

The Mechanism of Thermal Eliminations. Part 24.¹ Elimination from Mono-, Di-, and Trithiocarbonates. The Dependence of the Transition State Polarity, Thione to Thiol Rearrangement, and Ether Formation *via* Nucleophilic Substitution, on Compound Type

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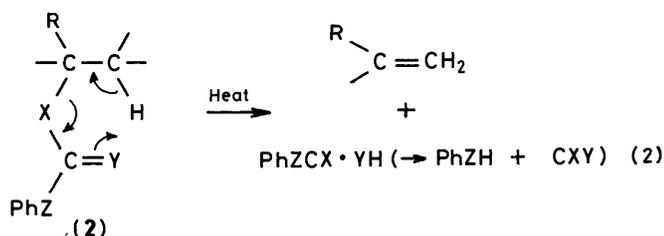
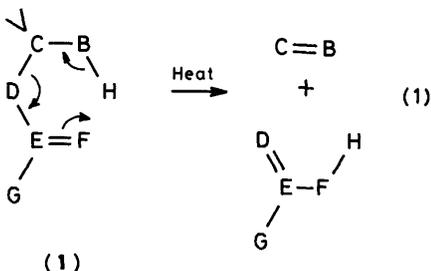
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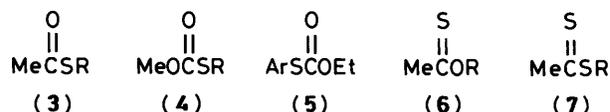
We have measured rates of thermal decomposition and Arrhenius parameters for *S*-alkyl *O*-phenyl thiocarbonates, *O*-alkyl *O'*-phenyl thiocarbonates, *S*-alkyl *O*-phenyl and *O*-alkyl *S*-phenyl dithiocarbonates (xanthates), and alkyl phenyl trithiocarbonates between 671.4 and 819.2 K. The reactivity order is: PhOCSOR > PhOCO₂R > PhSCSOR > PhSCO₂R > PhOCSSR > PhSCSSR > PhOCOSR > (PhSCOSR). Compared with the pyrolysis of acetates the rate decrease accompanying change of carbonyl to thiocarbonyl is smaller, whilst that accompanying change of OR to SR is greater, because the transition state for carbonate pyrolysis is more *E*₁-like within the overall semi-concerted process. The accelerating effect of thion sulphur is greatest for ethyl derivatives which have the least *E*₁-like transition state. The Pri/Et rate ratios at 700 K are: 30.7(PhOCO₂R), ≤17.4(PhOCOSR), 2.0(PhOCSSR), 1.6(PhSCSSR), and for the latter two classes of compounds attack on the β-C-H bond, rather than C_α-X bond breaking may be the most important rate-determining step. Compounds containing thione sulphur and *O*-alkyl groups (but not *O*-phenyl groups) undergo sulphur-oxygen exchange. A mechanism for this exchange is given which accounts both for these structural aspects and the much slower exchange in thionacetates. For carbonates, exchange is more severe for compounds which have the slowest competing elimination. Compounds PhSCSSPri, PhSCSSEt, PhOCSSEt, and PhOCOSEt each gave abnormally low activation energies (and low stoichiometry) due to competing nucleophilic substitution which gives ethers. This reaction is predicted to be important also for compounds PhSCOSR.

In previous parts of this series it has been shown that within the semi-concerted mechanism for pyrolytic eliminations involving 1,5-hydrogen shifts (1) a spectrum of transition-state structures exists. For some compounds, and especially carboxylic acid esters, breaking of the bond to the α-carbon [the C-D bond in (1)] is the most important rate-determining step, whilst for others it is nucleophilic (or basic) attack upon the β-hydrogen. Changes in structure within a given compound type have been shown to change the nature of the transition state within these limits (which correspond to either a more *E*₁-like, or a more *E*_T-like, transition state). In this paper we examine the pyrolysis of



carbonates (2) in which X, Y, and Z are variously sulphur, and R is H or Me.

S-Alkyl thioacetates (3) and *S*-alkyl *O*-methyl thiocarbonates (4) are less reactive than their oxygen-containing counterparts (by factors of 9 and 117 respectively, for the ethyl derivatives at 600 K).² They have less *E*₁-like transition states, though C_α-S bond breaking is still the most important step of the reaction. *S*-Aryl *O*-ethyl thiocarbonates (5) are also less reactive than the corresponding carbonates, but by a much smaller factor (1.86 at 600 K for the ethyl compounds³), and this is also consistent with a transition state in which C_α-O bond breaking is the most important step. This difference in the magnitude of the effect of sulphur at the two positions has also been found in other dialkyl carbonates.⁴ For *O*-alkyl thioacetate (6) the high nucleophilicity of the C=S bond compared with the C=O bond produces a substantial increase in rate,⁴⁻⁶ and this is more marked the less *E*₁-like the transition state.² Thus the rate differences are 187-fold and 83-fold for the ethyl and *t*-butyl compounds at 600 K.² Changing C=O to C=S in thioacetates (which have a less *E*₁-like transition state as noted above) should produce the largest rate increase, and thus ethyl dithioacetate (7; R = Et) is more reactive than *S*-ethyl thioacetate (3; R = Et) by a factor of 315 at 600 K.



