Radical Chain Reduction of Alkyl Halides, Dialkyl Sulphides and *O*-Alkyl *S*-Methyl Dithiocarbonates to Alkanes by Trialkylsilanes

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Saturated primary, secondary and tertiary alkyl halides RX (X = Cl, Br or I) are reduced to the corresponding alkanes RH in essentially quantitative yield by triethylsilane in refluxing hexane or cyclohexane in the presence of a suitable initiator and an alkanethiol catalyst. Reduction proceeds by a radical chain mechanism and the thiol acts as a polarity reversal catalyst which mediates hydrogen-atom transfer from the Si–H group of the silane to the alkyl radical R•. Triphenylsilanethiol and perfluorohexanesulphenyl chloride are also effective catalysts; the latter is probably reduced *in situ* to the corresponding fluorinated thiol. Other silanes R_3SiH (R = Pr^n, Pr^i or Ph) also bring about reduction. The silane–thiol couple therefore serves as a useful replacement for tributylstannane as a homolytic reducing agent for alkyl halides. Reduction of 6-bromohex-1-ene, to give a mixture of hex-1-ene and methylcyclopentane, is more sluggish than reduction of saturated halides and this is attributed to removal of the thiol catalyst by addition across the C=C bond. Ethyl 4-bromobutanoate is smoothly reduced to ethyl butanoate without interference from the ester function. Dialkyl sulphides are reduced to alkanes by triethylsilane in a radical chain reaction, but the effect of added thiol depends on the nature of the *S*-alkyl groups in the sulphide. The trialkylsilane–thiol couple can also successfully replace trialkylstannane as the reducing agent in the Barton–McCombie deoxygenation of primary and secondary alcohols *via* their *S*-methyl dithiocarbonate (xanthate) esters. Good yields of deoxy compounds are obtained from octan-1-ol, octan-2-ol, octadecan-1-ol, 5α-cholestan-3β-ol, cholesterol and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose.

The removal of a functional group G from an organic compound R–G and its replacement by hydrogen to give R–H is a basic transformation of considerable importance in synthetic chemistry. A wide variety of reducing agents is available for bringing about such reactions, which can proceed by heterolytic or homolytic mechanisms. Radical reductions, which involve R• as a reactive intermediate, are less susceptible to steric retardation and less prone to give rearranged products than the heterolytic routes [1] and have found a rapidly expanding role in synthetic methodology.

Tri-n-butyltin hydride is pre-eminent amongst reagents for bringing about homolytic reductive removal of functional groups and such reactions follow the radical chain mechanism generalised in reactions (1) and (2).[2,†] However, organotin

$$Bu_3Sn^\bullet + R\text{–}G \longrightarrow Bu_3Sn\text{–}G + R^\bullet \quad (1)$$

$$R^\bullet + Bu_3Sn\text{–}H \longrightarrow R\text{–}H + Bu_3Sn^\bullet \quad (2)$$

compounds are toxic and are often difficult to remove completely from the desired reaction product, as well as being rather costly and presenting disposal problems. Simple, low molecular weight trialkylsilanes (especially Et_3SiH) would be very acceptable alternatives, through the propagating cycle of reactions (3) and (4). However, although reaction (3) is generally more exothermic and faster than its tin counterpart [reaction (1)], because of the greater strength of the Si–H bond compared with Sn–H (see Table 1), reaction (4) is

$$Et_3Si^\bullet + R\text{–}G \longrightarrow Et_3Si\text{–}G + R^\bullet \quad (3)$$

$$R^\bullet + Et_3Si\text{–}H \longrightarrow R\text{–}H + Et_3Si^\bullet \quad (4)$$

relatively slow [3] and chain lengths are short at moderate temperatures.[4]

Polar factors are unfavourable for reaction (4), because a nucleophilic alkyl radical is abstracting an electron-rich hydrogen atom, and we have proposed that this reaction should be subject to polarity reversal catalysis (PRC) by thiols, when the single-step process would be replaced by the cycle of reactions (5) and (6).[5,6] Thiyl radicals are electrophilic and both

† The tin atom may not become attached to the leading atom of the group G in R–G and the abstraction of G by $Bu_3Sn^\bullet$ may take place in a two-step addition-elimination sequence.

