-thiazines when treated with hydrazine hydrate, hydroxylamine hydrochloride, thiourea and thiosemicarbazide, respectively. While treatment of 3-chloro-thiopyrylidenemalononitriles with acetylacetone gave the corresponding 3-chloro-spirothiopyran derivatives of pyran.

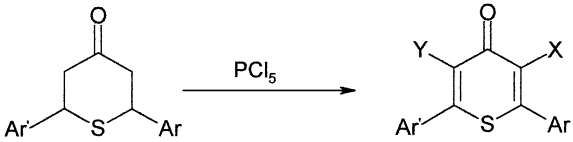
Keywords: 3-Chlorothiopyrones; 3-chlorothiopyrylidenemalononitriles; NMR spectra; mass spectra; 3-chlorospirothiopyranes

Thiopyranes and their derivatives have been subject of interest for chemists due to their importance as intermediates in the synthesis of pyrylium dyes[1] as well as their biological activities. Thiopyran-4-ones are reported to be fungicidal,[2] while 3-carboxylic acid of thiopyran-4-one itself has been used as precursor in the preparation of noval penicillins or the equivalent cephalosporins.[2] Moreover, the alkylamino substitution of fused thiopyran-4-ones affords analogues of the acridine antimalarials which have been shown to intercalate into DNA and

I would like to thank Dr. Bassam El Ali and King Fahd University of Petroleum and Minerals, Saudi Arabia, Chemistry Department for helping with the spectra and elemental analysis of this work.

Address correspondence to Abdel Moneim El-Ghanam, Chemistry Department, Faculty of Science, Alexandria University, Ibrahimia PO Box 426, Alexandria 21321, Egypt. E-mail: delghanam@yahoo.com

strongly mutagenic in test system.[2] On the basis of the above facts, the synthesis of new thiopyrones, 3-chloro-4H-thiopyran-4-ones and their reactions with bidentate and active methylene reagents have been studied. While both a mixture of 2,6-diphenyl (**2a**) and 3-chloro-2,6-diphenyl (**2b**)-4H-thiopyran-4-ones and a mixture of 2,6-di-p-anisyl-3,5-dichloro (**2c**) and 2,6-di-p-anisyl-3-chloro (**2d**)-4H-thiopyran-4-ones have been prepared by the reaction of 2,6-diphenyl (**1a**) and 2,6-di-p-anisyl (**1c**) -tetrahydro-4H-thiopyran-4-ones with phosphorus pentachloride[3] respectively. Under the same conditions, 2-phenyl-6-p-tolyl (**2e**) and 2,6-di-p-tolyl (**2f**)-thiopyran-4-ones were formed from 2-phenyl-6-p-tolyl (**1e**) and 2,6-di-p-tolyl (**1f**) -tetrahydrothipyran-4-ones[4] respectively (Scheme 1). In order to repair this gab, in the



