

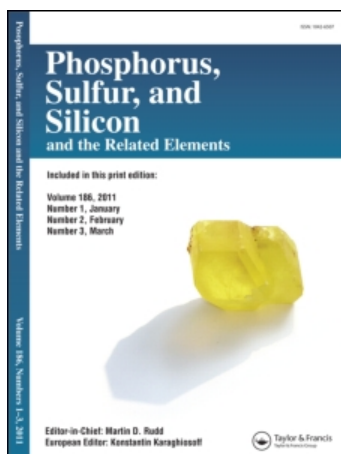
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A NEW SYNTHESIS OF 6-THIATHIOPHTHENES FROM ACETYLENIC β -DIKETONES

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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.

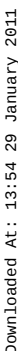
Thiathiophthenes derivatives have been used as antioxidants in lubricating oils.¹ They show herbicidal activity and may be used to reduce unwanted dicotyledenous plant growth and are also useful as dyestuffs for certain fibers.²

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-1-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.

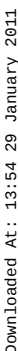
The structure of the 6-thiathiophthenes was confirmed from their analytical and spectral data. The reported NMR spectrum of 2,5-diphenyl-6-thiathiophthene in CDCl₃ showed a singlet at δ 8.22 for H-3 and H-4 protons.²³ In the present study, the spectra of **5a–g** exhibited these protons at δ 8.20–8.69 (Table I). Similar to the ¹³CNMR 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-diphenyl¹⁹- and 2-*p*-methoxyphenyl-5-phenyl-6-thiathiophthenes.¹⁷ The fact that the position as well as the intensity of these absorptions are



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TABLE I
Characterization data of the 6-thiathiophenes and 1-oxa-6,6a-dithia-2-azapentalenes

Compd.	IR (cm ⁻¹)		UV $\lambda_{\max}$, nm (ε)	NMR (δ/ppm)**		Relative intensity of				
	C=O	NO ₂		H-3&H-4 (s)	Ar-H (m)	Others (s)	M ⁺ (N-1)	7	8	9
<u>5a</u>			252 304 350* 510 (51316)(21758)(6568)(14779)	8.69	7.56		75	43	11	100
<u>5b</u>			251 310 352* 508 (61474)(25149)(10246)(18163)	8.66	7.63	2.38 (CH ₃)	100	55	14	45
<u>5c</u>			255 314 360* 512 (54474)(20868)(8688)(15024)	8.62	7.50	3.50 (OCH ₃)	46	45	13	78
<u>5d</u>			251 309 352* 510 (42074)(22579)(7498)(13164)	8.20	7.66					
<u>5e</u>			252 308 350* 512 (50474)(25230)(8232)(14239)	8.68	7.65		35,100	20,50	6,12	84
<u>5f</u>			253 300 350* 502 (48373)(23389)(9794)(16657)	8.60	7.64		3,13	3,8	6	45
<u>5g</u>			251 294 346* 504 (47218)(19382)(7794)(15657)	8.53	7.59		3,16	5,7	3,7	55
<u>12a</u>	1710	1345,1535	258 305* 475 (30302)(13789)(2632)		7.93					
<u>12b</u>	1707	1355,1545	254 298* 470 (33125)(12051)(2795)		8.00	2.48 (CH ₃)				
<u>12d</u>	1710	1355,1541	260 306* 478 (29789)(15984)(2906)		8.01					

* Shoulder. ** The solvents for NMR spectra were: CDCl₃ for 5d, 5f, 5g; DMSO-d₆ for 5a-5c, 5e, 12a, 12b, 12d.

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 4H-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** ($\text{PhC}\equiv\text{S}^+$) and **9** ($\text{R}-\text{C}\equiv\text{S}^+$).

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 enolate¹⁸ **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 pyrone³⁴ **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-aryl-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 $1707\text{--}1710\text{ cm}^{-1}$, two absorptions at $1345\text{--}1355$ and $1535\text{--}1545\text{ cm}^{-1}$ for the nitro group.³⁸ Their electronic spectra exhibited three absorption maxima in the regions $254\text{--}260$, $298\text{--}306$ (sh) and $470\text{--}478\text{ nm}$ (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 ¹³CNMR 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					X
				C	H	N	S		
<u>5a</u>	172	78	C ₁₇ H ₁₂ S ₃	65.5 (65.4)	3.8 3.9		30.9 30.8		)
<u>5b</u>	180	80	C ₁₈ H ₁₄ S ₃	66.5 (66.3)	4.4 4.3		29.7 29.5		)
<u>5c</u>	192	82	C ₁₈ H ₁₄ OS ₃	63.3 (63.2)	4.3 4.1		28.0 28.1		)
<u>5d</u>	178	80	C ₁₇ H ₁₁ BrS ₃	52.1 (52.2)	3.0 2.8		24.5 24.6	20.7 20.5	)
<u>5e</u>	170	85	C ₁₇ H ₁₁ ClS ₃	59.0 (58.9)	3.3 3.2		27.9 27.7	10.2 10.3	)
<u>5f</u>	170	79	C ₁₇ H ₁₁ ClS ₃	59.0 (58.9)	3.3 3.2		27.5 27.7	10.5 10.3	)
<u>5g</u>	200	86	C ₁₇ H ₁₀ Cl ₂ S ₃	53.8 (53.7)	2.8 2.6		25.2 25.3	18.3 18.4	)
<u>10g</u>	180	70	C ₁₇ H ₁₅ ClN ₄	65.5 (65.7)	4.9 4.8	18.1 18.0		11.2 11.4	)
<u>12a</u>	162	70	C ₁₇ H ₁₀ N ₂ O ₄ S ₂	55.0 (55.1)	2.7 2.7	7.6 7.6	17.1 17.3		)
<u>12b</u>	165	75	C ₁₈ H ₁₂ N ₂ O ₄ S ₂	56.5 (56.3)	3.2 3.1	7.4 7.3	16.9 16.7		)
<u>12d</u>	170	80	C ₁₇ H ₉ BrN ₂ O ₄ S ₂	45.5 (45.4)	1.9 2.0	6.0 6.2	14.2 14.3	17.6 17.8	)

(Na₂SO₄) 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. ¹³CNMR spectrum of **5d** (δ/ppm) (CDCl₃): 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-4H-pyran-4-one (**11h**) with hydrazine hydrate.³⁴ IR, $\nu_{\max}$ (cm⁻¹) for **10g**: 1654 (C = N, hydrazone), 1598 (C = N, pyrazole ring), 3205, 3330 (NH₂). NMR (δ/ppm) (DMSO-d₆): 3.98 (s, CH₂), 6.39 (s, H-4), 6.70 (s, NH₂), 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-4H-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 HNO₃; 1 H₂SO₄) 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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