Table 1 Reaction enthalpies (ΔH°) and rate coefficients (k) for hydrogen-atom abstraction from M–H by primary alkyl radicals at 50 °C

M–H	DH° (M–H)[a] /kJ mol^{-1}	ΔH°[b] /kJ mol^{-1}	Abstracting radical[c]	Solvent[d]	k[e]/ dm^3 mol^{-1} s^{-1}	$k_{rel.}$[e]
Et_3SiH	377[f]	−42	A	Benzene	7×10^3	(1)
Bu_3SnH	310[g]	−109	B	THF	4.9×10^6	700
Bu^{t}SH	384[h]	−35	B	THF	1.0×10^7	1429

[a] Data from ref. 13 unles noted otherwise. [b] For hydrogen-atom abstraction by the ethyl radical [ref. 13 gives DH° (Et–H) = 419 kJ mol^{-1}]. [c] A = cyclopentylmethyl radical, B = 2,2-dimethylbut-3-enyl radical. [d] THF = tetrahydrofuran. [e] Data from ref. 3. [f] Data from ref. 12. [g] For Me_3SnH. [h] For MeSH.

$$R^{\bullet} + XSH \longrightarrow RH + XS^{\bullet} \quad (5)$$

$$XS^{\bullet} + Et_3SiH \longrightarrow XSH + Et_3Si^{\bullet} \quad (6)$$

reactions (5) and (6) should benefit from favourable charge transfer interactions in the transition state[7,8] (see Table 1: note that the least exothermic hydrogen transfer, *viz.* abstraction from Bu^{t}SH, is also the fastest[3]). In accord with this proposal, our preliminary experiments have shown that alkyl halides, dialkyl sulphides and *O*-alkyl *S*-methyl dithiocarbonates can be effectively reduced by trialkylsilanes in the presence of a thiol catalyst.[5,6] Indeed, thiol catalysis would be suggested by the simplistic relationship between the C=O and R_3Si groups, along with the known[9,10] catalysis by thiols of the radical-chain decarbonylation of aldehydes [reactions (7) and (8)]. In this

$$R\dot{C}O \longrightarrow R^{\bullet} + CO \quad (7)$$

$$R^{\bullet} + RCHO \longrightarrow RH + R\dot{C}O \quad (8)$$

paper we present a full account of our work on the homolytic reduction of organic compounds using trialkylsilanes.

Table 2 Reduction of alkyl halides by triethylsilane in refluxing hexane in the presence of TBHN (5 mol%)[a] and t-dodecanethiol (2 mol%)[a]

Entry	Alkyl halide (RHal)	Yield RH (%)[b]
1	1-Bromooctane	99[c]
2		10[d]
3		0[e]
4	1-Chlorooctane	96
5	1-Iodooctane	91
6	2-Bromooctane	96
7	1-Bromoadamantane	99
8	1-Bromo-1-methylcyclohexane	95[f]

[a] Based on alkyl halide. [b] Unless otherwise noted, reaction mixtures consisted of Et_3SiH (10.0 mmol), alkyl halide (5.0 mmol) and decane internal standard (3.5 mmol) in hexane (15 cm^3). [c] The same yield was obtained after refluxing for 0.5 h. [d] No thiol present. [e] No TBHN present. [f] Et_3SiH (20.0 mmol) and t-dodecanethiol (4 mol%) present.

Results and Discussion

Reduction of Alkyl Halides.—Representative alkyl halides were heated for 1 h in refluxing hexane, under an atmosphere of dry argon, with two molar equivalents of triethylsilane. The initiator for these pilot studies was di-t-butyl hyponitrite (TBHN) (5 mol%) and t-dodecanethiol* (2 mol%) was present as an 'acceptor'[10] polarity reversal catalyst. The reaction mixtures were allowed to cool, washed with saturated aqueous sodium hydrogen carbonate, dried and analysed by GLC using decane as internal standard present during the reaction. The results are summarised in Table 2. Quantitative reduction of 1-bromooctane to octane was achieved in the presence of both thiol and TBHN, while without thiol only a 10% yield of octane was obtained. In the presence of thiol but without TBHN, no octane was produced, confirming the radical chain nature of the reduction. 1-Chloro- and 1-iodo-octane were also reduced in almost quantitative yield in the presence of the thiol catalyst, but no octane was produced from 1-fluorooctane under the same conditions. Furthermore, no octane was detected by GLC after 1-fluorooctane (2.5 mmol), Et_3SiH (5 mmol), t-$C_{12}H_{25}SH$ (2 mol%) and 1,1-di-t-butylperoxycyclohexane (DTBPC) initiator (2 mol%) in cyclohexane (7.5 cm^3) were heated in a sealed tube for 1 h at 115 °C. Evidently the triethylsilyl radical abstracts fluorine from the alkyl fluoride too slowly to maintain a chain hydrodehalogenation.