1 2

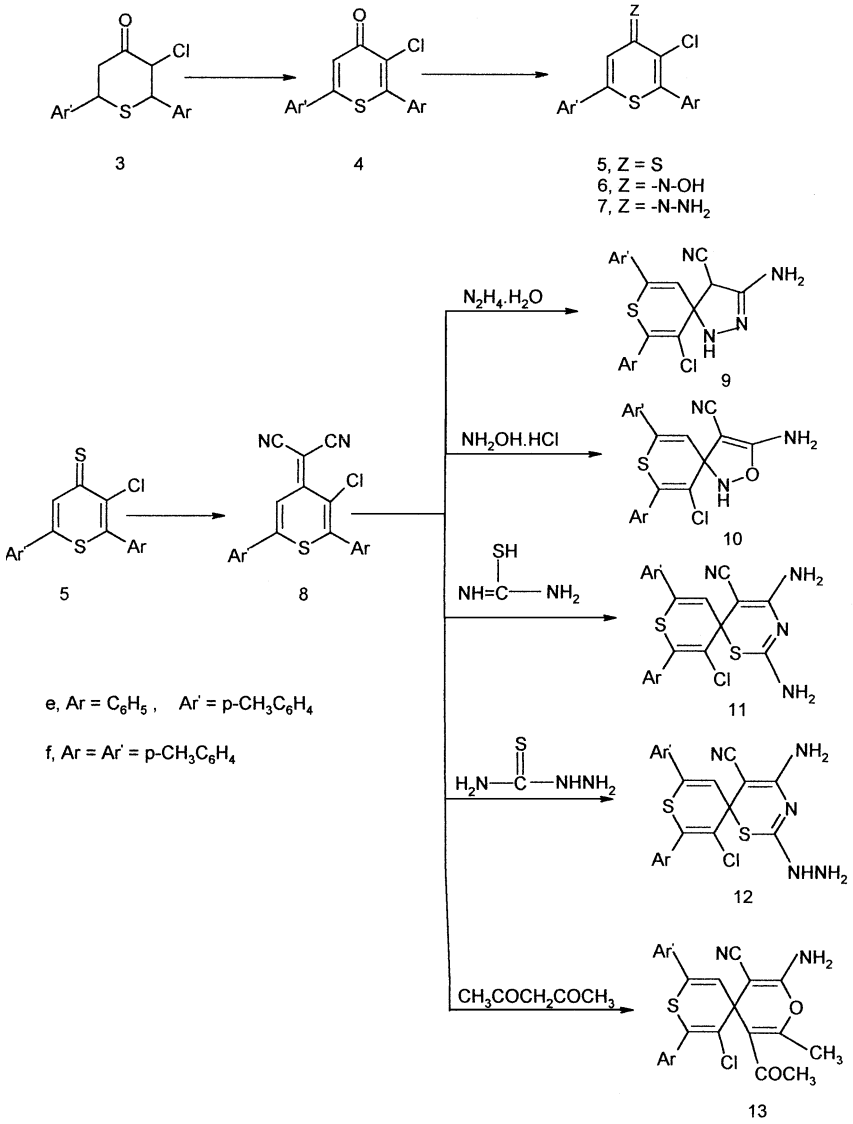
	Ar	Ar'	X	Y
a,	C_6H_5	C_6H_5	H	H
b,	C_6H_5	C_6H_5	Cl	H
c,	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	Cl	Cl
d,	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	Cl	H
e,	C_6H_5	p-$CH_3C_6H_4$	H	H
f,	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	H	H

SCHEME 1

present work, 3-chloro-2-phenyl-6-p-tolyl (**4e**) and 3-chloro-di-p-tolyl (**4f**)-4H-thiopyran-4-ones have been prepared in moderate yields from the dehydrogenation of 3-chloro-2-phenyl-6-p-tolyl (**3e**) and 3-chloro-2,6-di-p-tolyl (**3f**) –tetrahydro-4H-thiopyran-4-ones, prepared in the previous publication,[5] using phosphorus pentachloride in dry benzene (Scheme 2).

RESULTS AND DISCUSSION

The structure of the newly prepared 3-chloro-thiopyran-4-ones **4e,f** (Scheme 2), where established from their spectral and analytical data (Tables I and II). The IR spectra showed a strong carbonyl absorption



SCHEME 2

in the range 1645–1662 cm^{-1}, while their ^{1}H-NMR spectra showed beside other characteristics, a singlet for H-5 proton at 7.06–7.20 δ. Further weight was added to the structure of 3-chloro-thiopyrones **4e,f** by study of their electron impact mass spectra. These compounds gave a

