Pyrothiocarbonates. Part 2. Reaction of *S*-Ethoxycarbonyl *O*-Ethyl Dithiocarbonate with some Potassium *O*-Alkylthiocarbonates

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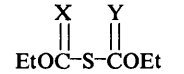
The thiolysis of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (1) has been examined in order to study both its transesterification reaction and the reactivities of its carbonyl and thiocarbonyl groups. The two symmetrical pyrothiocarbonates $(EtOCS)_2S$ (4) and $(EtOCO)_2S$ (5) are produced by reactions of (1) with $EtOCS_2K$ (7) or EtOCOSK (8) in 95% ethanol at 0 °C; (4) was always the main product in the reaction with (7) whereas (5) was initially the main product in the reaction with (8). The reaction of (1) with $BuOCS_2K$ yielded first $BuOCS_2CSOEt$ and then $BuOCS_2CO_2Et$ and $(BuOCS)_2S$. These results indicate that the thiocarbonyl group of (1) is more reactive than the carbonyl one.

In previous studies, it was established that the reaction of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (1) with primary and secondary aliphatic amines [1,2] gave rise to the thiocarbamate (2) and the carbamate (3) by two routes: (i) nucleophilic attack of the amine at the carbonyl and thiocarbonyl groups of (1); and (ii) aminolysis of the symmetrical pyrothiocarbonates (4) and (5) formed by transesterification of (1) with the nucleophiles $EtOCS_2^-$ and $EtOCOS^-$ involved in the above primary process.

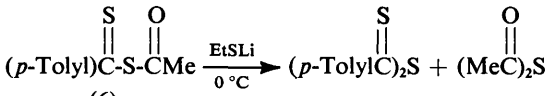


(1) X = S; Y = O
(4) X = Y = S
(5) X = Y = O

(2) X = S
(3) X = O

The aminolysis of (1) predominates during the first minute of the reaction and it was observed that the product (2) prevails over (3) during this time. On the other hand, assays of aminolyses carried out with representative substrates of the carbonyl and thiocarbonyl moieties of (1) indicate that the aminolysis is favoured for the substrate with the thiocarbonyl group. Both observations indicate that the thiocarbonyl group of (1) is more reactive towards amine attack.

An analogous transesterification to that produced by thiolysis of (1), before the secondary process of aminolysis takes place, has been described [3] for the acetic *p*-thiotoluic thioanhydride (6). The disproportionation of this compound is catalyzed by lithium ethanethiolate:



(6)

The thiolysis of (1) is reported as part of a detailed study of transesterification reactions; it completes a previous study [2] and provides further evidence for the reactivity differences of the carbonyl and thiocarbonyl groups of this substrate.[4]

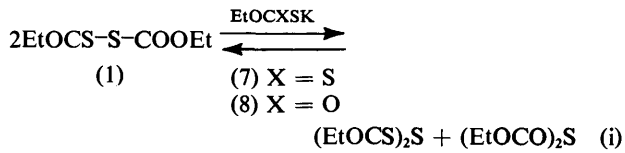
Results and Discussion

The reaction of (1) with a 10% molar amount of potassium *O*-ethyl dithiocarbonate (7) and potassium *O*-ethyl monothiocarbonate (8) was carried out following the reaction products with time. Potassium salts were used as being more stable than the ammonium ones. The reactions were performed in ethanol at 0 °C and aliquots taken from the reaction media were analyzed by v.p.c. after treatment with 5% cold HCl solution in order to decompose the thiocarbonates. The transesterification of (1) occurs in both cases giving the symmetrical thiocarbonates (4) and (5) [equation (i); see also Table 1].

Table 1. Reaction of (1) with (7) and (8) in ethanol at 0 °C

EtOCXSK [a]	Time (h)	Concentration (10^2 mol l^{-1}) (1) [b]	(4)	(5)
(7; X = S)	1	30.1	2.4	0.4
	4	28.3	2.8	0.8
	7	26.9	3.1	1.1
	24	23.2	5.4	1.9
	31	21.8	6.5	2.3
(8; X = O)	1	32.3	0.2	0.6
	4	31.0	0.8	0.8
	7	29.3	1.5	1.4
	24	25.2	3.6	2.4
	31	23.7	4.7	3.0

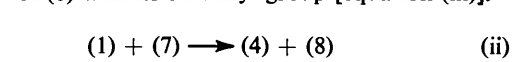
[a] $[(7)]_0 = [(8)]_0 = 3.4 \times 10^{-2}$ mol l^{-1}. [b] $[(1)]_0 = 33.5 \times 10^{-2}$ mol l^{-1}.