In addition to the primary elimination (2) for sulphur-containing carbonates, secondary reactions can occur. These are thione to thiol rearrangement, and nucleophilic substitution

Table 1. Kinetic data for pyrolysis of compounds PhZCYXR

R	Z Y X	T/K	$10^3 k/s^{-1}$	$E/kJ mol^{-1}$	$\log(A/s^{-1})$	$10^4 k/s^{-1}$ at 700 K	Corr. coeff.
Et	O O S	690.7	0.208	190.7	10.75	3.21	0.999 87
		705.7	0.428				
		722.6	0.890				
		731.2	1.45				
		786.5	12.0				
		796.4	17.4				
		803.1	22.1				
		810.6	28.8				
		819.2	38.7				
		819.2	38.7				
Pr ⁱ	O O S	671.4	1.20	207.9	13.26	56.4	0.999 49
		690.7	3.5				
		705.7	7.31				
		722.6	18.1				
		729.4	25.6				
		739.5	38.9				
		750.0	59.9				
		755.8	73.5				
Et	O S O	678.9	0.295	198.3	11.73	8.52	0.999 81
		706.2	1.20				
		721.6	2.37				
		731.2	3.65				
Pr ⁱ	O S O	671.4	1.51	See text	Too fast to measure		
Pr ⁱ	S S O	690.7	4.98				
705.7	9.96						
722.6	14.8						
Et	O S S	680.4	3.67	201.3	13.02	98.7	0.999 60
		689.5	5.97				
		693.2	6.72				
		698.2	9.18				
		708.2	14.7				
		718.4	22.7				
		726.5	34.5				
		734.5	51.3				
		739.5	63.4				
		739.5	63.4				
Pr ⁱ	O S S	671.4	4.18	209.0	13.89	196	0.999 50
		690.7	12.3				
		760.2	27.5				
		721.6	55.7				
Et	S S S	671.4	0.65	183.9	11.11	24.3	0.999 90
		698.2	2.22				
		708.2	3.51				
		718.4	5.52				
		726.5	7.85				
		732.5	10.1				
		732.5	10.1				
Pr ⁱ	S S S	671.4	1.09	167.2	10.06	38.2	0.999 15
		690.7	2.68				
		705.7	4.97				
		722.6	9.06				

Table 2. Prⁱ/Et rate ratios at 700 K for compounds PhZCYXR

Z	Y	X	$k(\text{Pr}^i):k(\text{Et})$
O	O	O	30.7 ^a
O	O	S	≥ 17.4 ^b
O	S	S	1.99
S	S	S	1.6

^a The Arrhenius parameters for the isopropyl and ethyl compounds are respectively, $E_{\text{act}} = 180.3, 189.5 \text{ kJ mol}^{-1}$; $\log A = 13.5, 12.7 \text{ s}^{-1}$. Note that in ref. 2 the Arrhenius parameters given for isopropyl and t-butyl carbonates are in fact the acetate values. The correct carbonate values are given in Table 1 of that paper. This error does not significantly affect the discussion. ^b See text.

side reactions depend upon the structures of the carbonates, and give the mechanisms for both in terms of current theories of gas-phase pyrolysis reactions. We also correct an earlier report on the pyrolysis of *O*-ethyl *O'*-methyl thiocarbonate and *O*-ethyl *S*-methyl thiocarbonate.¹²

Results and Discussion

Kinetic data are given in Table 1, and the Prⁱ/Et rate ratios, along with those previously obtained for PhOCO₂R¹³ are assembled in Table 2. The main features of the results are as follows:

1. *S*-Alkyl *O*-Phenyl Thiocarbonates (PhOCOSR) (Scheme 1, R = H, Me; X = S, Y = O).—(a) *Isopropyl compound*. The activation energy was higher than that for the oxygen analogue (*cf.* Table 2 footnote) whilst the $\log A$ values are almost identical. Accordingly the elimination rate is less than that of the