TABLE I Spectroscopic Data of Compounds **4–13**

Comp. no.	IR (KBr) ν cm^{-1}/ ^{1}H-NMR δ (ppm)
4e	IR: ν = 2932 (CH—Aliphatic), 1662 (C═O), 1595 (C═C); ^{1}HNMR: ($CDCl_3$): δ = 7.58 (m, 9H, Aromatic) 7.06 (s, 1H, H-5), 2.36 (s, 3, CH_3).
4f	IR: ν = 2946 (CH—Aliphatic), 1645 (C═O), 1590 (C═C); ^{1}HNMR: ($CDCl_3$): δ = 7.45 (m, 8H, Aromatic) 7.20 (s, 1H, H-5), 2.42 (s, 6H, $2CH_3$).
5e	IR: ν = 2920 (CH—Aliphatic), 1432 (C═S), 1588 (C═C); ^{1}HNMR: ($CDCl_3$): δ = 7.42 (m, 9H, Aromatic), 7.88 (s, 1H, H-5), 2.28 (s, 3H, CH_3).
5f	IR: ν = 2898 (CH—Aliphatic), 1450 (C═S), 1592 (C═C); ^{1}HNMR: ($CDCl_3$): δ = 7.62 (m, 8H, Aromatic), 8.36 (s, 1H, H-5), 2.48 (s, 6H, $2CH_3$).
6e	IR: ν = 3328 (OH), 2936 (CH—Aliphatic), 1622 (C═N), ^{1}HNMR ($CDCl_3$): δ = 9.24 (s, 1H, OH), 7.42 (m, 9H, Aromatic), 7.19 (s, 1H, H-5), 2.40 (s, 3H, CH_3).
6f	IR: ν = 3435 (OH), 2920 (CH—Aliphatic), 1618 (C═N), ^{1}HNMR ($CDCl_3$): δ = 8.88 (s, 1H, OH), 7.38 (m, 8H, Aromatic), 7.20 (s, 1H, H-5), 2.44 (s, 6H, $2CH_3$).
7e	IR: ν = 2300, 3216 (NH_2), 2886 (CH—Aliphatic), 1620 (C═N), ^{1}HNMR ($CDCl_3$): δ = 7.48 (m, 9H, Aromatic), 7.22 (s, 1H, H-5), 5.48 (s, 2H, NH_2), 2.30 (s, 3H, CH_3).
7f	IR: ν = 3318, 3220 (NH_2), 2922 (CH—Aliphatic), 1625 (C═N), ^{1}HNMR ($CDCl_3$): δ = 7.52 (m, 8H, Aromatic), 7.19 (s, 1H, H-5), 6.00 (s, 2H, NH_2), 2.42 (s, 6H, $2CH_3$).
8e	IR: ν = 2920 (CH—Aliphatic), 2196 (C≡N), 1586 (C═C); ^{1}HNMR ($CDCl_3$): δ = 7.56 (m, 9H, Aromatic), 6.92 (s, 1H, H-5), 2.38 (s, 3H, CH_3).
8f	IR: ν = 2892 (CH—Aliphatic), 2188 (C≡N), 1596 (C═C); ^{1}HNMR ($CDCl_3$): δ = 7.58 (m, 8H, Aromatic), 7.12 (s, 1H, H-5), 2.42 (s, 6H, $2CH_3$).
9e	IR: ν = 3386, 3332, 3220 (NH_2 + NH), 2920 (CH—Aliphatic), 2192 (C≡N), 1608 (C═C); ^{1}HNMR($CDCl_3$): δ = 10.92 (br, 1H, NH), 7.52 (m, 9H, Aromatic), 7.12 (s, 1H, H-5), 5.60 (br, 2H, NH_2), 2.38 (s, 3H, CH_3).