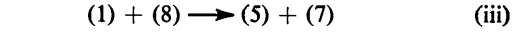
(1) (7) X = S; (8) X = O

$(EtOCS)_2S$ (4) + $(EtOCO)_2S$ (5) (i)

The formation of (4) and (5) can be explained by reaction of (7) with the thiocarbonyl group of (1) [equation (ii)] and interaction of (8) with its carbonyl group [equation (iii)].



(ii)



(iii)

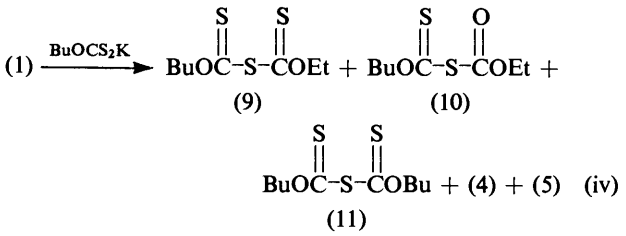
Reaction (2) must be faster than (3) during the first hour since (1) decreases more rapidly in the first reaction (Table 1). After 24 h the total concentrations of the symmetrical products (4) and (5) are larger than the initial concentration of (7) and (8), indicating that the reaction is catalyzed by either of the potassium thiocarbonates. Although these reactions must be reversible, an equilibrium value was not reached because of the slow decomposition of (8). As a consequence

Table 2. Reaction of (1) with $BuOCS_2K$ in ethanol at 0 °C [a]

Time (min)	Concentration (10^2 mol l^{-1}) (1)	(9)	(10)	(11)	(4)	(5)
1	33.4					
5	32.5	0.6				
15	30.9	1.6	0.4	0.1		
30	29.2	1.7	1.1	0.2	0.8	
60	26.0	1.5	2.8	0.2	2.2	
120	23.8	1.2	3.9	0.1	3.7	
180	21.6	1.1	4.8	0.1	4.8	0.3
360	18.8	0.9	4.3		5.1	0.8
1 260	15.7	0.9	3.6		5.3	1.7

[a] $[(1)]_0 = 33.9 \times 10^{-2}$ mol l^{-1}; $[BuOCS_2K]_0 = 8.8 \times 10^{-2}$ mol l^{-1}.

(4) is enriched in the reaction media.* Since the carbonyl and thiocarbonyl groups of (1) were also expected to react with (7) and (8) *via* indistinguishable reactions, the reaction with potassium *O*-butyl dithiocarbonate (which should give identifiable reactions) was undertaken. Thus, when 4 equiv. of (1) were allowed to react with potassium *O*-butyl dithiocarbonate in ethanol at 0 °C, *S*-ethoxythiocarbonyl *O*-butyl dithiocarbonate (9), *S*-ethoxycarbonyl *O*-butyl dithiocarbonate (10), bis(butoxythiocarbonyl) sulphide (11), (4), and (5) were obtained [equation (iv)].

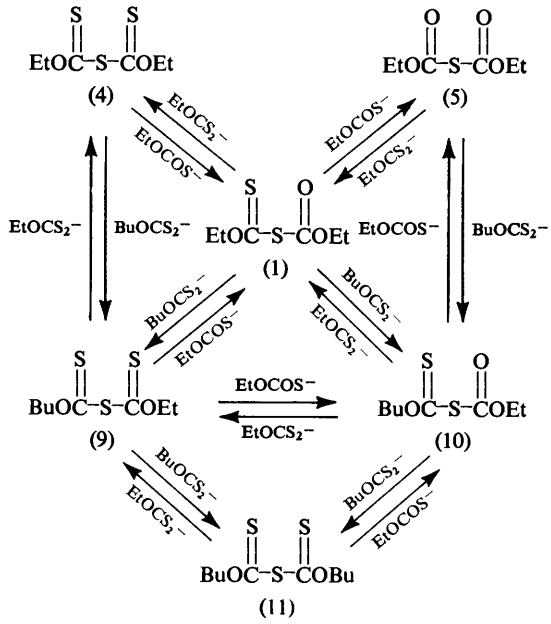


This thiolysis was studied in the same way as the reaction described by equation (1) and the results are shown in Table 2. No other covalent products than those appearing in Table 2 were detected.

