On the Mechanism of Reduction of Dithiocarbonates (Xanthates) with Tributylstannane

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Competition experiments with various dithiocarbonates show that the deoxygenation occurs by addition of stannyl radicals to give (**2**) followed by fragmentation rather than by direct S_H2 attack on sulphide sulphur.

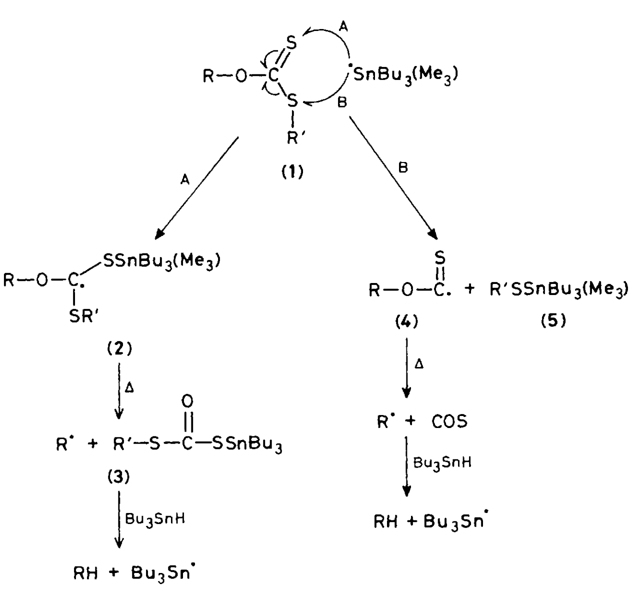
An alternative mechanism has recently been proposed for the reduction of dithiocarbonates (xanthates) with trialkylstannane.[1]

The original mechanism of Barton and McCombie[2] postulated an initial attack of the tin radical on the carbon–sulphur double bond followed by fission of the carbon–oxygen bond (Scheme 1, path A). Barker and Beckwith,[1] however, preferred a S_H2 step on the sulphide sulphur following the observation of e.s.r. signals attributed to alkoxythiocarbonyl radicals (**4**) (Scheme 1, path B), although under experimental conditions different from those normally used.

Given the importance of this reaction in the deoxygenation of secondary alcohols,[3] we have studied this reduction further and now adduce results which seem to weigh against an S_H2 process and in favour of the original mechanism.

Like other bimolecular substitutions, S_H2 reactions are subject to steric hindrance.[4] We therefore performed competition experiments between the *S*-methyl dithiocarbonate (**6**) and the more bulky isopropyl analogue (**7**). When an equimolar mixture of (**6**) and (**7**) was treated with one equivalent of Bu_3SnH at 80 °C, a rapid reaction took place (a few minutes), but only the isopropyl derivative (**7**) reacted. No cholestane (**8**) was produced however. Only the *S*-tributylstannyl dithiocarbonate (**9**) [from n.m.r., u.v., alkylation with MeI to (**6**) and further reduction to cholestane (**8**) with another equivalent of Bu_3SnH] and (presumably) propane are formed.

Although the nature of the products can be explained by an S_H2 attack on the sulphide sulphur and expulsion of an isopropyl radical, the surprisingly large rate of reaction is difficult to understand in terms of an S_H2 process. Moreover, even the *S*-mesityl dithiocarbonate (**11**) reacts at room temperature (but not to give deoxygenation, *vide infra*).



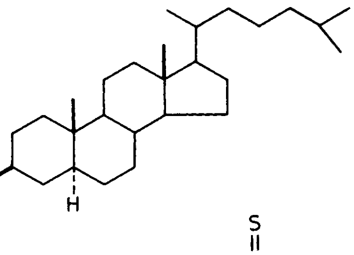
Scheme 1

We next studied arylthio systems of type –C(=S)–S–Ar where –S–Ar bond fission is improbable owing to the relatively strong sulphur–aryl bond.[4] Dithiocarbonates (**10**) and (**11**) were prepared in high yield by treating the imidazolide (**12**) with thiophenol and with 2,4,6-trimethylthiophenol respectively in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Competition experiments [0.1 mmol each of two dithiocarbonates in toluene (3 ml) with 0.15 mmol of tributylstannane] at 110 °C using a trace of AIBN (azoisobutyronitrile) as initiator under argon showed (**10**) to react fastest, followed by (**11**), and finally (**6**) (*ca.* 4:1.5:1). At this temperature only deoxygenation is observed. The effect of PhS relative to MeS is not unexpected.[5]

More important however is the observation that when fragmentation is not fast, each of (**6**), (**10**), and (**11**), when treated separately with Bu_3SnH in refluxing benzene (80 °C) [0.3 mmol of dithiocarbonate and 0.6 mmol of tributylstannane in benzene (4 ml) under argon with AIBN initiation], under as identical experimental conditions as possible, gave different results. Thus the mesitylene derivative (**11**) gives significantly more cholestane (**8**) (75%) than (**10**) (29%) or (**6**) (40%) (average of two experiments). The other major product is the hemi-monothioacetal (**13**) in the yields: 13% [from (**11**)], 35% [from (**10**)], and 35% [from (**6**)], originally formed as its tributylstannyl derivative.