9f	IR: ν = 3362, 3346, 3262 (NH_2 + NH), 2868 (CH—Aliphatic), 2194 (C≡N), 1612 (C═C); ^{1}HNMR ($CDCl_3$): δ = 11.22 (br, 1H, NH), 7.58 (m, 8H, Aromatic), 7.16 (s, 1H, H-5), 5.82 (s, 2H, NH_2), 2.42 (s, 6H, $2CH_3$).
10e	IR: ν = 3386, 3350, 3262 (NH_2 + NH), 2960 (CH—Aliphatic), 2190 (C≡N), 1608 (C═C); ^{1}HNMR (DMSO-d_6): δ = 11.22 (br, 1H, NH), 7.58 (m, 9H, Aromatic), 7.12 (s, 1H, H-5), 5.82 (br, 2H, NH_2), 2.32 (s, 3H, CH_3).
10f	IR: ν = 3392, 3370, 3256 (NH_2 + NH), 2896 (CH—Aliphatic), 2202 (C≡N), 1612 (C═C); ^{1}HNMR (DMSO-d_6): δ = 10.98 (br, 1H, NH), 7.48 (m, 8H, Aromatic), 7.08 (s, 1H, H-5), 6.00 (s, 2H, NH_2), 2.42 (s, 6H, $2CH_3$)
11e	IR: ν = 3392, 3342 (NH_2), 2976 (CH—Aliphatic), 2190 (C═N), 1630 (C═N); 1598 (C═C); ^{1}HNMR (DMSO-d_6): δ = 7.54 (m, 9H, Aromatic), 7.16 (s, 1H, H-5), 5.46 (br, 4H, NH_2), 2.36 (s, 3H, CH_3).
11f	IR: ν = 3378, 3336 (NH_2), 2896 (CH—Aliphatic), 2182 (C═N), 1622 (C═N); 1602 (C═C); ^{1}HNMR (DMSO-d_6): δ = 7.56 (m, 8H, Aromatic), 7.08 (s, 1H, H-5), 2.82 (br, 4H, $2NH_2$), 2.40 (s, 6H, $2CH_3$).
12e	IR: ν = 3388, 3336, 3246 (NH_2 + NH), 2960 (CH—Aliphatic), 2186 (C≡N), 1636 (C═N); 1608 (C═C); ^{1}HNMR ($CDCl_3$): δ = 11.12 (br, 1H, NH), 2.54 (m, 9H, Aromatic), 6.98 (s, 1H, H-5), 5.46 (br, 4H, $2NH_2$), 2.38 (s, 3H, CH_3).
12f	IR: ν = 3378, 3342, 3258 (NH_2 + NH), 2982 (CH—Aliphatic), 2179 (C≡N), 1628 (C═N); 1598 (C═C); ^{1}HNMR ($CDCl_3$): δ = 10.98 (s, 1H, NH), 7.48 (m, 8H, Aromatic), 7.12 (s, 1H, H-5), 5.68 (br, 4H, $2NH_2$), 2.42 (s, 6H, $2CH_3$).
13e	IR: ν = 3396, 3332 (NH_2), 2938 (CH—Aliphatic), 2188 (C═N), 1674 (C═O); 1602 (C═C); ^{1}HNMR (DMSO-d_6): δ = 7.52 (m, 9H, Aromatic), 6.98 (s, 1H, H-5), 5.62 (br, 2H, NH_2), 2.32 (s, 3H, CH_3), 2.22 (s, 3H, $COCH_3$).
13f	IR: ν = 3388, 3362 (NH_2), 2962, 2932 (CH—Aliphatic), 2164 (C≡N), 1670 (C═O); 1612 (C═C); ^{1}HNMR (DMSO-d_6): δ = 7.58 (m, 8H, Aromatic), 7.16 (s, 1H, H-5), 5.92 (br, 2H, NH_2), 2.38 (s, 6H, $2CH_3$), 2.20 (s, 3H, $COCH_3$).

