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

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SHORT COMMUNICATION

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

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(Received January 26, 1977)

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 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 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

RCO(CH₂)₂CO₂Me
$$\xrightarrow{\text{H}_2S}$$
1

R
HS
S
O
R
S
O
R
S
O
R
S
O
R
S
O

NMR spectra of compounds 2 (CCl₄):

 $2a \delta = 2.0 (s, 3H); 2.25-3.2 (m, 4H); 3.0 (s, 1H)$

2b δ = 1.2 (t, 3H); 1.9-3.5 (m, 6H); 2.9 (s, 1H)

 $2c \delta = 0.83-1.18 \text{ (m, 3H)}; 1.2-3.4 \text{ (m, 8H)}; 2.5 \text{ (s, 1H)}.$

TABLE I

Esters	Sulfur compounds %			
	2	3	4	Yield
1a R = Me	95	ϵ	€	50%
1b R = Et	73	9	18	45%
1c R = Pr	59	13	28	30%
1d R = iPr	0	25	75	30%
le 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:

$$1 \xrightarrow{\text{H}_2\text{S}}$$

This is confirmed by the fact that γ -oxo esters (with R \neq CH₃) 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):

$$Ar \xrightarrow{O \quad CO_2Et} \xrightarrow{H_2S \quad HCl} Ar \xrightarrow{S \quad OEt}$$

8a Ar = C_6H_5 ; mp = 30°C (petroleum ether); yield = 10%; nmr (CCl₄) δ = 1.23 (t, 3H); 3.87 (q, 2H); 5.95 (d, 1H) and 6.75 (d, 1H) J \sim 4 Hz; 6.9-7.5 (m, 5H).

8b Ar = $p \cdot ClC_6H_4$; mp = 78°C (petroleum ether); yield = 20%; nmr (CCl₄) 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 = pCH₃C₆H₄; mp = 28°C (petroleum ether); yield = 10%; nmr (CCl₄) 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 = pCH₃OC₆H₄; mp = 58° C (methanol); yield = 15%; nmr (CCl₄) δ = 1.37 (t, 3H); 3.68 (s, 3H); 3.99 (q, 2H); 5.97 (d, 1H) and 6.60 (d, 1H) J \sim 4 Hz; 6.7 \sim 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 instable⁶).

Chemical properties of 2a

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

$$2a \xrightarrow{CH_2N_2} MeS \xrightarrow{S} O \xrightarrow{CS_2/ICH_3} DMSO/HN_2$$

$$\begin{bmatrix} SMe \\ SMe \end{bmatrix} \xrightarrow{P_4S_{10}} S$$

$$\begin{bmatrix} P_4S_{10} \\ \hline xylene \end{bmatrix} \xrightarrow{S} S$$

11 nmr (CC1₄) δ = 1.85 (s, 3H); 2.15 (s, 3H); 2.1–3.0 (m, 4H)

12 red solid; mp = 132° C; yield = 15%; nmr (CS₂) δ = 2.55 (d, 3H) and 6.89 (q, 1H) J \sim 1,1 Hz. The 1,2-dithiole-3-thione 12 can be synthesized by another method⁷.

Chemical properties of 3a and 4a

In a basic medium carbon disulfide and methyl iodide react with 3a to yield heterocyclic product 13⁸ 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 published⁹).

$$3a \xrightarrow{CS_2} 1Me \xrightarrow{SMe} SMe \xrightarrow{MeO^-} MeO \xrightarrow{SMe} S$$

$$13 \text{ yield} = 15\% \qquad 14 \text{ yield} = 85\%$$

14 mp = 91° C; nmr (CCl₄) 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/ICH₃ gives compound 15 (yield = 55%) which can produce the thioketone 17 (or the ketone 18) according to the following scheme:

$$3a + 4a \xrightarrow{DMSO}_{HNa/IMe}$$

$$S = CO_2Me$$

$$16$$

$$S = CO_2Me$$

$$S = CO_2Me$$

$$16$$

$$S = CO_2Me$$

$$17 \text{ yield} = 40\%$$

$$18$$

17 red liquid; nmr (CCl₄) δ = 1.25 (s, 6H); 2.62 (s, 3H); 3.13 (s, 2H); 3.63 (s, 3H). This thicketone is decomposed completely within one hour. 18 colourless liquid; nmr (CCl₄) 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.

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REFERENCES AND NOTES

- J. Brunet, D. Paquer and P. Rioult, C. R. Acad. Sci. Paris, C, 277, 323 (1973).
- W. Steinkopf and F. Thormann, Ann. Chem. 540, 1 (1939).
- 3. S. Gronowitz and R. Hoffman, *Arkiv. Chem.* 15, 499 (1960).
- 4. D. Paquer, Int. J. Sulfur. Chem. 7, 269 (1972).
- 5. A. B. Hornfeldt, Arkiv, Kemi, 22, 211 (1963).
- A. I. Kosak, R. J. F. Palchak, W. A. Steele and C. M. Selwitz J. Am. Chem. Soc. 76, 4450 (1946).

- P. Rioult and J. Vialle, Bull. Soc. Chim. Fr. 4483 (1968).
- P. Rioult and J. Vialle, Bull. Soc. Chim. Fr. 3315 (1965) and 4477 (1968).
- 9. G. Brisset, L. Morin, D. Paquer and P. Rioult, Rec. Trav. Chim. Pays-Bas, "sous presse" (1977).
- B. Cederlund and A. B. Hornfeldt, Acta. Chem. Scand. 25, 3324 and 3546 (1971).
- 11. B. Cederlund, A. Jesperon and A. B. Hornfeldt, *Acta. Chem. Scand.* 25, 3656 (1971).
- 12. E. B. Pedersen and S. O. Lawesson, *Tetrahedron*, 27, 3861, (1971).