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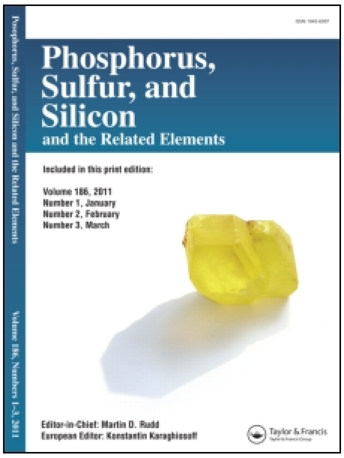

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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To cite this Article Barillier, Daniel(1978) 'Synthesis of 3,5-Diaryl and 3,5-Dialkyl-1,2-dithiolylium-4-olates', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 2, 251 — 255

To link to this Article: DOI: 10.1080/03086647808069895

URL: http://dx.doi.org/10.1080/03086647808069895

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Phosphorus and Sulfur
1978, Vol. 5, pp. 251–255

SHORT COMMUNICATION

Synthesis of 3,5-Diaryl and 3,5-Dialkyl-1,2-dithiolylium-4-olates

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(*Received February 6, 1978; in final form May 31, 1978*)

Sulfurization of 2-acetoxy or 2-benzoyloxy-1,3-propanediones gives the corresponding 1,2-dithiolylium salts which are used as starting materials for preparation of 1,2-dithiolylium-4-olates.

The reaction was studied under different conditions in order to obtain the best sulfurization yields.

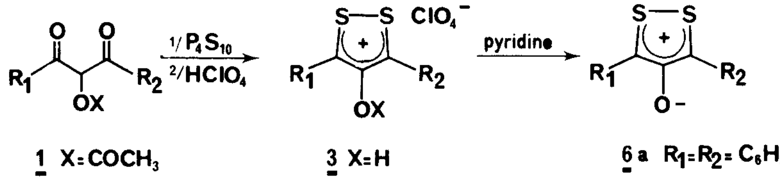
A new 3-*p*-dimethylaminophenyl-5-phenyl-1,2-dithiolylium-4-olate is also described. It is formed by nucleophilic attack on a 3-alkylthio substituted or a 5 unsubstituted position of a 1,2-dithiolylium ion by *N,N*-dimethylaniline.

In our previous papers we have described the synthesis of 3,5-diaryl-1,2-dithiolylium-4-olates.[1,2] These products, such as **6** were generally obtained by a basic attack of 1,2-dithiolylium perchlorates obtained in the sulfurization of β-diketones **1** or **2**. These starting materials being usually easy to prepare, the decisive step in the preparation of compound **6** is the sulfurization for which we have heretofore reported rather low yields.

In this paper we report some methods allowing an increase in sulfurization yields. We also describe two new compounds **6f** and **6g**. These have been prepared for a structural study of a series of compounds **6** to be published later.

Sulfurization of **1** was first studied in the case of 2-acetoxy-1,3-diphenyl-1,3-propanedione, **1a**. The results are summarized in Table I: they clearly show that no C—Oσ bond cleavage occurs at room temperature and perchlorate **4a** is the sole product obtained in this case, but with a poor yield. At about 140°C (boiling xylene), the reaction leads to the cleavage of the C—Oσ bond of the acetoxy group and gives only the perchlorate **3a** with a rather good yield. A mixture of the two salts **3a** and **4a** is obtained at intermediate temperatures (boiling carbon disulfide or benzene).