If an S_H2 process is operating, cholestane (**8**) and the hemithioacetal (**13**) must be produced by competing pathways from the *same* alkoxythiocarbonyl radical (**4**). Under identical experimental conditions similar ratios of (**8**) and (**13**) should be obtained irrespective of the nature of R′ in the original dithiocarbonate (**1**) (Scheme 1, path B). This is clearly not the case, the ratios of (**8**) to (**13**) being *ca.* 6 [from (**11**)], *ca.* 0.8 [from (**10**)], and *ca.* 1.1 [from (**6**)].

These various observations are easily accommodated by the original mechanism (path A). The attack of the stannyl radical



(**6**) $X = -O-\overset{S}{\overset{\|}{C}}-SMe$

(**7**) $X = -O-\overset{S}{\overset{\|}{C}}-SPr^i$

(**8**) $X = H$

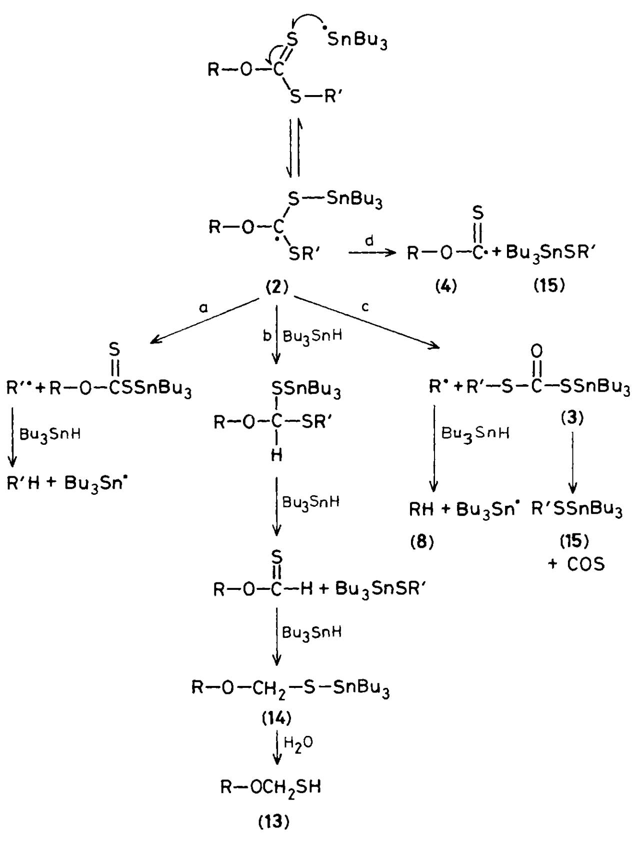
(**9**) $X = -O-\overset{S}{\overset{\|}{C}}-SSnBu_3$

(**10**) $X = -O-\overset{S}{\overset{\|}{C}}-SPh$

(**11**) $X = -O-\overset{S}{\overset{\|}{C}}-S-C_6H_2(2,4,6\text{-}Me_3)$

(**12**) $X = -O-\overset{S}{\overset{\|}{C}}-\text{Imidazole}$

(**13**) $X = -O-CH_2SH$



Scheme 2

on the carbon–sulphur double bond is rapid and reversible.[6] The carbon radical (**2**) thus formed can evolve in various ways depending on the experimental conditions and substituents R and R'.

When R' is isopropyl (and presumably any other secondary substituent), scission of the C–S– bond is favoured (Scheme 2, path a). In other cases and when reaction temperatures are relatively low, further reduction of radical (**2**) can compete with fragmentation to give finally the hemi-monothioacetal [such as (**13**)] after hydrolysis of the tin salt (**14**) (path b).

In the case of the mesityl derivative, release of steric strain conceivably favours fragmentation and therefore relatively higher yields of cholestane are obtained. Increasing the temperature (*e.g.* refluxing toluene) strongly favours the fragmentation and the alkane becomes practically the sole product (path c).

If the reaction is performed at a low temperature with photochemically generated tin radicals and in the absence of Bu_3SnH, as in the study by Beckwith and Barker, the intermediate radical (**2**) cannot fragment or be further reduced. It eliminates to give the apparently more persistent alkoxythiocarbonyl radical observed by e.s.r. (path d). In a similar way, species (**3**) can extrude carbonyl sulphide[7] to give sulphide (**15**) explaining the absence of carbonyl absorptions in the i.r. spectra of crude reaction mixtures.[2]

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