Secondary alkyl bromides and 1-bromoadamantane were successfully reduced (Table 2, entries 6 and 7), although a tertiary alkyl bromide capable of eliminating HBr (entry 8) required higher concentrations of silane and thiol to give a near-quantitative yield of alkane.

A systematic investigation of the homolytic reduction of 1-bromooctane by trialkylsilanes was conducted in order to examine the effects of changing the reagents and reaction conditions. The results are summarised in Table 3.

Dilauroyl peroxide (DLP) is a readily-available initiator which decomposes at a convenient rate ($t_{\frac{1}{2}}$ *ca.* 1 h) in refluxing

* This is the mixture of isomers t-$C_{12}H_{25}SH$ as obtained from the Aldrich Chemical Company.

Table 3 Reduction of 1-bromooctane by two molar equivalents of trialkylsilane

Entry	Silane	Solvent	Initiator[a] (mol%)[b]	Catalyst (mol%)[b]	Reaction conditions	Yield of octane (%)
1	Et_3SiH	Cyclohexane	DLP (2)	None	Reflux, 1 h	10
2				t-$C_{12}H_{25}SH$ (2)		100
3				t-$C_{12}H_{25}SH$ (1)		99
4				1-AdSH (2)		100
5				1-AdSH (10)		100
6				Ph_3CSH (2)		1
7				Bu^{t}C(O) SH (2)		15
8				Ph_3SiSH (2)		99
9				n-$C_6F_{13}SCl$ (2)		100
10				Bu$^t_2S_2$ (2)		17
11	Ph_3SiH					98
12	Pr^n_3SiH					100[c]
13	Pr^i_3SiH					63
14	Pr^i_3SiH				Reflux, 2h	99
15	Et_3SiH	Cyclohexane	AIBN (2)	t-$C_{12}H_{25}SH$ (2)	Reflux, 1h	12
16		Cyclohexane	DBP (2)			100
17		Hexane	DBCPD (2)			97
18		Benzene	DLP (2)			36
19		Benzene	AIBN (2)			0
20		Cyclohexane	TBPB (2)		Sealed tube, 115 °C, 1 h	100
21		Cyclohexane	DTBPC (2)			100
22		Cyclohexane	DTBPC (2)	None		19

[a] DLP = dilauroyl peroxide, AIBN = azobisisobutyronitrile, DBP = dibenzoyl peroxide, DBCPD = bis (4-t-butylcyclohexyl) peroxydicarbonate, TBPB = t-butyl peroxybenzoate, DTBPC = 1,1-di-t-butylperoxycyclohexane. [b] Based on 1-bromooctane. [c] Nonane was used as internal standard for GLC purposes.

cyclohexane.[11] Under these conditions, 1 or 2 mol% of t-$C_{12}H_{25}SH$ raises the yield of octane from *ca.* 10% to quantitative (Table 3, entries 1–3). Adamantane-1-thiol (1-AdSH) is also an effective catalyst, but triphenylmethanethiol actually inhibits the reduction, perhaps because $Ph_3C^{\bullet}$ is generated in this system (entries 4–6).