From this result one may conclude that the yield and the selectivity of the sulfurization depend mainly on the temperature. However, as carbon disulfide appears to be a better solvent than benzene, it follows that the rôle of the solvent should not be neglected. This is confirmed by the results obtained in sulfurization of β-diketone **1b**, which are given in Table I. The importance of the solvent is shown in this case by the fact that the perchlorate yield when carbon disulfide is used is higher than when xylene is used. One can easily explain this result, which was reported previously,[3] considering that the reaction



1 X=$COCH_3$
2 X=COC_6H_5

3 X=H
4 X=$COCH_3$
5 X=COC_6H_5

6 a R1=R2=C_6H_5
b R1=R2=$CH_3C_6H_4$
c R1=R2=ClC_6H_4
d R1=R2=2-thienyl
e R1=C_6H_5 R2=t-butyl
f R1=R2=t-butyl

TABLE I

Yields (%) in the sulfurization of **1a** and **1b** in various conditions of temperature and solvent

$\mathbf{1} \rightarrow \mathbf{3} + \mathbf{4}$

Starting material	R_1	R_2	Perchlorate yield C_6H_6 20° **3**	 **4**	 CS_2 20° **3**	 **4**	 Boiling C_6H_6 **3**	 **4**	 Boiling CS_2 **3**	 **4**	 Boiling xylene **3**	 **4**
1a	C_6H_5-	C_6H_5-	0	15	0	30	20	15	20	30	60	0
1b	$CH_3C_6H_4-$	$CH_3C_6H_4-$			0	35			65	0	55	0

mixture remains heterogeneous when using xylene (or benzene) instead of carbon disulfide, which is a better solvent for P_4S_{10}.

These experiments on compounds **1a** and **1b** show that the reactions in boiling carbon disulfide or boiling xylene give the best yields of dithiolic products. Also, β-diketones **1** and **2** were treated according to these methods and yields of corresponding dithiolylium perchlorates are given in Table II; the solvent which appears in this table was chosen after experimentation with the two methods.

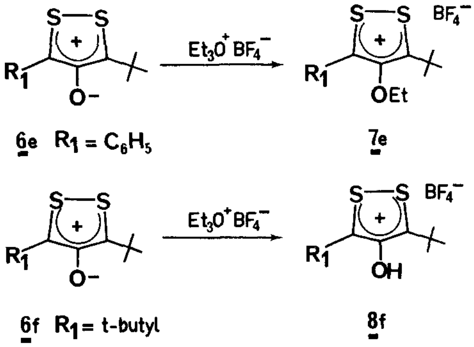
The sulfurization of β-diketones **1** generally gives the 4-hydroxy dithiolylium salts **3** (with C—O bond cleavage) whereas sulfurization of β-diketones **2** gives the 4-benzoyloxy salts **5** (with no cleavage).

Some remarks should be made about the preparation of the new *t*-butyl disubstituted perchlorate **3f**:

— the sulfurization of β-diketones **1f** and **2f** always affords the 3,5-di-*t*-butyl-4-hydroxy-1,2-dithiolylium perchlorate **3f** resulting from a C—O bond cleavage of the starting material, which is not observed in the sulfurization of **1e** and **2e**.

— the reaction is much slower than in the other cases and the yield is poor.

This particular behaviour of *t*-butyl disubstituted products is most probably due to the steric hindrance of the bulky *t*-butyl groups attached to the planar ring in the dithiolic compounds. This can be confirmed by the reaction of the compounds **6e** and **6f** with triethyloxonium fluoroborate:[4] the alkylation of compound **6e** by means of this reagent leads to the corresponding 4-ethoxydithiolylium fluoro-

