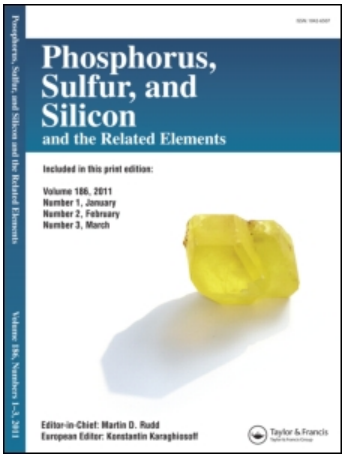

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Sulfurization of γ-oxo esters; study of the resulting sulfur compounds

Jacques Brunet[a]; Daniel Paquer[a]; Philippe Rioult[a]
[a] UER de Sciences, Université de Caen, Caen Cédex, France

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SHORT COMMUNICATION

Sulfurization of γ-oxo esters; study of the resulting sulfur compounds.

JACQUES BRUNET, DANIEL PAQUER and PHILIPPE RIOULT

UER de Sciences, Université de Caen, 14032 Caen Cédex, France

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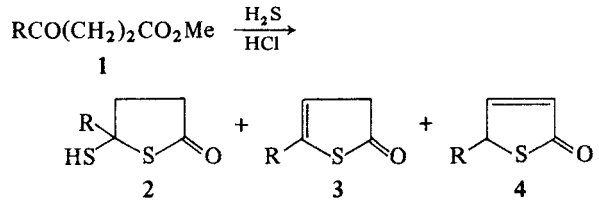
Treatment of aliphatic γ-oxo esters with hydrogen chloride/hydrogen sulfide gives three sulfur compounds: an alkyl-5-mercaptothiolan-2-one, an alkyl-4-thiolen-2-one and an alkyl-3-thiolen-2-one. Chemical properties of these products are reported. With aromatic γ-oxo esters we obtain a thiophenic compound.

In a previous paper[1] we have described conditions for preparation of γ-oxo esters; we report here the sulfurization reaction of some γ-oxo esters and the chemical properties of the sulfur products obtained. Some reports exist in the literature concerning the sulfurization of γ-oxo esters[2,3]. However, we have used a new technique in this field: the direct reaction of hydrogen sulfide with esters in the presence of hydrogen chloride[4]. Aliphatic γ-oxo esters **1** give three sulfur compounds (see Table 1):

- –a 5-alkyl-5-mercaptothiolan-2-one, **2**
- –a 5-alkyl-4-thiolen-2-one, **3**
- –a 5-alkyl-3-thiolen-2-one, **4**



NMR spectra of compounds **2** (CCl_4):
2a δ = 2.0 (s, 3H); 2.25–3.2 (m, 4H); 3.0 (s, 1H)
2b δ = 1.2 (t, 3H); 1.9–3.5 (m, 6H); 2.9 (s, 1H)
2c δ = 0.83–1.18 (m, 3H); 1.2–3.4 (m, 8H); 2.5 (s, 1H).

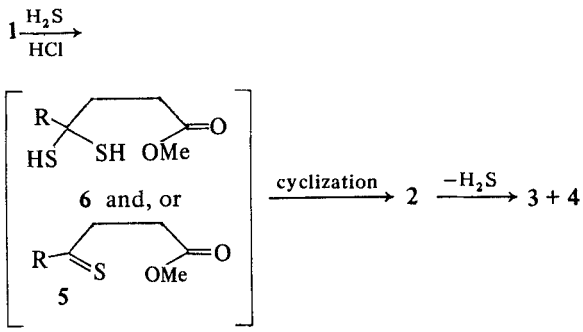
TABLE I

Esters	Sulfur compounds % 2	3	4	Yield
1a R = Me	95	ε	ε	50%
1b R = Et	73	9	18	45%
1c R = Pr	59	13	28	30%
1d R = iPr	0	25	75	30%
1e R = t-Bu	0	23	77	25%

The NMR spectra of compounds **3** and **4** have been previously described[3,5].

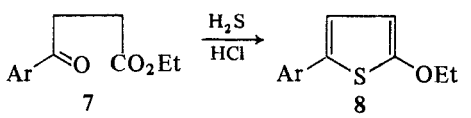
In addition, a sample of 5-mercapto-5-methylthiolan 2-one **2a**, in refluxing pyridine, gave a mixture of the two sulfur products **3a** (25%) and **4a** (75%).

Therefore the mechanism of the sulfurization reaction is probably as follows:



This is confirmed by the fact that γ-oxo esters (with $R \neq CH_3$) give increased relative yields of thiolenone when the alkyl group R increases in size (elimination of hydrogen sulfide is favored in this case).

With aromatic γ-oxo esters **7** the same reaction affords mainly the thiophenic compound **8** which is isolated by liquid phase chromatography (silica gel):



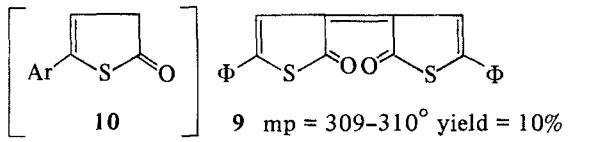
8a Ar = C_6H_5; mp = 30°C (petroleum ether); yield = 10%; nmr (CCl_4) δ = 1.23 (t, 3H); 3.87 (q, 2H); 5.95 (d, 1H) and 6.75 (d, 1H) J ~ 4 Hz; 6.9–7.5 (m, 5H).