Literature values for the strengths of the Si–H bond in Et_3SiH (377 kJ mol^{-1})[12] and of the S–H bond in an alkanethiol (384 kJ mol^{-1})[13,14] indicate that the hydrogen abstraction reaction (9) is slightly exothermic in the forward direction. The errors in these measurements imply that hydrogen abstraction by $RS^{\bullet}$

$$RS^{\bullet} + Et_3SiH \rightleftharpoons RSH + Et_3Si^{\bullet} \quad (9)$$

could be thermoneutral or even slightly endothermic. However, for the [alkanethiol]:[silane] concentration ratios employed in this work, the equilibrium (9) will almost certainly favour $Et_3Si^{\bullet}$. Polar effects will facilitate hydrogen transfer in either direction through the transition state $[RS\cdots H\cdots SiEt_3]^{\bullet}$ and both forward and back reactions are probably very fast at 80 °C and above. Thiopivalic acid [Bu^{t}C(O)SH] is an ineffective catalyst (entry 7), probably because the S–H bond is weaker than that in an alkanethiol and the equilibrium analogous to (9) will be unfavourable to $Et_3Si^{\bullet}$. Even with an alkanethiol, most of the exothermicity of reaction (4) is associated with the first step of the catalytic cycle [reaction (5)] because reaction (9) is close to thermoneutral. A more effective thiol catalyst should be one which has a rather stronger S–H bond than that in an alkanethiol, because abstraction of hydrogen from Et_3SiH by $XS^{\bullet}$ would then be essentially irreversible and presumably more rapid than abstraction by $AlkylS^{\bullet}$.

The trimethylsiloxyl radical $Me_3SiO^{\bullet}$ is more electrophilic and reactive in hydrogen-atom abstraction than $Me_3CO^{\bullet}$ and these differences have been associated with the π acceptor character of the trialkylsilyl group.[15] For similar reasons, we might expect $R_3SiS^{\bullet}$ to be a more efficient abstractor of hydrogen than $R_3CS^{\bullet}$. *ab initio* MO Calculations using the GAUSSIAN 86 package[16,17] for H_3MSH and $H_3MS^{\bullet}$ (M = C or Si) predict that the S–H bond in silanethiol is stronger by 10.5 kJ mol^{-1} than that in methanethiol.* In practice, triphenylsilanethiol[18] was found to be an effective catalyst for the reduction of 1-bromooctane (entry 8).

Increasing the electronegativity of the group X in XSH would be expected to increase the strength of the S–H bond, provided that the unpaired electron is not significantly more delocalised in $XS^{\bullet}$ than in an alkanethiyl radical. This suggests that perfluoroalkanethiols R^FSH should be efficient acceptor catalysts, although these compounds have a tendency to lose HF if an α-C–F bond is present. However, the corresponding sulphenyl chlorides R^FSCl are quite stable and perfluorohexanesulphenyl chloride (n-$C_6F_{13}SCl$) is commercially available. We reasoned that n-$C_6F_{13}SCl$ was likely to be reduced *in situ* by triethylsilane to give n-$C_6F_{13}SH$. Entry 9 shows that quantitative reduction of bromooctane was realised in the presence of 2 mol% n-$C_6F_{13}SCl$.

The reaction between the sulphenyl chloride and triethylsilane was investigated briefly using ^1H NMR spectroscopy. The silane (0.50 mmol), n-$C_6F_{13}SCl$ (0.50 mmol), dilauroyl peroxide (0.01 mmol) and 1,3,5-tri-t-butylbenzene (0.15 mmol) as internal concentration standard in perdeuteriocyclohexane (0.6 cm^3) were heated at 70 °C in an NMR tube under argon for 3 h. After this time, about 50% of the silane had been consumed, as evidenced by the decrease in intensity of the Si*H* septet at δ 3.70. Formation of Et_3SiCl was confirmed by addition of authentic material and at least one other triethylsilyl compound, probably mainly Et_3SiSCl, was present in lower concentration. Key multiplets (both triplets of triplets) appeared at δ 3.18 and δ 5.88. That at δ 5.88 is assigned to 1*H*-perfluorohexane [$CF_3(CF_2)_4CF_2H$] and, on this basis, $^2J_{HF}$ = 52.0 Hz and $^3J_{HF}$ = 5.1 Hz. The multiplet at δ 3.18 is ascribed to n-$C_6F_{13}SH$, whence $^3J_{HF}$ = 15.7 Hz and $^4J_{HF}$ = *ca.* 1.5 Hz (the latter splitting was poorly resolved). The combined yields of thiol and 1*H*-perfluorohexane were approximately equal to the amount of silane consumed and the [thiol]:[fluoroalkane] ratio was *ca.* 3:1. These results suggest that triethylsilyl radicals react with the fluoroalkanesulphenyl chloride mainly by abstraction of chlorine and displacement of n-$C_6F_{13}^{\bullet}$; the latter process would yield triethylsilanesulphenyl chloride,[19] which would be expected to be reduced to Et_3SiSH (presumably also on efficient polarity reversal catalyst) under the normal conditions used for alkyl halide reduction.