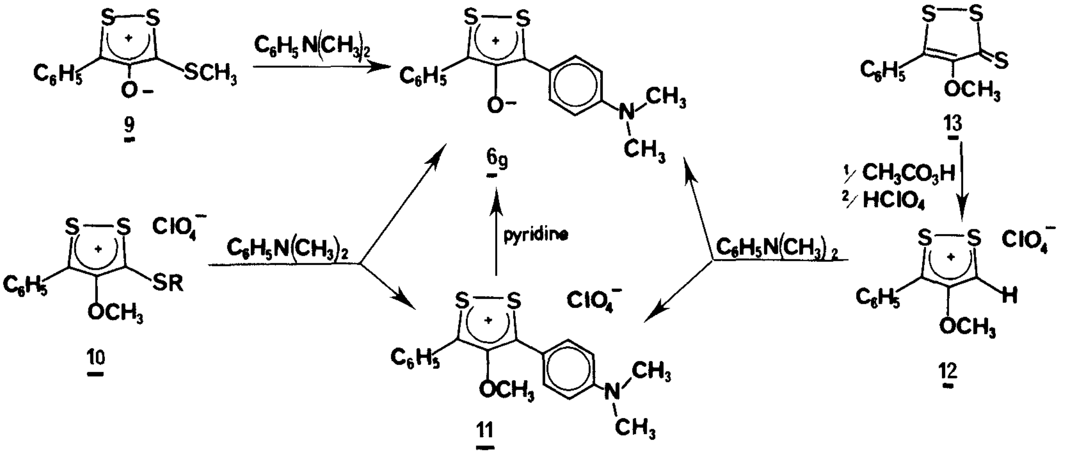


6e $R_1 = C_6H_5$

7e

6f R_1 = t-butyl

8f



9

6g

10

11

12

13

TABLE II

Yields (%) in the sulfurization of β-diketones **1** and **2** in boiling CS_2 or xylene

Starting[a] material	R_1	R_2	Perchlorate yield **3**	**4**	**5**	Method
1c	ClC_6H_4-	ClC_6H_4-	45			boiling xylene
1e	C_6H_5-	*t*-butyl		45		boiling CS_2
1f	*t*-butyl	*t*-butyl	35			boiling xylene
2c	ClC_6H_4-	ClC_6H_4-			55[b]	boiling CS_2
2d	2-thienyl	2-thienyl			55	—
2e	C_6H_5-	*t*-butyl			60	—
2f	*t*-butyl	*t*-butyl	25			boiling xylene

[a] Sulfurization of compounds **1a** and **1b** is given in Table I, sulfurization of compounds **1d**, **2a** and **2b** was previously reported (see Ref. 2).

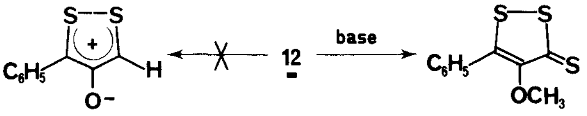
[b] In this case the compound isolated is dithiolylium chloride because crystallization of the perchlorate is difficult.

borate **7e** whereas, under the same conditions, **6f** is only protonated to give 4-hydroxydithiolylium fluoroborate, **8f**, probably by an elimination mechanism involving triethyloxonium fluoroborate.

Last, we wish to report the synthesis of 3-*p*-dimethylaminophenyl-5-phenyl-1,2-dithiolylium-4-olate, **6g**. This product is obtained by a well known method according to Klingsberg *et al.*[5,6] and Mollier *et al.*[7]: it involves nucleophilic attack on the 3 or 5 position of the dithiole ring by the *para* carbon of a tertiary aromatic amine.

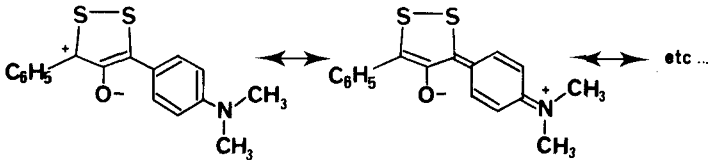
In our case treatment of previously described[3] 3-methylthio-5-phenyl-1,2-dithiolylium-4-olate, **9**, by *p*-dimethylaniline leads to the mesoionic compound **6g**. Under the same conditions treatment of the corresponding 4-methoxydithiolylium perchlorate **10** gives a mixture of **6g** and the intermediate perchlorate **11**.

