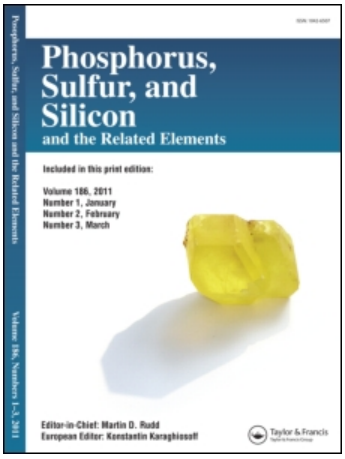

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A NEW SYNTHESIS OF 6-THIATHIOPHTHENES FROM ACETYLENIC β-DIKETONES

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A NEW SYNTHESIS OF 6-THIATHIOPHTHENES FROM ACETYLENIC β-DIKETONES

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A new method for the synthesis of 2,5-diaryl-6-thiathiophthenes is described involving the reaction of 1,5-diarylpent-1-yne-3,5-diones with phosphorus pentasulfide. The reaction of 3-chloro-6-thiathiophthenes with hydrazine hydrate gave pyrazole derivatives. Nitration of the 6-thiathiophthenes afforded the corresponding 4-nitro-1-oxa-6,6a-dithia-2-azapentalenes.

Key words: Acetylenic β-diketones; thiathiophthenes and dithia-2-azapentalenes; synthesis and structure elucidation.

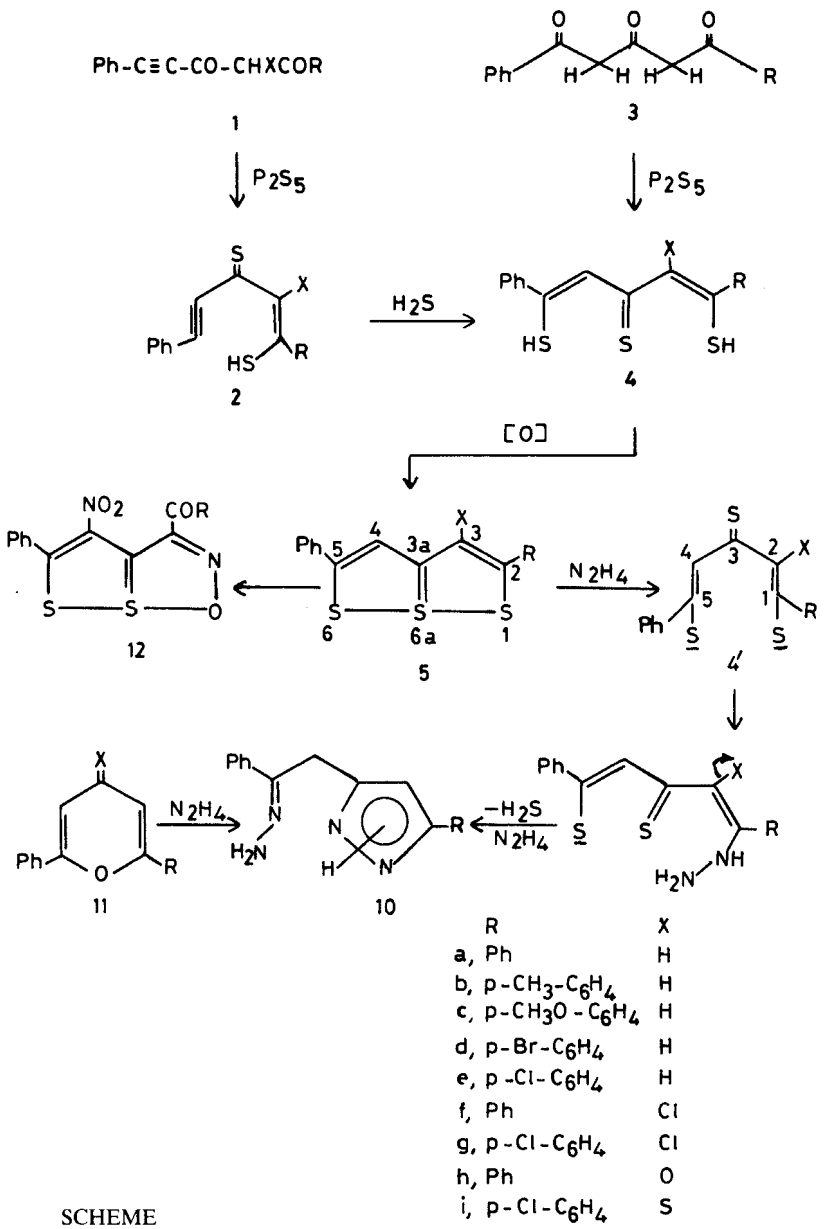
Thiathiophthenes derivatives have been used as antioxidants in lubricating oils.[1] They show herbicidal activity and may be used to reduce unwanted dicotyledenous plant growth and are also useful as dyestuffs for certain fibers.[2]