TABLE II Physical and Analytical Data of Compounds **4–13**

Comp. no.	m.p.°C	Yield%	Formula	Calculated/Found %				
				C	H	N	S	Cl
4e	142	62	$C_{18}H_{13}ClOS$	69.12	4.16	—	10.24	11.3
				69.23	4.30	—	10.16	11.18
4f	166	58	$C_{19}H_{15}ClOS$	69.98	4.59	—	9.80	10.87
				69.68	4.38	—	9.72	10.70
5e	171	53	$C_{18}H_{13}ClS_2$	65.75	3.92	—	19.48	10.81
				65.52	3.92	—	19.32	10.86
5f	182	56	$C_{19}H_{15}ClS_2$	66.57	4.38	—	18.69	10.36
				66.38	4.52	—	18.86	10.32
6e	148	70	$C_{18}H_{14}ClNOS$	65.95	4.27	4.27	9.77	10.84
				65.73	4.29	4.28	9.70	10.94
6f	156	71	$C_{19}H_{16}ClNOS$	66.76	4.69	4.10	9.37	10.39
				66.80	4.86	4.32	9.40	10.18
7e	172	76	$C_{18}H_{15}ClN_2S$	66.16	4.59	8.57	9.80	10.87
				65.98	4.64	8.52	9.64	10.92
7f	183	80	$C_{19}H_{17}ClN_2S$	66.96	4.99	8.22	9.40	10.43
				66.70	5.02	8.16	9.38	10.46
8e	198	68	$C_{21}H_{13}ClN_2S$	69.90	3.61	7.77	8.88	9.85
				69.78	3.42	7.61	8.92	9.68
8f	160	70	$C_{22}H_{15}ClN_2S$	70.49	4.01	7.48	8.54	9.48
				70.50	4.22	7.28	8.50	9.62
9e	226	77	$C_{21}H_{17}ClN_4S$	64.20	4.33	14.27	8.15	9.04
				64.38	4.16	14.22	8.30	9.12
9f	216	82	$C_{22}H_{19}ClN_4S$	64.94	4.67	13.78	7.87	8.73
				64.72	4.51	13.62	7.85	8.88
10e	186	69	$C_{21}H_{16}ClN_3OS$	64.04	4.07	10.67	8.13	9.02
				63.96	4.12	10.56	8.06	9.12
10f	202	71	$C_{22}H_{18}ClN_3OS$	63.23	4.31	10.06	7.66	8.50
				63.46	4.30	10.21	7.52	8.70
11e	194	68	$C_{22}H_{17}ClN_4S_2$	60.48	3.89	12.83	14.66	8.13
				60.36	3.91	12.68	14.62	8.16
11f	212	66	$C_{23}H_{19}ClN_4S_2$	61.26	4.22	12.43	14.21	7.88
				61.32	4.10	12.41	14.21	7.90
12e	202	61	$C_{22}H_{18}ClN_5S_2$	58.47	3.99	15.50	14.17	7.86
				58.28	3.71	15.76	14.32	7.68
12f	221	63	$C_{23}H_{20}ClN_5S_2$	59.29	4.30	15.04	13.75	7.63
				59.40	4.32	15.16	13.80	7.15
13e	188	58	$C_{26}H_{21}ClN_2O_2S$	67.46	4.54	6.05	6.92	7.68
				66.96	4.11	6.23	6.90	7.72
13f	212	62	$C_{27}H_{23}ClN_2O_2S$	68.28	4.85	5.90	6.74	7.48
				67.76	4.81	6.34	6.72	7.61

moderately intense molecular ion peaks followed by a carbonyl lost to give the base peak fragment, which undergo a subsequent fragmentation characteristic to 2,5-diaryl thiophens[6] (Experimental section). Treatment of **4e,f** with phosphorus pentasulfide in dry benzene

afforded the corresponding 3-chloro-thiopyran-4-thiones **5e,f**. On the other hand, the reaction of 3-chloro-thiopyran-4-ones **4e,f** as well as the thiones **5e,f** with hydroxylamine hydrochloride in ethanol led to the formation of the respective oximes **6e,f** (Scheme 2). The IR spectra of the oximes **6e,f** are characterized by a strong intensity C=N absorption at 1618–1622 cm^{-1} as well as a broad hydroxyl absorption at 3328–3435 cm^{-1}. On the other hand the ^{1}H-NMR spectra of the thiones **5e,f** showed an downfield shift in the resonance of H-5 protons (7.88–8.36 δ) comparing to the parent 3-chloro-thiopyran-4-ones **4e,f**. Similar deshielding on replacement of carbonyl with thiocarbonyl were also observed for other 4H-pyran-4-thiones.[7,8] Such significant deshielding in the resonance of H-5 protons of **5e,f** can be attributed to the increased magnetic anisotropy of the thione over carbonyl. On the other hand, the reaction of 3-chloro- thiopyran-4-ones **4e,f** with hydrazine hydrate gave the corresponding hydrazone derivatives **7e,f**. The structures of the above hydrazones were fully characterized by their spectral (IR, ^{1}H-NMR) and analytical data (Tables I and II). Also, 3-chloro-2-phenyl-6-p-tolyl and 3-chloro-2,6-di-p-tolyl-4-thiopyrylidenemalononitriles, **8e,f**, were synthesized from the reaction of 3-chloro-2-phenyl-6-p-tolyl and 3-chloro-2,6-di-p-tolyl-4H-thiopyran-ones, **4e,f** or their thiones **5e,f** with malononitrile in refluxing ethanol in the present of triethylamine, respectively (Scheme 2). The structures of 3-chloro-thiopyrylidenemalononitriles, **8e,f** are confirmed from their spectral and analytical data (Tables I and II). The IR showed a moderately C≡N absorption in the range 2188–2196 cm^{-1}, while their ^{1}HNMR spectra showed beside other characteristics, a singlet at 6.92–7.12 δ for H-5 protons of thiopyran ring. Treatment of **8e,f** with hydrazine hydrate, hydroxylamine hydrochloride, thiourea, or thiosemicarbazide in refluxing ethanol in the present of pipredine afforded the corresponding 3-chloro- spirothiopyran derivatives of pyrazole, **9e,f**, isoxazole, **10e,f**, 1,3-thiazines, **11e,f** and **12e,f** respectively (Scheme 2). The reaction involve the addition of the amino or marcapto groups at the ethylenic double bond and then nucleophilic attack of the amino or imino group to give the cyclized spiro compounds.[9] Also, the reaction of 3-chlorothiopyrylidenemalononitriles **8e,f** with active methylene compound, acetylacetone, in ethanol in the present of pipredine gave the spirothiopyran derivatives **13e,f** (Scheme 2). A carbanion formation is assumed in these reactions followed by nucleophilic addition at the ethylenic double bond and cyclization to give the spirothiopyran derivatives[9] **13e,f**. All spirothiopyran derivatives, **9e, f–13e, f** were confirmed from their spectral and analytical data (Tables I and II).