A similar result is also observed when the 4-methoxy-3-phenyl-1,2-dithiolylium salt **12**, owing to a vulnerable site on the nonsubstituted 5 position, is used as starting material. This perchlorate, **12**, results from the peracetic oxidation of the dithiolethione **13**.[8] On the contrary, sodium hydroxide or pyridine, on reacting with **12**, lead to the dithiolethione **13**, and not to the mesoionic compound 3-phenyl-1,2-dithiolylium-4-olate. This result is not surprising because similar results had been obtained in our preceding work[3]: it seems that one fraction of the compound **12** undergoes a basic cleavage of the ring and the resulting materials contribute to sulfurization of the unaltered part by nucleophilic attack on the reactive 5 position of the dithiole ring.

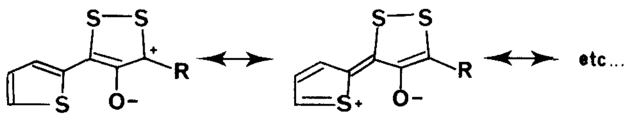


13

Compound **6g** may be described as a resonance hybrid in which either dithiolylium or ammonium canonical forms can be written. Similarly, com-



6g



6d R= thienyl

pound **6d** may be written as a resonance hybrid including dithiolylium and sulfonium forms.

This point is of current interest and will be discussed among other structural problems in a study soon to be published.

EXPERIMENTAL

Solid products **1**, **2** and **6** were recrystallized until stable melting points were obtained. The reported yields correspond to this final stage. Melting points of dithiolylium salts are generally approximative because they correspond to a melting region and sometimes to decomposition.

All liquid and solid samples were analysed (C, H, S ±0.3%).

The ^1H nmr spectra were recorded in $CDCl_3$ or CF_3CO_2D using tetramethylsilane ($\delta = O$) as internal standard.

Products **1a–e**, **2a–c**, **3a–d**, **5a–c** and **6a–e** were described previously.[1,2]

Preparation of β-diketones **1** *and* **2**

β-diketones were prepared as described previously.[1,2]

4-acetoxy-2,2,6,6-tetramethyl-3,5-heptanedione **1f**: pale yellow oil (yield: 90%); bp = 125°/20 mm; ir: ν_{CO} = 1705, 1725 and 1755 cm^{-1}. Nmr ($CDCl_3$): δ = 1.20 (s, 18H); 2.18 (s, 3H); 6.29 (s, 1H). Compound **1f** crystallizes slowly at room temperature (F < 30°).

2-benzoyloxy-1,3-di(2-thienyl)-1,3-propanedione **2d**: colourless crystals (yield: 90%); mp = 113°; ir: ν_{CO} = 1640 and 1705 cm^{-1}. Nmr ($CDCl_3$): δ = 6.96 (s, 1H); 7.15 to 8.50 (m, 11H).

2-benzoyloxy-4,4-dimethyl-1-phenyl-1,3-pentanedione **2e**: colourless crystals (yield: 90%); m; = 109°; ir: ν_{CO} = 1675 and 1710 cm^{-1}. Nmr ($CDCl_3$): δ = 1.18 (s, 9H); 7.27 (s, 1H); 7.60 to 8.50 (m, 10H).

4-benzoyloxy-2,2,6,6-tetramethyl-3,5-heptanedione **2f**: colourless crystals (yield: 75%); mp = 85°; ir: ν_{CO} = 1695 cm^{-1}. Nmr ($CDCl_3$): δ = 1.25 (s, 18H); 6.67 (s, 1H); 7.52 to 7.78 and 8.10 to 8.35 (m, 5H).

Sulfurization of β-diketones. Preparation of 1,2-dithiolylium perchlorates **3**, **4** *or* **5**

2 g of β-diketone and 1 g of acetophenone were added to a rapidly stirred suspension of 4 g phosphorus pentasulfide in 50 ml of dry carbon disulfide, xylene or benzene (see Tables I and II). The mixture was stirred under reflux for 2 h (compounds **1a**, **1b**, **1c**, **2c**) or 24 h (compounds **1e**, **1f**, **2d**, **2e**, **2f**). After cooling to room temperature a solid residue X and a solution Y were obtained.