A considerable quantity of work has been carried out on the bonding[3,4] and structure[5–10] of thiathiophthenes. However, the chemistry of this important heterocycle has been little explored. Several methods are reported for the synthesis of 2,5-diaryl-6-thiathiophthenes.[8,11–20] In the present study, a new route for the synthesis of the latter is described. A series of 2-aryl-5-phenyl-6-thiathiophthenes (**5a–g**) were obtained from 1,5-diarylpent-1-yne-3,5-diones[21,22] (**1a–g**) and phosphorus pentasulfide. Their formation is assumed to proceed by addition of hydrogen sulfide on the triple bond of the 1,5-diarylpent-l-yne-3,5-dithiones (**2**) initially formed leading to the trithiones **4**. Subsequent oxidation of the latter affords the 6-thiathiophthenes **5**. The intermediacy of the trithiones in the above reaction is supported by the fact that the 6-thiathiophthenes **5a,c** are reported[13,15] to be formed from the reaction of the triketones **3a,c** and phosphorus pentasulfide. Moreover, **5b** was also obtained, in the present study, by the same route (Scheme).

Evidently, the above reaction is among the best routes for the synthesis of thiathiophthenes **5** since in most of the alternative methods poor yields are reported.

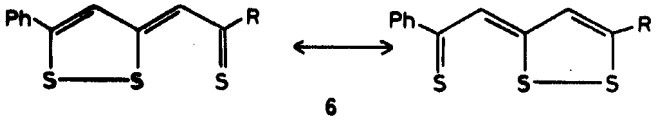
The structure of the 6-thiathiophthenes was confirmed from their analytical and spectral data. The reported NMR spectrum of 2,5-diphenyl-6-thiathiophthene in $CDCl_3$ showed a singlet at δ 8.22 for H-3 and H-4 protons.[23] In the present study, the spectra of **5a–g** exhibited these protons at δ 8.20–8.69 (Table I). Similar to the ^{13}CNMR spectrum of 2,5-diphenyl-6-thiathiophthene,[24] 2-*p*-bromophenyl-5-phenyl-6-thiathiophthene (**5d**) gave five signals for the 6-thiathiophthene ring carbons besides six signals for phenyl and *p*-bromophenyl carbons (cf. Experimental).

The electronic spectra of the 6-thiathiophthenes **5a–g** in methanol gave three absorption maxima in the ranges 251–255, 294–314 and 504–512 nm, besides a shoulder in the region 346–360 nm (Table I). The above data correlated well with that reported for 2,5-diphenyl[19]- and 2-*p*-methoxyphenyl-5-phenyl-6-thiathiophthenes.[17] The fact that the position as well as the intensity of these absorptions are



SCHEME

not affected in the presence of 0.1 M sodium methoxide or 0.1 M sulfuric acid confirms the bicyclic structure **5** of these compounds rather than structure **6**.



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The structure of the 6-thiathiophthenes **5** was further confirmed from their mass spectral data. The relative intensities of the most prominent peaks in their spectra

TABLE I

Characterization data of the 6-thiathiophthenes and 1-oxa-6,6a-dithia-2-azapentalenes

Compd.	IR (cm^{-1})		UV λ_{max}, nm(ϵ)	NMR (δ /ppm)**			Relative intensity of				
	C=O	NO_2		H-3&H-4 (s)	Ar-H (m)	Others (s)	M^+	(M-1)	7	8	9
5a			252 304 350* 510 (51316)(21758)(6568)(14779)	8.69	7.56		75	43	11	100	100
5b			251 310 352* 508 (61474)(25149)(10246)(18163)	8.66	7.63	2.38 (CH_3)	100	55	14	45	47
5c			255 314 360* 512 (54474)(20868)(8688)(15024)	8.62	7.50	3.50 (OCH_3)	46	45	13	78	96
5d			251 309 352* 510 (42074)(22579)(7498)(13164)	8.20	7.66						
5e			252 308 350* 512 (50474)(25230)(8232)(14239)	8.68	7.65		35,100	20,50	6,12	84	25,91
5f			253 300 350* 502 (48373)(23389)(9794)(16657)	8.60	7.64		3,13	3,8	6	45	45
5g			251 294 346* 504 (47218)(19382)(7794)(15657)	8.53	7.59		3,16	5,7	3,7	55	4,12
12a	1710	1345,1535	258 305* 475 (30302)(13789)(2632)		7.93						
12b	1707	1355,1545	254 298* 470 (33125)(12051)(2795)		8.00	2.48 (CH_3)					
12d	1710	1355,1541	260 306* 478 (29789)(15984)(2906)		8.01						