8b Ar = p · ClC_6H_4; mp = 78°C (petroleum ether); yield = 20%; nmr (CCl_4) δ = 1.37 (t, 3H); 4.01 (q, 2H); 6.0 (d, 1H) and 6.73 (d, 1H) J = 4 Hz; 7.0–7.4 (m, 4H).

8c Ar = p$CH_3C_6H_4$; mp = 28°C (petroleum ether); yield = 10%; nmr (CCl_4) δ = 1.17 (t, 3H); 2.16 (m, 3H); 3.81 (q, 2H); 5.94 (d, 1H) and 6.7 (d, 1H) J = 4 Hz; 6.92–7.28 (m, 4H).

8d Ar = p$CH_3OC_6H_4$; mp = 58°C (methanol); yield = 15%; nmr (CCl_4) δ = 1.37 (t, 3H); 3.68 (s, 3H); 3.99 (q, 2H); 5.97 (d, 1H) and 6.60 (d, 1H) J ~ 4 Hz; 6.7–7.2 (m, 4H).

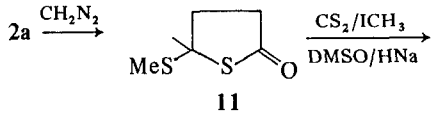
When compound **7a** (Ar=C_6H_5) is employed as a starting material we have characterized a second component **9** which was described by A. I. Kosak *et al*[6]. This leads us to consider that the 5-arylthiolen-2-one **10** is produced during the sulfurization reaction, but not isolated (indeed such compounds are very instable[6]).



10 **9** mp = 309–310° yield = 10%

Chemical properties of **2a**

It is possible with **2a** to observe the following reactions:



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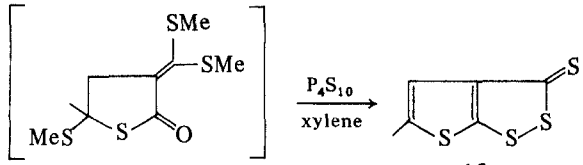


12

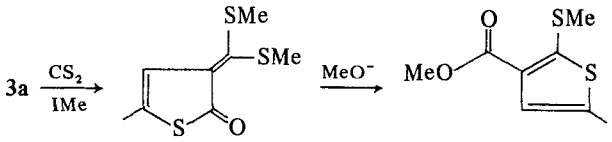
11 nmr (CCl_4) δ = 1.85 (s, 3H); 2.15 (s, 3H); 2.1–3.0 (m, 4H)

12 red solid; mp = 132°C; yield = 15%; nmr (CS_2) δ = 2.55 (d, 3H) and 6.89 (q, 1H) J ~ 1,1 Hz. The 1,2-dithiole-3-thione **12** can be synthesized by another method[7].

Chemical properties of **3a** *and* **4a**

In a basic medium carbon disulfide and methyl iodide react with **3a** to yield heterocyclic product **13**[8] which can produce with phosphorus pentasulfide 1,2-dithiole-3-thione **12**.

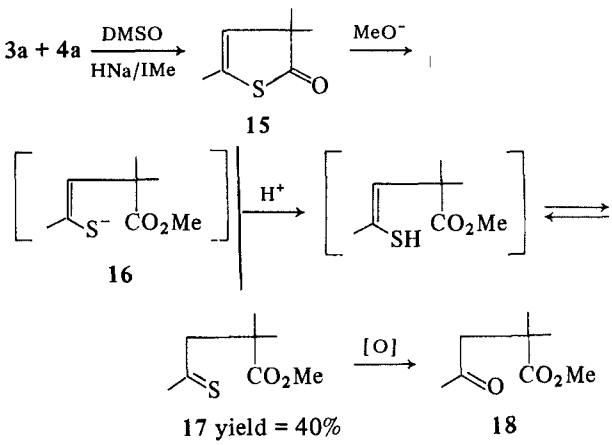
Addition of **13** to a solution of sodium methoxide gives, after chromatography, a pure solid identified as the compound **14** (the mechanism of this rearrangement has been previously published[9]).



13 yield = 15% **14** yield = 85%

14 mp = 91°C; nmr (CCl_4) δ = 2.45 (d, 3H); 2.52 (s, 3H); 3.48 (s, 3H) 7.05 (1, 1H, J = 1.5 Hz).

Alkylation of the mixture **3a** + **4a**[10,11,12] by DMSO/HNa/ICH_3 gives compound **15** (yield = 55%) which can produce the thioketone **17** (or the ketone **18**) according to the following scheme:

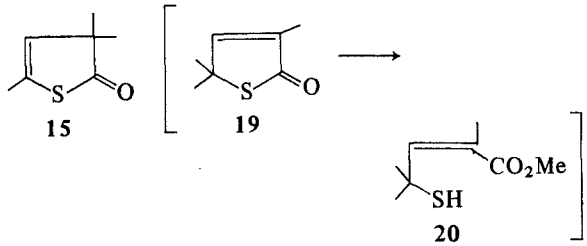


17 yield = 40% **18**

17 red liquid; nmr (CCl_4) δ = 1.25 (s, 6H); 2.62 (s, 3H); 3.13 (s, 2H); 3.63 (s, 3H). This thioketone is decomposed completely within one hour.

18 colourless liquid; nmr (CCl_4) δ = 1.22 (s, 6H); 2.06 (s, 3H); 2.63 (s, 2H) 3.63 (s, 3H).

This leads us to consider that the structure **15** proposed in 1971 by E. B. Pedersen *et al.*[12] for methylated thiolenone is the right one. Indeed compound **15** can give the thioketone **17**; in contrast, a compound such as **19** would probably give compound **20**.



15 **19** **20**

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