The attack of $BuOCS_2^-$ at the thiocarbonyl carbon of the substrate produces the unsymmetrical thiocarbonate (9) which is detected before the mixed pyrodithiocarbonate (10) which is, in turn, the product arising from the attack of $BuOCS_2^-$ at the substrate carbonyl group. This fact suggests that the thiocarbonyl carbon of (1) is more reactive than the carbonyl carbon in the thiolysis. The formation of (10) also provides evidence that (1) reacts with (7) and (8) and with amines *via* indistinguishable reactions.

From Table 2 it is seen that after a 15 min reaction period the symmetrical sulphide (11) is observed. This would result from $BuOCS_2^-$ attack at the thiocarbonyl group of (9) and/or (10), giving rise to the corresponding thiocarbonates $EtOCS_2^-$ and $EtOCOS^-$ as leaving groups. These may also react with (1) to yield the symmetrical pyrothiocarbonates (4) and (5) and also with the electrophilic species (9), (10), and (11). All the transformations described above give rise to a complex mixture of reversible reactions as indicated by the Scheme.

Lack of balance between initial and final species after 21 h (see Table 2) arises as a result of the gradual decomposition



Scheme.

of the potassium thiocarbonates. Because of this, none of the transformations described strictly reached equilibrium.

Since most of the compounds utilized as references for v.p.c. analyses were thermally unstable liquids, both new and known compounds were synthesized in order to minimize purification problems. Thus (4) and (5) were prepared by acylation of sodium sulphide utilizing a phase-transfer catalyst.[5] The thiocarbonates (9) and (11) were formed by reaction of the potassium *O*-alkyl dithiocarbonates (in small excess) with the *O*-alkyl chlorothiocarbonates; the latter were prepared by a drastic modification of the Rivier's method.[6] The pyrothiocarbonates procedure affords products of high purity (yields >90%).

$$R^1OCS_2K + R^2OCSCl \longrightarrow R^1OCS\text{-}S\text{-}CSOR^2 + KCl$$

(9) $R^1 = Bu$, $R^2 = Et$
(11) $R^1 = R^2 = Bu$

Application of the desulphurization procedure with potassium cyanide [7] to bis(butoxythiocarbonyl) disulphide (12) gave *S*-butyl *O*-butyl dithiocarbonate (13).

$$(BuOCS)_2S_2 \xrightarrow{KCN} BuOCS_2Bu + COS$$

(12) (13)

Finally (10) was prepared by slow addition of potassium *O*-butyl dithiocarbonate to an excess of ethyl chlorocarbonate in acetone at 0 °C, which is the same method as that for the formation of (1).

$$BuOCS_2K + ClCO_2Et \longrightarrow BuOCS\text{-}S\text{-}CO_2Et + KCl$$

(10)

Experimental

^1H N.m.r. spectra at 100 MHz were run on a Varian XL-12 WG instrument. Solutions were in $CDCl_3$ ($SiMe_4$ as internal reference). I.r. spectra were run using KBr plates on a Perkin-Elmer 567 machine.

Preparation of (1),[1] (4),[5] (5),[5] (7),[8] (8),[9] (12),[7] (13),[10]

* After three weeks *S*-ethyl *O*-ethyl dithiocarbonate was detected among other products in the reactions mixtures according to equations (ii) and (iii).

$BuOCS_2K$,[8] EtOCSCl [6] and BuOCSCl [6] have been previously described. Ethanol (95%), toluene and acetone were analytical reagent grade.