* Shoulder. ** The solvents for NMR spectra were: $CDCl_3$ for 5d,f,g; DMSO-d_6 for 5a-c,e, 12a,b,d.

are listed in Table I. The compounds studied **5a–c, e–g** gave a strong molecular ion peaks which were the base peaks in the case of **5b** and **5e**. A major fragmentation route is the elimination of hydrogen radical giving the (M-1) species.[25] It is worthy to mention that the base peak in the spectra of **5f, g** was the (M-Cl) species. The ease of loss of a halogen radical had been also reported in the mass spectra of other halo-heterocyclic systems.[26–29] Loss of sulfur atom from the (M—X; X=H or Cl) species gave rise to an intense peak which may be formulated as the 4**H**-thiopyran-4-thione cation **7**. Similar to the mass spectra of other 6-thiathiophthenes,[25] an important fragmentation route involves the formation of the two species **8** ($PhC{\equiv}S^+$) and **9** ($R{-}C{\equiv}S^+$).

6-Thiathiophthenes are generally inert towards carbonyl reagents.[30] However, in certain cases, they undergo ring opening by nucleophilic reagents with subsequent recyclization to new cyclic compounds.[31–33] In the present study, the reaction of **5f, g** with hydrazine hydrate in ethanol gave 5(3)-aryl-3(5)-(2-hydrazono-2-phenylethyl)pyrazoles (**10f, g**). This reaction is assumed to involve ring opening to the resonance-stabilized enolate[18] **4′**, followed by attack of hydrazine molecule at C-1 of the trithione anion **4′** and subsequent cyclization to the pyrazole **10** with the expulsion of chlorine atom. The structure of the above pyrazoles **10f, g** was confirmed by their formation from the reaction of hydrazine hydrate with the pyrone[34] **11h** and thiopyrone **11i**, respectively (Scheme).

It is to be noted that the presence of chlorine at position 3 of the 6-thiathiophthene greatly facilitated the nucleophilic attack on the ring since treatment of the non-chlorinated members **5** with methylamine, hydrazine or potassium hydroxide under various conditions gave unchanged material.

Little work has been reported on the electrophilic attack on 6-thiathiophthenes: formylation of 2-*p*-methoxyphenyl-5-phenyl-6-thiathiophthene affords the 3-formyl derivative,[35] while 2-phenyl-6-thiathiophthenes yield the 4-formyl analogue.[36] 2-Methylthio-5-phenyl-6-thiathiophthene undergoes nitration or bromination in the 3-position.[37] It has been mentioned that nitration or nitrosation of 2,5-diphenyl-6-thiathiophthene gave 3-benzoyl-5-phenyl-1-oxa-6,6a-dithia-2-azapentalene.[37] However, in the present study, nitration of **5a, b, d**, under more vigorous conditions, gave 3-aroyl-4-nitro-5-phenyl-1-oxa-6,6a-dithia-2-azapentalenes (**12a,b,d**). The infrared spectra of these compounds showed, besides the carbonyl absorption at 1707–1710 cm^{-1}, two absorptions at 1345–1355 and 1535–1545 cm^{-1} for the nitro group.[38] Their electronic spectra exhibited three absorption maxima in the regions 254–260, 298–306 (sh) and 470–478 nm (Table I).

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 and electronic spectra were measured with a Unicam SP 1750 spectrophotometer for solutions in methanol. The NMR spectra were recorded 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. The ^{13}CNMR spectrum was recorded on a Joel JNM-FX 100 NMR spectrometer.