The residue X was heated on a water bath during 1.5 h with a mixture of perchloric acid (5 ml) and acetic acid (40 ml). The perchlorates were obtained by addition of ether to the filtrate of the resulting medium.

The solution Y was poured in a flask and treated with a new portion of phosphorus pentasulfide (4 g), so an additional part of perchlorate was isolated according to the same procedure.

3,5-di-t-butyl-4-hydroxy-1,2-dithiolylium perchlorate **3f**: colourless crystals; decomposition about 252°. Nmr (CF_3CO_2D): δ = 1.86 (s).

4-acetoxy-3,5-diphenyl-1,2-dithiolylium perchlorate **4a**: yellow crystals; m.p. = 171–174°; ir: ν_{CO} = 1780 cm^{-1}. Nmr (CF_3CO_2D): δ = 2.30 (s, 3H); 7.50 to 8.50 (m, 10H).

4-acetoxy-3,5-di(4-methylphenyl)-1,2-dithiolylium perchlorate **4b**: yellow crystals; mp = 159–162°; ir: ν_{CO} = 1780 cm^{-1}. Nmr (CF_3CO_2D): δ = 2.32 (s, 3H); 2.53 (s, 6H); 7.58 to 7.88 (q AB, 8H, J = 8 Hz).

4-acetoxy-3-t-butyl-5-phenyl-1,2-dithiolylium perchlorate **4e**: colourless crystals; mp = 220–230°; ir: ν_{CO} = 1780 cm^{-1}. Nmr (CF_3CO_2D): δ = 1.80 (s, 9H); 2.42 (s, 3H); 7.89 (extended S, 5H).

4-benzoyloxy-3,5-di-(2-thienyl)-1,2-dithiolylium perchlorate **5d**: bright brown crystals; decomposition about 220°; ir: ν_{CO} = 1750 cm^{-1}. Nmr (CF_3CO_2D): δ = 7.20 to 8.50 (m).

4-benzoyloxy-3-t-butyl-5-phenyl-1,2-dithiolylium perchlorate **5e**: colourless crystals; mp = 229–233°; ir: ν_{CO} = 1750 cm^{-1}. Nmr (CF_3CO_2D): δ = 1.82 (s, 9H); 7.60 to 8.60 (m, 10H).

Preparation of 1,2-dithiolylium-4-olates **6**

Preparation of compounds **6a–e** was previously reported.[1,2] The compound **6f** was prepared according to the following procedure: a mixture of 5 g of perchlorate **3f** and 50 ml of pyridine was stirred under reflux for 5 minutes. The resulting orange solution was cooled and poured into 200 ml of water. The product was extracted with chloroform. The organic layer was washed with water and the extract was dried and concentrated to afford a solid mass which was recrystallized with benzene. Yields of the compounds **6** are given in Table III.

TABLE III

Yields of compounds **6** from perchlorates **3**, **4** and **5**

	3	4	5
6a	85	80	(Refs. 1 and 2)
6b	90	70	(Refs. 1 and 2)
6c	85		80
6d	(Ref. 2)		50
6e		65	35
6f	40		

3,5-di-t-butyl-1,2-dithiolylium-4-olate **6**: yellow crystals; sublimation about 120°; ir: ν_{CO} and dithiolic cycle = 1463, 1475 and 1488 cm^{-1}; uv (dioxane): $\pi^* \leftarrow \pi$, λ = 463 nm (ε = 5950). Nmr ($CDCl_3$): δ = 1.59 (s).

Treatment of **6e** *and* **6f** *by triethyloxonium fluoroborate*

To a stirred solution of **6e** or **6f** (100 mg) in 20 ml of methylene chloride, 0.6 g of triethyloxonium fluoroborate was added. After two days at room temperature the 1,2-dithiolylium fluoroborate was precipitated by addition of ether. The isolated salt was recrystallized in a mixture methylene chloride/ether.