Reaction of (1) *with Potassium* O-*Alkyl Thiocarbonates.*—A solution of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (1) (20 mmol) in 95% ethanol (10 ml) at 0 °C was added to a solution of potassium *O*-ethyl thiocarbonate or *O*-ethyl dithiocarbonate (2 mmol) or potassium *O*-butyl dithiocarbonate (5 mmol), in 95% ethanol (50 ml) at 0 °C with stirring which was stopped after 30 s. Samples (5 ml) were taken from the reaction solution at different periods of times. The aliquots were quickly quenched by pouring them into an excess of cold 5% aqueous HCl and extracted with chloroform (2 × 25 ml). The combined chloroform extracts were washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), filtered, and the solvent evaporated under reduced pressure. The residue was diluted to 10 ml with toluene and analyzed by v.p.c.

Analytical Method.—V.p.c. was performed with a Perkin-Elmer 900 machine equipped with a flame-ionization detector and a 5 ft × 1/8 in stainless-steel column filled with 5% SE-30 on Chromosorb W. An oven programmed temperature of 140—200 °C was used. Peak integration was carried out by a Perkin-Elmer M-1 integrator. The concentrations are reported as the average of at least two measurements interpolated from a calibration curve determined by injection of samples of known concentrations of differents standard compounds.

Synthesis of Pyrothiocarbonates.—S-*Ethoxythiocarbonyl* O-*butyl dithiocarbonate* (9). A solution of potassium *O*-butyl dithiocarbonate (50 mmol) in acetone (50 ml) was cooled in an ice-bath and a solution of *O*-ethyl chlorothiocarbonate (55 mmol) in acetone (25 ml) was added. The mixture was stirred; after 5 min an excess of 10% aqueous HCl was added and then extracted with chloroform (2 × 50 ml). The combined chloroform extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), filtered, and the solvent evaporated under reduced pressure to leave a yellow oil, b.p. 115—116 °C at 0.1 mmHg; n_D^{24} 1.5795; $\nu_{max.}$ 1 270 (C=S) and 1 000 (C–O–C); δ_H 0.98 (3 H, t, $CH_3CH_2CH_2CH_2O$), 1.49 (3 H, t, CH_3CH_2O), 1.3—1.7 (2 H, m, $CH_3CH_2CH_2CH_2O$), 1.83 (2 H, m, $CH_3CH_2CH_2CH_2O$), 4.66 (2 H, q, CH_3CH_2O), and 4.72 (2 H, t, $CH_3CH_2CH_2CH_2O$) (Found: C, 40.6; H, 6.1; S, 39.95. Calc. for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92; S, 40.35%).

S-*Ethoxycarbonyl* O-*butyl dithiocarbonate* (10). This compound was prepared by a similar procedure [1] to that of (1), it was a yellow oil, b.p. 120—121 °C at mmHg, n_D^{24} 1.5130; $\nu_{max.}$ 1 750 (C=O), 1 270 (C=S), and 1 030 (C–O–C); δ_H 1.00 (3 H, t, $CH_3CH_2CH_2CH_2O$), 1.36 (3 H, t, CH_3CH_2O), 1.52 (2 H, m, $CH_3CH_2CH_2CH_2O$), 1.86 (2 H, m, $CH_3CH_2CH_2CH_2O$), 4.33 (2 H, q, CH_3CH_2O), and 4.66 (2 H, t, $CH_3CH_2CH_2CH_2CH_2O$) (Found: C, 42.95; H, 6.5; S, 29.05. Calc. for $C_8H_{14}O_3S_2$: C, 43.22; H, 6.35; S, 28.84%).

Bis(*butoxythiocarbonyl*) *sulphide* (11). This compound was prepared by a similar method to that for (9) except that *O*-butyl chlorothiocarbonate was used; it was a yellow oil, decomp. at 120 °C at 0.1 mmHg; n_D^{24} 1.5542; $\nu_{max.}$ 1 275 (C=S) and 1 000 (C–O–C); δ_H 1.00 (3 H, t, CH_3), 1.47 (2 H, m, CH_3CH_2), 1.83 (2 H, m, $CH_3CH_2CH_2$), and 4.63 (2 H, t, CH_2O) (Found: C, 45.2; H, 6.55; S, 35.85. Calc. for $C_{10}H_{18}O_2S_3$: C, 45.08; H, 6.81; S, 36.10%).

Acknowledgements

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