*2-Aryl-5-phenyl-(***5a-e***)- and 2-Aryl-3-chloro-5-phenyl-(***5f, g***)-6-thiathiophthenes (Tables I, II)*: A solution of **1a–g** (0.8 g; 0.0032 mol) in dry xylene (30 mL) was refluxed with phosphorus pentasulfide (2.0 g; 0.0089 mol) for 1 h. The reaction mixture was washed with ammonium sulfide, water, dried

TABLE II

Analytical data of the 6-thiathiophthenes and 1-oxa-6,6a-dithia-2-azapentalenes

Compd.	m.p. (°C)	Yield (%)	Molecular Formula	% Found/Required C	H	N	S	X
5a	172	78	$C_{17}H_{12}S_3$	65.5 (65.4	3.8 3.9		30.9 30.8	)
5b	180	80	$C_{18}H_{14}S_3$	66.5 (66.3	4.4 4.3		29.7 29.5	)
5c	192	82	$C_{18}H_{14}OS_3$	63.3 (63.2	4.3 4.1		28.0 28.1	)
5d	178	80	$C_{17}H_{11}BrS_3$	52.1 (52.2	3.0 2.8		24.5 24.6	20.7 20.5)
5e	170	85	$C_{17}H_{11}ClS_3$	59.0 (58.9	3.3 3.2		27.9 27.7	10.2 10.3)
5f	170	79	$C_{17}H_{11}ClS_3$	59.0 (58.9	3.3 3.2		27.5 27.7	10.5 10.3)
5g	200	86	$C_{17}H_{10}Cl_2S_3$	53.8 (53.7	2.8 2.6		25.2 25.3	18.3 18.4)
10g	180	70	$C_{17}H_{15}ClN_4$	65.5 (65.7	4.9 4.8	18.1 18.0		11.2 11.4)
12a	162	70	$C_{17}H_{10}N_2O_4S_2$	55.0 (55.1	2.7 2.7	7.6 7.6	17.1 17.3	)
12b	165	75	$C_{18}H_{12}N_2O_4S_2$	56.5 (56.3	3.2 3.1	7.4 7.3	16.9 16.7	)
12d	170	80	$C_{17}H_9BrN_2O_4S_2$	45.5 (45.4	1.9 2.0	6.0 6.2	14.2 14.3	17.6 17.8)

(Na_2SO_4) and evaporated. The isolated 6-thiathiophthenes **5a**–g were crystallized from benzene in reddish brown plates. The 6-thiathiophthenes **5a**–**c** were found to be completely identical (m.p. mixed m.p., IR and NMR spectra) with authentic samples prepared from the reaction of 1,5-diarylpent-1,3,5-triones (**3a**–**c**) with phosphorus pentasulfide. ^{13}CNMR spectrum of **5d** (δ/ppm) ($CDCl_3$): 174.9 (C-2), 124.2 (C-3), 178.2 (C-3a), 123.5 (C-4), 174.3 (C-5), 157.1, 126.2, 127.6 and 130.7 for phenyl and 157.1, 126.2, 129.2 and 135.9 for *p*-bromophenyl carbons.

*5(3)-Aryl-3(5)-(2-hydrazono-2-phenylethyl)pyrazoles (**10f, g**)*: A solution of **5f, g** (0.5 g; 0.0016 mol) in 95% ethanol (10 mL) was refluxed with 99% hydrazine hydrate (1 mL; 0.0199 mol) for 3 h. After removal of most of the solvent and dilution with water, the separated pyrazoles **10f, g** were crystallized from benzene in needles. The pyrazole **10f** (80% yield) was found to be completely identical (m.p. mixed m.p., IR and NMR spectra) with authentic sample prepared from 2,6-diphenyl-4**H**-pyran-4-one (**11h**) with hydrazine hydrate.[34] IR, ν_{max} (cm^{-1}) for **10g**: 1654 (C = N, hydrazone), 1598 (C = N, pyrazole ring), 3205, 3330 (NH_2). NMR (δ/ppm) (DMSO-d_6): 3.98 (s, CH_2), 6.39 (s, H-4), 6.70 (s, NH_2), 12.90 (s, NH), 7.60 (m, Ar-H). MS: m/z (relative abundance) M^+ 312, 310 (4, 15), 311, 309 (12, 40), 296, 294 (35, 100), 193, 191 (5, 16), 151, 149 (7, 22), 119 (30), 77 (18).

The pyrazole **10g** was also prepared (75%) from 2-*p*-chlorophenyl-6-phenyl-4**H**-pyran-4-thione (**11i**) and 99% hydrazine hydrate in ethanol as described earlier.[39]

*3-Aroyl-4-nitro-5-phenyl-1-oxa-6,6a-dithia-2-azapentalenes (**12a, b, d**) (Tables I, II)*: A solution of **5a, b, d** (0.7 g; 0.0022 mol) in glacial acetic acid (12 mL) was refluxed with nitrating mixture (3 mL, 1 HNO_3: 1 H_2SO_4) for 3–5 h. The reaction mixture was then poured into ice-cold water and the yellow solid **12a, b, d** which separated crystallized from methanol in yellow needles.

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