Compound **6e** always gives the ethylated product **7e** and compound **6f** the protonated product **8f** (3 experiences).

3-t-butyl-4-ethoxy-5-phenyl-1,2-dithiolylium fluoroborate **7e**: white needles (yield: 50%); mp = 150°. Nmr ($CDCl_3$): $\delta = 1.27$ (t, 3H); 1.69 (s, 9H); 3.95 (q, 2H); 7.50 to 8.20 (m, 5H).

3,5-di-t-butyl-4-hydroxy-1,2-dithiolylium fluoroborate **8f**: colourless crystals (yield: 40%); mp = 185–195°. Nmr ($CDCl_3$): $\delta = 1.65$ (s).

Treatment of **9** *by N-N-dimethylaniline*

A mixture of the mesoionic compound **9**[3] (1 g), ethanol (20 ml) and amine (5 ml) was stirred under reflux for 0.5 h. After cooling the mixture was diluted with ether. A dark green mass was isolated and recrystallized into 31 mg of sparkling crystals (ethanol).

3-dimethylaminophenyl-5-phenyl-1,2-dithiolylium-4-olate **6g**: dark green sparkling crystals (yield: 20%); mp = 203°; ir: ν_{CO} and dithiolic cycle: 1475 and 1485 cm^{-1}, $\nu_{CN} = 1600$ cm^{-1}. Nmr (CF_3CO_2D): $\delta = 3.67$ (s, 6H); 7.80 to 8.30 (m, 5H); 8.17 and 8.45 (q AB, $J = 9$ Hz, 4H).

Treatment of the perchlorates **10** *and* **12** *by N,N-dimethylaniline*

(a) A mixture of compound **10**[3] (1 g), acetic acid (5 ml) and amine (2 ml) was stirred under reflux for 20 minutes. After cooling the violet resulting solution was diluted with water and a solid red mass obtained (60 mg). The separation of perchlorate **11** (90%) and mesoionic compound **6g** (10%) was achieved by divided recrystallization.

(b) An alternative method of preparation consisted in dissolving the perchlorate **12** (0.5 g) and potassium persulfate (0.4 g) in a mixture of ethanol (100 ml) and amine (5 ml). This solution was then heated for 3 h. The violet final solution was diluted with ether and 35 mg of a mixture of perchlorate **11** (95%) and mesoionic compound **6g** (5%) obtained.

3-dimethylaminophenyl-4-methoxy-5-phenyl-1,2-dithiolylium perchlorate **11**: red sparkling crystals; mp = 192–196°; ir: $\nu_{CN} = 1600$ cm^{-1}; ClO_4^- ion = large and wide band about 1080 cm^{-1}. Nmr (CF_3CO_2D): $\delta = 3.60$ (s, 6H); 3.72 (s, 3H); 7.50 to 8.50 (m, 10H).

The treatment of this perchlorate in boiling pyridine gives compound **6g**.

Preparation of perchlorate **12**

To a stirred solution of dithiolethione **13**[10] (1 g) in 30 ml of acetic acid, cooled at 0° in an ice bath, was added dropwise 10 ml of commercial hydrogen peroxyde (110 vol). After stirring for 2 h at this temperature the resulting pale yellow solution was treated with 5 ml of perchloric acid and the salt **12** was precipitated by addition of ether.

4-methoxy-3-phenyl-1,2-dithiolylium perchlorate **12**: lemon coloured crystals (yield: 75%); mp = 178–180°. Nmr (CF_3CO_2D): $\delta = 4.33$ (s, 3H); 7.50 to 8.35 (m, 5H); 9.51 (s, 1H).

Upon heating in boiling pyridine, this perchlorate **12** gives as main reaction product the 4-methoxy-5-phenyl-1,2-dithiole-3-thione **13** (yield: 50%). The same result is observed with different experimental conditions and demethylating reagents.

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