EXPERIMENTAL

Elemental analysis were preformed on a Perkin-Elmer 240 microanalyzer. Melting points were recorded on a Kofler Block and are uncorrected. Infrared spectra were measured with a Unicam SP 1025 spectrophotometer for KBr pellets. Theb ^{1}H-NMR spectra were recorded on Jeol Lambada-500 MHz spectrometer using TMS as internal standard. Mass spectra were recorded at 70 eV with an AEI MS-9 spectrometer coupled to a DS-50 data System using a direct insertion probe for introduction of samples.

Synthesis of 3-Chloro-2,6-diaryl-4H-Thiopyran-4-ones 4e,f (Tables I and II)

A solution of 3-chloro-2,6-diaryl-tetrahydrothiopyran-4-ones,[5] **3e,f** (55 mmol) in dry benzene (370 ml) was treated with phosphorus pentachloride (40 gm; 190 mmol) in one portion, with shaking and cooling under the tap, and the mixture was heated under reflux for one hour. The reaction mixture was treated as described earlier[3] to give **4e,f** which crystallized from methanol as needles. MS: m/z (relative abundance) **4e**: M^+ 314 (22), 312 (61), 284 (100), 248 (16), 148 (29), 135 (23), 91 (12), 77 (16).

Synthesis of 3-Chloro-2,6-diaryl-4H-Thiopyran-4-thiones 5e,f (Tables I and II)

A solution of 3-chloro-thiopyrones **4e,f** (2 mmol) in dry benzene (30 ml) was heated under reflux with phosphorus pentasulfide (14 mmol). The reaction mixture was worked up as described earlier.[3] The isolated thiopyran-4-thiones **5e,f** was crystallized from benzene-petroleum ether (b.p 40–60°C) as brown needles.

Synthesis of 3-Chloro-2,6-diaryl-4H-Thiopyran-4-one Oximes 6e,f (Tables I and II)

A solution of 3-chloro-thopyrones **4e,f** or their thiones **5e,f** (2 mmol) in ethanol (40 ml) was heated under reflux with hydroxylamine hydrochloride (8 mmol) and sodium acetate (8 mmol) in water (2 ml) for 3 h. The reaction mixture was then poured into ice-cold water to give the corresponding oximes **6e,f** which crystallized from ethanol as needles. MS: m/z (relative abundance) **6e**: M^+ 329 (36), 327 (100), 311 (14), 286 (26), 275 (35), 262 (11), 229 (43), 150 (23), 91 (32), 77 (18).