Homolytic substitution by $Et_3Si^{\bullet}$ at sulphur in Bu^{t}SSBu^t should give Bu^{t}S$^{\bullet}$ and thus Bu^{t}SH *in situ*. However, this reaction is evidently not efficient enough under the usual conditions to render the disulphide an effective catalyst for reduction of bromooctane by Et_3SiH (Table 3, entry 10).

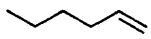
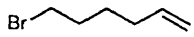
With t-$C_{12}H_{25}SH$ as catalyst, a number of other silanes were examined as potential reducing agents. Triphenyl- and tripropylsilanes both gave quantitative yields of octane (entries 11 and 12). One potential problem with the use of silanes for reduction of alkyl halides is that R_3SiHal is a reaction product. Triethylhalogenosilanes, especially the bromide and iodide are reactive towards nucleophiles (the still more reactive Me_3SiI is well-known for its ability to cleave C–O bonds in ethers, epoxides, lactones *etc.*), but the triisopropylhalogenosilanes are much less reactive electrophiles for steric reasons.[20] Although Pr^i_3SiH is evidently a somewhat less effective reducing agent for bromooctane than Et_3SiH, a quantitative yield of octane was still achieved when the reflux period was extended to 2 h (entries 13 and 14). Reaction mixtures containing Pr^i_3SiH remained colourless throughout, while with Et_3SiH a pale yellow colour developed during heating. Carbon dioxide was evolved only very slowly when the reaction mixture from Pr^i_3SiH was washed with aqueous $NaHCO_3$, while gas evolution was rapid when Et_3SiH was the reducing agent, reflecting the relative ease of hydrolysis of Pr^i_3SiBr and Et_3SiBr.

Initiators other than dilauroyl peroxide were investigated. Azobisisobutyronitrile (AIBN), which is sparingly soluble in cold cyclohexane and dissolved only when the reaction mixture was heated, is an ineffective initiator (entry 15). Possibly this is because the azo compound traps $Et_3Si^{\bullet}$ to give a hydrazyl radical which itself then acts as a radical scavanger. Dibenzoyl peroxide (DBP) and bis(4-t-butylcyclohexyl) peroxydicarbonate (DBCPD) are both efficient initiators (entries 16 and 17). Benzene is an unsuitable solvent (as presumably are most other arenes). Trialkylsilyl radicals add rapidly to arenes to give cyclohexadienyl radicals[21] and the problem can presumably be traced back to this behaviour. Although AIBN is readily soluble in benzene, this combination of solvent and initiator is totally ineffective (entries 18 and 19). The more thermally stable t-butyl perbenzoate (TBPB) and DTBPC are both successful initiators at 115 °C (entries 20 and 21). Although direct abstraction of hydrogen from Et_3SiH by alkyl radicals will be faster at this higher temperature, thiol catalysis still raises the yield very significantly, from 19% to quantitative (entries 21 and 22).

Alkyl halides are also reduced to hydrocarbons by organosilanes in the presence of aluminium trichloride.[22] However, this reaction proceeds through carbocation intermediates which are subject to rearrangement and is

* Geometries were fully optimised within C_s symmetry at the (U)HF/6-31G** level. Total energies (hartree) at the (U)MP3 (Full)/6-31G**//(U)HF/6-31G** level, including zero-point vibrational energies scaled[17] by a factor of 0.9 are: −437.987 795 (H_3CSH), −437.362 801 ($H_3CS^{\bullet}$), −689.023 128 (H_3SiSH) and −688.394 140 ($H_3SiS^{\bullet}$). (1 hartree = 2625.5 kJ mol^{-1}).