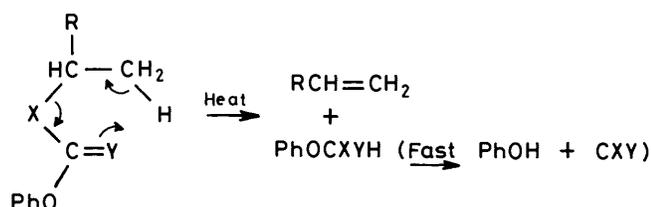
to give ethers, which have been observed on a number of previous occasions⁷⁻¹¹ though the mechanisms have not been adequately described. We now show the extent to which these

Table 3. RO/RS rate ratios at 600 K for compounds GCO·XR

G	$k(\text{Pr}^i\text{O}):k(\text{Pr}^i\text{S})$	$k(\text{EtO}):k(\text{EtS})$
Me ^{2,14}	17	9
MeO ²	157	117
PhO ^a	484	≥91

^a This work.

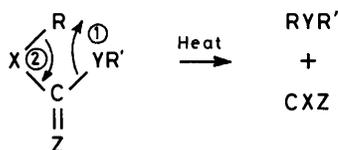
oxygen analogues and by a factor of 195 at 700 K (484 at 600 K), consistent with a less polar C–X bond. One of us has previously established that for a semi-concerted elimination with *E1* character, the elimination rate is proportional to the polarity of this bond.¹³ Because the transition state for carbonate pyrolysis is more *E1*-like than that for acetate pyrolysis, the rate reductions on going to compounds with thiol sulphur are much greater in the former compounds (Table 3). Likewise the factor for the phenyl carbonates (Table 3) is greater than for the methyl carbonates since the former have the more *E1*-like transition state.²



Scheme 1. R = H, Me;

S-Alkyl *O*-phenyl thiocarbonates, X = S, Y = O*O*-Alkyl *O*'-phenyl thiocarbonates, X = O, Y = S*S*-Alkyl *O*-phenyl dithiocarbonates, X = Y = S

(b) *Ethyl compound*. The activation energy, the log *A* value, and the stoichiometry were each anomalously low, indicating that concurrent nucleophilic substitution was taking place (confirmed in separate product runs). Nucleophilic substitution produces the ether (Scheme 2, R = Et, R' = Ph, X = S, Y = Z = O), and has a stoichiometry of only 2.0 compared with 3.0 for the elimination. It has a lower activation energy because the strong C–H bond is not broken (*cf.* elimination) and decreases in importance along the series: Et > Prⁱ > Bu^t.¹⁵ It has previously been found to accompany the pyrolysis of *O*-alkyl *O*'-aryl thiocarbonates (after rearrangement to *S*-alkyl *O*-phenyl thiocarbonates—see below)¹⁰ but no mechanism for the reaction was given.



Scheme 2. Nucleophilic substitution in carbonates to produce ethers.

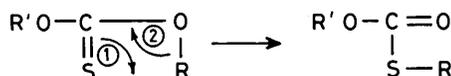
The lower activation energy for substitution means that it will produce increasingly enhanced overall reaction rates the lower the temperature. Hence the Prⁱ/Et rate ratio of 17.4 at 700 K is a minimum value, the true value being probably greater but cannot be more than 30.7, the value for the oxygen analogues which have a more *E1*-like transition state.

Because the transition state for pyrolysis of ethyl esters is less *E1*-like than that for pyrolysis of isopropyl esters, the rate reducing effect of thiol sulphur should be smaller for the former

than for the latter. This is precisely observed (Table 3) and as for the isopropyl esters the effect is larger in the carbonates than acetates which again reflects the differences in the transition states for the two classes of compounds.

2. *O*-Alkyl *O*'-Phenyl Thiocarbonates (PhOCSOR) (Scheme 1, R = H, Me; X = O, Y = S).—(a) *Isopropyl compound*. This pyrolysed very rapidly and rate data could not be obtained at temperatures at which we could be certain that surface-catalysed reactions would not intrude. It is evident however that this compound is significantly more reactive than the oxygen analogue, consistent with the higher nucleophilicity of the C=S versus the C=O bond.

(b) *Ethyl compound*. This gave a good Arrhenius plot and correct stoichiometry, but the elimination rate was slower than that of PhOCO₂Et. Now this cannot arise from the normal elimination mechanism and shows that thion to thiol rearrangement must be occurring (Scheme 3, R = Et, R' = Ph). In principle this could give either PhSCO₂Et or PhOCOS₂Et, but separate product runs showed that only the latter is formed. The reason for this specificity and further aspects of the mechanism are discussed below.



Scheme 3. Thione to thiol rearrangement in thiocarbonates

Since the observed rate is a little faster than that of PhOCOS₂Et (shown above to be very slow), it must arise from a combination of this slow elimination, and rapid elimination from PhOCSOEt. The rate coefficients indicates that *ca.* elimination 10% takes place *via* the latter compound.

