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DEOXYGENATION OF ALCOHOLS BY THE REACTIONS OF THEIR XANTHATE ESTERS WITH TRIETHYLSILANE: AN ALTERNATIVE TO TRIBUTYLTIN HYDRIDE IN THE BARTON-McCOMBIE REACTION

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Summary: O-Alkyl S-methyl dithiocarbonates derived from primary or secondary alcohols (ROH) react with trialkylsilanes in non-aromatic solvents to give the corresponding hydrocarbons RH in good yields; the reductions are promoted by thiols which act as polarity reversal catalysts.

The deoxygenation of a secondary alcohol by the reaction of the derived O-alkyl-S-methyl dithiocarbonate with tributyltin hydride [equation (1)] is a transformation of considerable importance, particularly in the carbohydrate and natural product fields. The general procedure, which is also applicable to a number of other

$$ROC(S)SMe + Bu_3SnH \longrightarrow RH + Bu_3SnSC(O)SMe \qquad (1)$$

thiocarbonyl derivatives,[1-5] is usually known as the Barton-McCombie reaction and the methodology has been extended to the deoxygenation of primary[6] and tertiary[7] alcohols. The available evidence indicates that, under normal conditions, the Barton-McCombie reaction proceeds by the radical chain mechanism shown in equations (2)-(4).[5,8,9]

$$Bu_3Sn^{\bullet} + ROC(S)SMe \rightleftharpoons RO\dot{C}(SMe)SSnBu_3 \qquad (2)$$

$$RO\dot{C}(SMe)SSnBu_3 \longrightarrow R^{\bullet} + Bu_3SnSC(O)SMe \qquad (3)$$

$$R^{\bullet} + Bu_3SnH \longrightarrow RH + Bu_3Sn^{\bullet} \qquad (4)$$

However, organotin compounds are toxic and are often difficult to remove completely from the reaction products, as well as being rather costly and presenting disposal problems. Simple, low molecular weight trialkylsilanes (e.g. Et_3SiH) would be acceptable alternatives, but apparently have not been seriously considered, presumably because it was thought that reaction (7) of the propagation sequence (5) - (7) would be too slow to give an adequate chain length.[10] We also suspect that simple trialkylsilanes may have been tried previously, but

$$Et_3Si^{\bullet} + ROC(S)SMe \longrightarrow RO\dot{C}(SMe)SSiEt_3 \qquad (5)$$

$$RO\dot{C}(SMe)SSiEt_3 \longrightarrow R^{\bullet} + Et_3SiSC(O)SMe \qquad (6)$$

$$R^{\bullet} + Et_3SiH \longrightarrow RH + Et_3Si^{\bullet} \qquad (7)$$

in the absence of effective initiation and using aromatic solvents, which are likely to prove less suitable than saturated solvents because silyl radicals add rapidly to arenes.[11]

We have reported recently[12] that reaction (7) is subject to polarity reversal catalysis by thiols, when the single step abstraction is replaced by the cycle of reactions (8) and (9).

$$R^{\bullet} + XSH \longrightarrow RH + XS^{\bullet} \quad (8)$$

$$XS^{\bullet} + Et_3SiH \longrightarrow XSH + Et_3Si^{\bullet} \quad (9)$$

We now report that S-methyl xanthates derived from primary and secondary alcohols react smoothly with triethylsilane in non-aromatic solvents in the presence of a thiol and an efficient source of initiation to give good yields of deoxygenated hydrocarbon products.

A series of pilot reactions of 1- and 2-octyl xanthates was carried out in sealed tubes at 115 °C. The reaction mixture consisted of the xanthate (2.5 mmol), triethylsilane (5.0 mmol), and decane (0.250 g) in cyclohexane (3.8 cm^3), together with 1,1-di-t-butylperoxycyclohexane initiator and t-dodecanethiol[13] catalyst. The yield of octane was determined by g.l.c. analysis (decane internal standard) and the results are summarised in Table 1.