Synthesis of 3-Chloro-2,6-diaryl-4H-Thiopyran-4-one Hydrazones 7e,f (Tables I and II)

A solution of the 3-chloro-thiopyran-4-ones **4e,f** (2 mmol) in ethanol (20 ml) was heated under reflux with hydrazine hydrate (2 ml) for 2 h. The reaction mixture was worked up as described earlier and crystallized from methanol as needles. MS: M/z (relative abundance) **7e**: 328 (34), 326 (100), 311 (16), 297 (22), 284 (20), 262 (25), 229 (17), 216 (22), 189 (13), 149 (24), 91 (11), 77 (8).

Synthesis of 3-Chloro-4-Thiopyrylidenemalononitriles 8e,f (Tables I and II)

3-Chloro-thiopyran-4-ones **4e,f** was added to an equimolar amount of malononitrile in ethanol (40 ml) and few drops of triethylamine. The reaction mixture was refluxed for 5 h, concentrated and cold to give **8e,f** which crystallized from ethanol . MS: m/z (relative abundance) **8b**: M^+ 377 (14), 375 (51), 359 (22), 323 (12), 299 (100), 263 (32), 172 (25), 96 (27), 91 (42).

Synthesis of 3-Chloro-Spirothiopyran Derivatives 9e,f—12e,f (Tables I and II). General Procedure

A solution of 3-chloro-4-thiopyrylidenemalononitriles **8e,f** (2 mmol) in ethanol (40 ml) was treated with equimolar amount of hydrazine hydrate or hydroxylamine hydrochloride or thiourea or thiosemicarbazide and few drops of pipredene.

The reaction mixture was refluxed for 4 h, concentrated, cooled, and filtered off and recrystallized from ethanol. MS: m/z (relative abundance) **9e**: M^+ 394 (12), 392 (38), 376 (22), 350 (13), 326 (25), 295 (28), 283 (100), 218 (27), 206 (31), 174 (37), 91 (11), 77 (8); **10e**: 395 (13), 393 (38), 377 (25), 351 (21), 327 (11), 311 (15), 296 (7), 284 (100), 252 (23), 207 (11),175 (21), 91 (14), 77 (19); **11e**: 437 (15), 435 (44), 419 (21), 393 (23), 377 (27), 253 (11), 339 (17), 307 (32), 295 (100), 218 (21), 186 (23), 95 (7), 91 (20), 77 (8).

Synthesis of 3-Chloro-Spirothiopyran Derivative 13e,f (Tables I and II)

3-Chloro-thiopyrylidenemalononitriles **8e,f** (2 mmol) was added to a stirred mixture of equimolar amount of acetylacetone in ethanol (40 ml) and a few drops of pipredine. The reaction mixture was refluxed for 4 h, concentrated, cooled, and the separated solid was filtered off and

crystallized from ethanol. MS: m/z (relative abundance) **13e**: M^+ 462 (11), 460 (32), 444 (23), 428 (11), 402 (23), 359 (27), 333 (15), 309 (18), 285 (25), 273 (100), 241 (31), 196 (23), 150 (34), 91 (26), 77 (12).

REFERENCES

[1] I. R. Wilt, G. A. Rynolds, and J. A. Van Allan, *Tetrahedron*, **29,** 795 (1973).
[2] A. H. Ingall, *Comprehensive Heterocyclic Chemistry*, **3,** 99, 885 (1984).
[3] F. Arndt, P. Nachtwey, and J. Push, *Ber*., **58B,** 1633 (1925).
[4] A. M. El-Ghanam, *AFINIDAD*, **453,** 386 (1994).
[5] A. M. El-Ghanam, *Phosphorus, Sulfur, and Silicon*, **108,** 93 (1996).
[6] J. H. Bowia, R. G. Cooks, S.-O. Lawesson, and C. Nolde, *J. Chem. Soc*., **B,** 616 (1967).
[7] F. M. Dean, J. Coodchild, A. W. Hill, S. Murray, and A. Zahman, *J. Chem. Soc.*, *Perkin Trans. I*, 1335 (1975).
[8] I. E. El-Kholy, M. M. Mishrikey, and H. M. Faid-Alla, *J. Heterocycl. Chem*., **14,** 845 (1977).
[9] A. M. El-Ghanam, *Phosphorus, Sulfur, and Silicon*, **178,** 863 (2003).