3. *S*-Alkyl *O*-Phenyl Dithiocarbonates (*Xanthates*) (PhOCSSR) (Scheme 1, R = H, Me; X = Y = S).—(a) *Isopropyl compound*. The log *A* value was similar to that obtained with PhOCOSPrⁱ. Thione to thiol rearrangement is unlikely here, but nucleophilic substitution is more likely (see discussions below), and the latter was confirmed both by the low stoichiometry, and the isolation of PhOPrⁱ among the reaction products. Since this is a secondary carbonate, nucleophilic substitution is relatively minor, and product runs at 643 K showed it to be less important than for the primary (ethyl) carbonate (below).

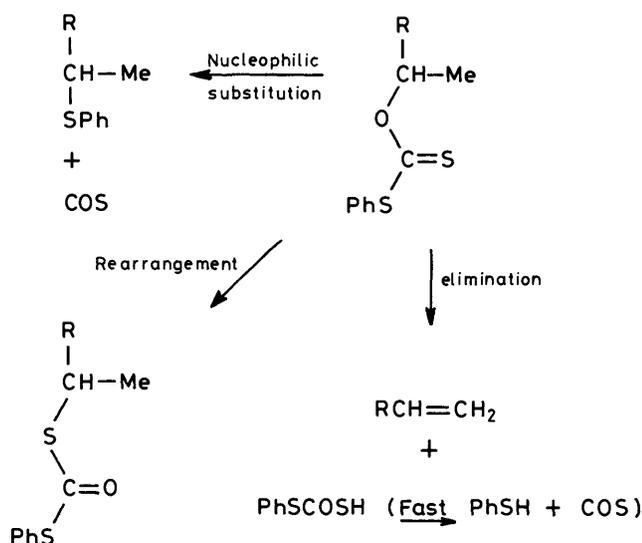
Comparison with the results in 2(a) gives a very low C=S/C=O rate ratio of 3.5 at 700 K which may be compared with that for *O*-alkyl thioacetates:acetates of 187 (ethyl) and 83 (*t*-butyl), both at 600 K,² and *ca.* 50–100 fold between *O*,*O*'-dialkyl thiocarbonates and dialkyl carbonates at 629 K.¹² The transition state for carbonate (and especially phenyl carbonate) pyrolysis is more *E1*-like than for acetate pyrolysis¹³ so a smaller factor would be expected, but on the other hand the comparison being made is between PhOCS·SPrⁱ and PhOCO·SPrⁱ, so for thiocarbonates the transition state should be appreciably less *E1*-like, making the smallness of the factor unexpected. It may arise from the nucleophilicity of thione sulphur being critically dependent upon the electron supply from G [see (1)]. For acetates G is methyl which can release electrons *via* C–H hyperconjugation, and in dialkyl carbonates G is alkoxyl which is also strongly electron-releasing. However for phenyl carbonates resonance between oxygen and the phenyl ring may result in poor conjugation between oxygen and C=S. Evidence that this is an important factor is adduced under 5 below.

(b) *Ethyl compound*. This gave a good Arrhenius line but low stoichiometry showing that some nucleophilic substitution was occurring, confirmed by isolation of PhOEt among the reaction products at 643 K. At 700 K the rate of pyrolysis was

30.5 times faster than for PhOCSEt, a larger factor than in 3(a) because of the more E_i -like transition state.

The relative rate of elimination of the isopropyl and ethyl compounds is 2.0 at 700 K which indicates a much more E_i -like transition state. Given that factor, the modest increase in reactivity relative to the carbonyl-containing analogues is very surprising and it could be argued that this is due to the incursion of nucleophilic substitution (see below). However, this would produce unexpectedly fast rates which is certainly not the case. A similarly low value is obtained with the *S*-alkyl *S'*-phenyl trithiocarbonates under 5 below.

4. *O*-Isopropyl *S*-Phenyl Dithiocarbonate (*Xanthate*) (PhSC-SOPrⁱ).—This compound did not give a satisfactory Arrhenius line and in the light of the other results this can be explained. Compared with PhOC SOPrⁱ it will be less reactive towards elimination, and therefore more susceptible to both nucleophilic substitution and thione to thiol rearrangement (Scheme 4). The