Surprisingly high yields of octane were obtained from both primary and secondary octyl xanthates in the absence of thiol catalyst (entries 2 and 5). Although alkyl radicals do abstract hydrogen from trialkylsilanes quite rapidly at high temperatures,[14] it seems likely that SH-containing compounds could be generated in situ by side reactions and that these thiols may act as catalysts. Neither xanthate gave any octane in the absence of initiator (entries 1 and 4), confirming the radical chain nature of the reduction. These latter results highlight the importance of the initiation step of any chain process and suggest that the unexpectedly[5] efficient tin hydride-mediated reductions of primary[15] and secondary[16] alkyl xanthates which have been reported may be explained in terms of inefficient initiation under 'normal' reaction conditions. The need for effective initiation will be especially important if, as seems possible for the Barton-McCombie reaction, there is a heterolytic process which can compete.

Next, trialkylsilane reductions of the O-alkyl S-methyl dithiocarbonates derived from octadecan-1-ol and from 5α-cholestan-3β-ol were carried out in open flasks. The xanthate (2-2.5 mmol) and triethyl- or tripropyl-silane (2 or 4 molar equivalents) together with thiol catalyst and dicumyl peroxide initiator were heated in a hydrocarbon solvent (7.5 cm^3) under argon. After removal of all volatile material (40 °C, 0.1 Torr), the octadecane or 5α-cholestane was isolated from the residue by flash chromatography on silica using hexane eluant. The results are summarised in Table 2.

It is clear that primary and secondary alcohols can be efficiently deoxygenated by the reactions of the derived S-methyl xanthates with trialkylsilanes in non-aromatic solvents. Octadecyl xanthate and tripropylsilane in decane solvent at 140 °C (entry 4) gives a good yield of octadecane, while in m-xylene under otherwise identical conditions (entry 5) the yield of octadecane was lower, a significant amount of the xanthate remained unreacted, and by-products (including at least one aromatic compound) were formed.

TABLE 1

Reduction of O-octyl S-methyl dithiocarbonates by triethylsilane in cyclohexane at 115 °C

Entry	Xanthate	Initiator[a] (mol%)[b]	t-$C_{12}H_{25}SH$ (mol%)[b]	Reaction time/h	Octane yield (%)
1	2-Octyl	0	2	1	0
2		2	0	1	63
3		2	2	1	92
4	1-Octyl	0	2	1	0
5		2	0	1	46
6		2	2	1	63
7		5	2	4	82

[a] 1,1-Di-t-butylperoxycyclohexane, for reasons of safety handled as a 50% w/w solution in white oil.

[b] Based on xanthate.

TABLE 2

Reduction of O-alkyl S-methyl dithiocarbonates ROC(S)SMe by trialkylsilanes[a]

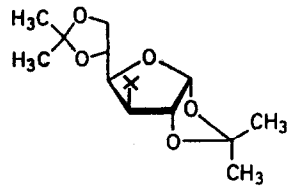
Entry	R	Solvent	t-$C_{12}H_{25}SH$ (mol%)[b]	Reaction conditions	Isolated Yield of RH (%)
1	Octadecyl	Octane	0	Reflux, 4 h	60
2		Octane	2	Reflux, 4 h	70
3[c]		Octane	2	Reflux, 4 h	80
4[d]		Decane	2	140 °C, 2 h	79
5[d]		m-Xylene	2	140 °C, 2 h	45
6	Cholestanyl	Octane	0	Reflux, 2 h	49
7		Octane	2	Reflux, 2 h	72
8[c]		Octane	2	Reflux, 4 h	89

[a] Two molar equivalents of triethylsilane unless noted otherwise. The initiator was dicumyl peroxide (4 mol%, based on xanthate).

[b] Based on xanthate.

[c] Four molar equivalents of triethylsilane.

[d] Two molar equivalents of tripropylsilane.



(1)

Deoxygenation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (1; X = OH), using classical Barton-McCombie methodology with Bu_3SnH as the reducing agent, gives (1; X = H) in 75% yield from the xanthate [1; X = OC(S)SMe].[1,17] When the xanthate was heated under reflux (bath temp. 140 °C) in octane for 6 h with four molar equivalents of triethylsilane and 2 mol% t-dodecanethiol, using di-t-butyl peroxide (20 mol%) as initiator, (1; X = H) was isolated in 60% yield.

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