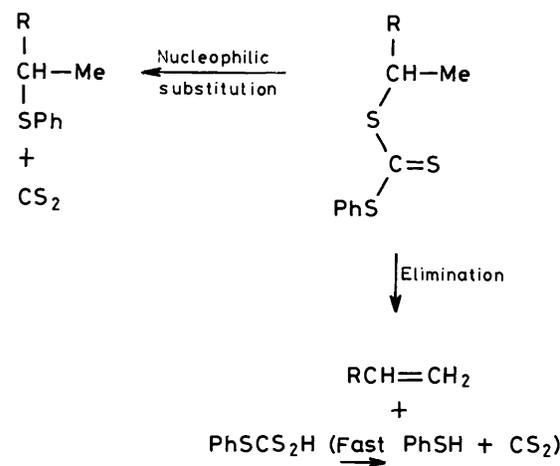


Scheme 4. R = H, Me

presence of these reactions was confirmed by the isolation in product runs of both PhSCOSPrⁱ and PhSPrⁱ, the proportion of the latter increasing with increasing temperature; the latter was also formed exclusively on fractional distillation of one batch preparation. The presence of two substantial competing side reactions prevents meaningful analysis of the rate data.

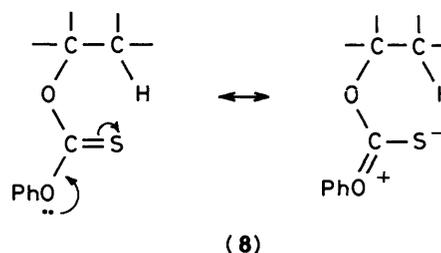
5. *S*-Alkyl *S'*-Phenyl Trithiocarbonates, (PhSCSSR) (Scheme 5, R = H, Me).—(a) *Isopropyl compound*. The compound gave a good Arrhenius line, but again low stoichiometry and isolation of some PhSPrⁱ in product runs at 643 K showed that nucleophilic substitution, the only possible side reaction here, was occurring (Scheme 5). Towards elimination one would expect that this compound would be less reactive than PhOCSSPrⁱ, and this is found, the factor being 5.1-fold at 700 K.

(b) *Ethyl compound*. This also gave a good Arrhenius line, but nucleophilic substitution was partially occurring shown by the stoichiometry and isolation of some PhSEt at 643 K, the relative amount being greater than for the isopropyl compound (above) as expected. The elimination rate relative to the isopropyl compound was 1.6 at 700 K, similar to but slightly smaller than that (2.0 at 700 K) between the *S*-alkyl *O*-phenyl dithiocarbonates, the same reason applying [cf. 3(b)]. This compound is less reactive than PhOCSSEt by a factor of 4.15-fold at 700 K. This is larger than that (1.86 at 600 K) which applies between PhSCO₂Et and PhOCO₂Et, and is consistent



Scheme 5. R = H, Me

with the greater importance of nucleophilic attack at the β -hydrogen in the former pair of compounds such that the resonance (8) becomes more important. This analysis reinforces that in 3 above in which it was also concluded that the nucleophilicity of the C=S bond (or thione sulphur) is critically dependent on the electron supply from the group G [in (1)].



Gas-phase Nucleophilic Substitution.—Little is known about this 4-centre S_Ni reaction of carbonates (Scheme 1) apart from its tendency to be surface-catalysed, retarded by steric hindrance in the alkyl group R, and aided by electron-withdrawal in the aryl group (Scheme 2, R' = Ar).¹⁵ The reaction has previously been observed in pyrolysis of sulphur-containing carbonates *viz.* *O*-alkyl *O'*-aryl thiocarbonates ArOCSSOMe which gave aryl methyl ethers (after initial rearrangement to the *S*-methyl carbonate), and *O*-alkyl *S*-methyl dithiocarbonates which gave dialkyl sulphide;¹⁶ no mechanistic details were given in either case.

The literature results and those we have obtained indicate that the reaction is semi-concerted, such that movement of the electron pair 1 in Scheme 2 somewhat precedes movement of pair 2, *i.e.* the reaction has S_N2 rather than S_N1 character. As a result C-Y bond-breaking and attack on R is more important than R-X bond-breaking. Consistent with this view are the following:

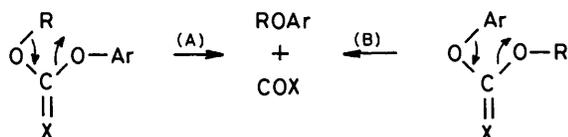
(i) *S*-Alkyl *O*-aryl thiocarbonates (RSCO-OR') (Scheme 2) undergo substitution more readily than carbonates (ROCO-OR'). This may be an apparent rather than a real effect arising from the greater importance of C_α-X bond polarisation and breakage for elimination, but not substitution. Hence elimination is so much faster for carbonates that substitution is not observed.

(ii) *O*-Alkyl *O'*-aryl thiocarbonate (ROCS-OR') are probably more reactive towards substitution than are carbonates. It is difficult to be certain of this at present because *O*-alkyl *O'*-aryl thiocarbonates can only be satisfactorily examined if a thiol sulphur is also present to prevent rearrangement, and this

introduces a third factor noted under (iii). Nevertheless, for nucleophilic substitution to occur rather than elimination, electron-withdrawal from Y by Z (Scheme 2) should be minimal, and hence for the reaction to occur $Z = S$ is more favourable than $Z = O$.

(iii) The reaction is favoured in *O*-alkyl *S*-aryl thiocarbonates (ROCO-SR') (Scheme 2), which follows from the greater nucleophilicity of sulphur compared with oxygen. Since electron-withdrawal in R' appears to increase the reaction rate,¹⁵ presumably through aiding polarisation of the C-Y bond, nucleophilic substitution should be more rapid in alkyl aryl carbonates than in dialkyl carbonates (and likewise in the various sulphur derivatives). As yet there is no accurate information on this point.

(iv) The reaction (A) in Scheme 6 is preferred to reaction (B). This is because the ArO bond is stronger than the

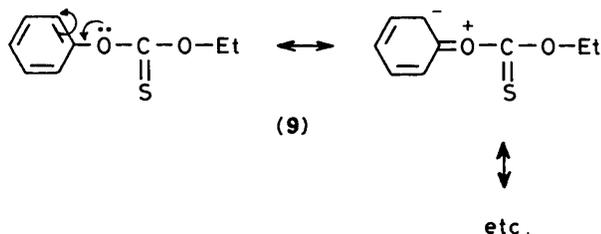


Scheme 6. Alternative pathways for nucleophilic substitution in carbonates

RO bond as a result of resonance in the former [see (9)]. This preference is not detectable in carbonates or *O*-alkyl *O'*-aryl thiocarbonates with ¹⁸O-labelling, but the correctness of the conclusion is provided by the isolation [see 3(b)] of phenetole (but not thiophenetole) from pyrolysis of PhOCOS₂Et. Thus although, as noted in (iii) above, sulphur is more nucleophilic than oxygen, nucleophilic attack by SEt would involve simultaneous Ph-O bond-breaking whereas attack by PhO requires S-Et bond-breaking only so this latter is preferred.

Thus for carbonates which are unsymmetrical with regard to the nature of the groups R/Ar, nucleophilic substitution will take place with increasing ease according to the nature of the attacking group as follows: SAr > OAr > SR > OR.

Thione to Thiol Rearrangement.—This reaction probably involves nucleophilic attack of thione sulphur upon one of the R groups shown in Scheme 3. As with most (if not all) electrocyclic reactions, it is unlikely that the process is fully concerted, and nucleophilic attack will partially precede breaking of the *O*-alkyl bond, *i.e.* movement of electron pair 1 will precede to some extent movement of pair 2. Our finding that *O*-alkyl *O'*-phenyl thiocarbonates rearrange only to the *S*-alkyl *O*-phenyl thiocarbonates follows because resonance between oxygen and the aryl ring (9) strengthens the aryl oxygen bond, so this factor accounts for the behaviour in both nucleophilic substitution and rearrangement.



All of the available information in the literature is consistent with this mechanism:

(i) The mechanism requires the central carbon to be electron-deficient so rearrangement should be aided by electron supply in the non-migrating group. Hence the yield of *O*-aryl *S*-methyl

thiocarbonate on rearrangement of *O*-aryl *O'*-methyl thiocarbonates ArOCSOMe increased, the more electron-releasing the substituent in the aryl ring.¹⁰ (In this work an ionic mechanism was proposed for the rearrangement which is clearly incorrect.) Because electron release to the central carbon increases the rate of rearrangement, it follows that *O*-alkyl *N*-aryl thiocarbonates (in which R'O is replaced by R'NH) rearrange much more readily than the corresponding *O*-alkyl *O'*-aryl thiocarbonates.¹⁷ Likewise the rearrangement is slower in *O*-alkyl thiocarbonates because R' is not so electron releasing as R'O.

(ii) Since nucleophilic attack upon R is the most important step of the reaction it follows that electron-withdrawal in R should increase the reaction rate. This has been found to be the case for the rearrangement of *O*-aryl thiobenzoates PhCSOAr to *S*-aryl thiobenzoates PhCOSAr in diphenyl ether at 200.5 °C, the ρ -factor for substituents in the aryl ring being 2.11.⁹ Similarly the rearrangement of *O,S*-diaryl dithiocarbonates ArSCSOAr' gave a correlation with $\rho = 1.87$ for the effects of substituents in the aryl ring Ar', whilst the electron deficiency at the central carbon in the transition state is also confirmed by the ρ -factor of -0.41 found for the effects of substituents in the aryl ring Ar'.⁹ For rearrangement of *N,N*-dialkyl *O*-aryl thiocarbonates R₂NC₂SOAr, the ρ -factor for the effects of substituents in the aryl ring was 1.97.^{18,19}

(iii) The greater importance of nucleophilic attack upon R (Scheme 3) is confirmed by the greater ease of rearrangement of *O, O'*-diaryl thiocarbonates if both aryl groups contain electron-withdrawing substituents.⁸

Rearrangement in *O, O'*-Dialkyl Thiocarbonates.—Previously one of us reported rates of thermal decomposition of some *O, O'*-dialkyl thiocarbonates and *O, S'*-dialkyl dithiocarbonates, but failed to find any evidence of thione to thiol rearrangement, or nucleophilic substitution though the reaction stoichiometry was not checked.¹² The present results indicated that for *O*-ethyl *O'*-methyl thiocarbonate MeOC₂SOEt, and *O*-ethyl *S*-methyl dithiocarbonates MeSC₂SOEt, rearrangement should have been considerable. Separate product runs have confirmed that rearrangement occurs readily, so that the reported kinetic data on these compounds¹² should be treated cautiously.

Correction of a Printing Error.—In reference 2, the rate data in the Scheme on page 294 were printed wrongly, which makes the argument in the text difficult to follow. It should be noted therefore that the rate coefficients and relative rate data shown under compounds (6)–(9) should be interchanged with those under compounds (10)–(13).

Experimental

Kinetic Studies.—These were mainly carried out by the static method using a stainless steel reactor. Recent improvements to the method and leading references have been given previously.³ For compounds especially prone to nucleophilic substitution, runs were carried out in a flow reactor in order to reduce surface contact time. For compounds where this was not a problem, runs carried out by both methods over a common temperature range, gave rate coefficients identical within experimental error.

***O*-Ethyl *S*-phenyl thiocarbonate.** This compound has been described previously.³

***S*-Ethyl *O*-Phenyl Thiocarbonate.**—Pyridine (15 ml) was slowly added to a cooled mixture of ethanethiol (6.2 g, 0.1 mol) and phenyl chloroformate (28.2 g, 0.2 mol), the mixture being then heated under reflux during 1 h. Normal work-up and fractional distillation gave *S*-ethyl *O*-phenyl thiocarbonate (13.3 g, 73%), b.p. 43 °C at 0.75 mmHg; δ (CDCl₃) 7.0–7.4 (5 H, m,

ArH), 2.8 (2 H, q, CH₂), and 1.28 (3 H, t, Me) (Found: C, 59.2; H, 5.5; S, 17.7. C₉H₁₀O₂S requires C, 59.3; H, 5.5; S, 17.6%).

S-Isopropyl O-phenyl thiocarbonate. The literature method²⁰ gave *S-isopropyl O-phenyl thiocarbonate* (70%), b.p. 81–82 °C at 0.3 mmHg; δ (CDCl₃) 7.0–7.5 (5 H, m, ArH), 3.87 (1 H, sept., CH), and 1.45 (6 H, d, Me₂) (Found: C, 61.3; H, 6.3; S, 16.3. C₁₀H₁₂O₂S requires C, 61.2; H, 6.1; S, 16.3%).

O-Ethyl O'-phenyl thiocarbonate. The general literature method⁸ employing reaction of preformed *O*-phenyl chloroformate with ethanol in pyridine gave *O-ethyl O'-phenyl thiocarbonate* (60%), b.p. 45–46 °C at 0.5 mmHg; δ (CDCl₃) 7.2–7.4 (5 H, m, ArH), 4.3 (2 H, q, CH₂), and 1.35 (3 H, t, Me).

O-Isopropyl O'-phenyl thiocarbonate. Adaptation of the literature method²⁰ gave *O-isopropyl O'-phenyl thiocarbonate* (50%), b.p. 64 °C at 1.0 mmHg; δ (CDCl₃) 7.2–7.6 (5 H, m, ArH), 5.5 (1 H, sept., CH), and 1.5 (6 H, d, Me₂) (Found: C, 61.2; H, 6.2; S, 16.3%).

O-Isopropyl S-Phenyl Dithiocarbonate.—Pyridine (10 ml) was added to phenyl chlorodithioformate (PhSCSCL, made from thiophenol and thiophosgene by the literature method²¹) (18.8 g, 0.1 mol) and propan-2-ol (13 ml) in cold dry benzene. The mixture was heated during 1 h. Normal work-up and fractional distillation yielded *O-isopropyl S-phenyl dithiocarbonate* (13.4 g, 63%), b.p. 51–52 °C at 0.8 mmHg; δ (CDCl₃) 7.2–7.6 (5 H, m, ArH), 5.4 (1 H, sept., CH), and 1.4 (6 H, d, Me₂) (Found: C, 56.7; H, 5.7; S, 30.4. C₁₀H₁₂OS₂ requires C, 56.6; H, 5.6; S, 30.2%). A second batch of this compound gave δ (CCl₄) 7.2–7.4 (5 H, m, ArH), 5.56 (1 H, sept., CH), and 1.28 (6 H, d, Me₂) for the crude product. However the product from fractional distillation gave δ (CCl₄) 7.0–7.4 (5 H, m, ArH), 3.27 (1 H, sept., CH), 1.25 (6 H, d, Me₂) but no carbonyl group in the i.r. spectrum (Found: C, 71.0; H, 7.9. C₉H₁₂S₂ requires C, 71.0; H, 7.95%). This product is therefore PhSPrⁱ and the result suggests that nucleophilic substitution occurs faster than rearrangement or β -elimination, at least when surfaces are not deactivated.

S-Ethyl O-Phenyl Dithiocarbonate.—The reaction of phenyl chlorothioformate²⁰ with ethanethiol in the presence of pyridine gave *S-ethyl O-phenyl dithiocarbonate* (70%), b.p. 50 °C at 0.08 mmHg; δ (CDCl₃) 7.2 (5 H, m, ArH), 3.22 (2 H, q, CH₂), and 1.40 (3 H, t, Me) (Found: C, 54.7; H, 5.2; S, 32.5. C₉H₁₀OS₂ requires C, 54.5; H, 5.1; S, 32.3%).

S-Propyl O-Phenyl Dithiocarbonate.—The reaction of phenyl chlorothioformate²⁰ with ethanethiol in the presence of pyridine gave *S-ethyl O-phenyl dithiocarbonate* (70%), b.p. 50 °C at 0.08 mmHg; δ (CDCl₃) 7.2 (5 H, m, ArH), 4.3 (2 H, q, CH₂), and 1.28 (3 H, t, Me) (Found: C, 54.7; H, 5.3; S, 32.7. C₉H₁₀OS₂ requires C, 54.5; H, 5.1; S, 32.3%).

S-Isopropyl O-Phenyl Dithiocarbonate.—The reaction of phenyl chlorothioformate²¹ with propane-2-thiol in the presence of pyridine gave *S-isopropyl O-phenyl dithiocarbonate* (67%), b.p. 110 °C at 1.0 mmHg, δ (CDCl₃) 7.0–7.4 (5 H, m, ArH), 3.70 (1 H, sept., CH), and 1.4 (6 H, d, Me₂) (Found: C, 56.5; H, 5.6; S, 30.3%).

Ethyl Phenyl Trithiocarbonate.—Reaction of phenyl chlorodithioformate²¹ with ethanethiol according to the literature method²² gave *ethyl phenyl trithiocarbonate* (63%), b.p. 70 °C at 0.13 mmHg (lit.,²² b.p. 144–147 °C at 2 mmHg); δ (CDCl₃) 7.2–7.5 (5 H, m, ArH), 2.8 (2 H, q, CH₂), and 1.30 (3 H, t, Me)

(Found: C, 50.5; H, 4.6; S, 44.9. C₉H₁₀S₃ requires C, 50.4; H, 4.7; S, 44.8%).

Isopropyl Phenyl Trithiocarbonate.—Reaction between phenyl chlorodithioformate and propane-2-thiol in the presence of pyridine according to the literature method²² gave *isopropyl phenyl trithiocarbonate* (60%), b.p. 42–43 °C at 1.8 mmHg (lit.,²³ b.p. 130–132 °C at 2.0 mmHg); δ (CDCl₃) 7.1–7.5 (5 H, m, ArH), 3.70 (1 H, sept., CH), and 1.4 (6 H, d, Me₂) (Found: C, 52.7; H, 5.3; S, 42.3. C₁₀H₁₂S₃ requires C, 52.6; H, 5.2; S, 42.1%).

O-Ethyl S-Phenyl Dithiocarbonate.—Slow addition of pyridine (10 ml) to a cooled solution of phenyl chlorodithioformate (0.15 mol) and ethanol (15 ml) in dry benzene, followed by heating under reflux during 1 h gave, after normal work-up, *O-ethyl S-phenyl dithiocarbonate* (70%), b.p. 87–88 °C at 1.0 mmHg; δ (CDCl₃) 6.7–7.2 (5 H, m, ArH), 4.0 (2 H, q, CH₂), and 1.4 (3 H, t, Me) (Found: C, 54.5; H, 5.2; S, 32.5%). Kinetics were not carried out on this compound because it underwent rapid isomerisation on heating (see Discussion).

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