Table 4 Reduction of 6-bromohex-1-ene by triethylsilane in decane[a]

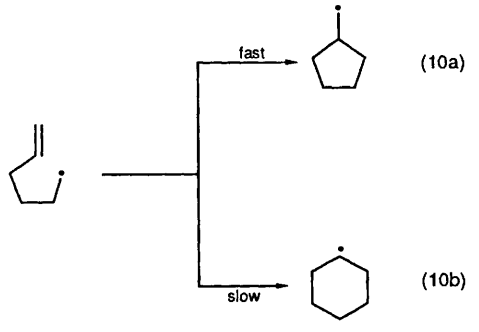
Entry	T/°C	Molar equivs. Et_3SiH[b]	Thiol catalyst	Initial thiol conc./mol dm^{-3} (mol%)[b]	Initiator[c] (mol%)[b]	Products and unreacted bromohexene[d] (mol%)[b]		
								
1	70	2	$t\text{-}C_{12}H_{25}SH$	0.005 (2)	TBHN (5)	30	3	56
2	70	2	$t\text{-}C_{12}H_{25}SH$	0.050 (20)	TBHN (5)	46	21	28
3	70	2	1-AdSH	0.013 (5)	TBHN (5)	44	3	33
4	70	2	1-AdSH	0.125 (50)	TBHN (5)	20	13	56
5	80	2	1-AdSH	0.003 (1)	DLP (5)	11	0.2	69
6	80	2	1-AdSH	0.025 (10)	DLP (5)	24	5	53
7	80	2	Ph_3SiSH	0.005 (2)	DLP (2)	12	5	79
8	80	2	Ph_3SiSH	0.025 (10)	DLP (2)	7	13	69
9	80	8	Ph_3SiSH	0.025 (10)	DLP (4)	11	22	56
10	70	8	Ph_3SiSH	0.005 (2)	DPCPD (4)	17	11	65

[a] Reaction mixtures were heated in sealed glass tubes for 1 h. [b] Based on bromohexene. [c] TBHN = di-t-butyl hyponitrite, DLP = dilauroyl peroxide, DPCPD = bis(4-t-butylcyclohexyl) peroxydicarbonate. [d] Cyclohexane was also formed; for each reaction the yield was about 2% of that of methylcyclopentane.

mechanistically quite distinct from the radical chain reductions described in this paper.

Alkanethiols might also promote the homolytic reduction of organic halides by tris(trimethylsilyl)silane,[4,12,23] because they should act as efficient polarity reversal catalysts for hydrogen-atom abstraction from silicon by R$^{\bullet}$. The Si–H bond in $(Me_3Si)_3SiH$ is appreciably weaker than that in Et_3SiH and thus thiyl radicals should abstract hydrogen very rapidly, irreversibly and regioselectively from silicon in the former silane.

Reduction of Unsaturated Alkyl Halides.—Cyclisation of the hex-5-enyl radical to give mainly the cyclopentylmethyl radical [eqn. (10a)] is one of the best known radical rearrangements.[24] In recent years, ring formation by radical cyclisation reactions has become a very important tool in organic synthesis.[25] A problem sometimes arises because hydrogen-atom transfer from tin hydrides can compete successfully with cyclisation, thereby reducing the yield of the desired product. The use of less reactive hydrogen donors such as trialkylgermanes has been proposed to overcome this difficulty,[26] but the silane–thiol couple appears potentially useful in this regard because the thiol is the actual hydrogen donor and its nature and concentration can be varied independently of the silane.



(10a)

(10b)

Reduction of 6-bromohex-1-ene by triethylsilane in the presence of thiol catalyst was examined in decane solvent (octane GLC standard) using sealed reaction tubes to prevent the loss of products by evaporation. The results are collected in Table 4. Formation of methylcyclopentane, but only traces of cyclohexane, along with hexene confirms the radical mechanism of the reduction.[24] Comparison of the pairs of entries, 1/2, 3/4, 5/6 and 7/8 shows that the ratio [methylcyclopentane]:[hexene] decreases as the thiol concentration increases, while entries 8 and 9 show that this ratio is essentially independent of the silane concentration. Clearly it is the thiol that donates a hydrogen atom to the alkyl radical.

However, conversions are much lower than those achieved with saturated alkyl bromides under similar conditions and the extent of reduction was also less reproducible. The C=C bond evidently interferes, probably by competing with the silane for reaction with thiyl radicals, leading to the removal of thiol from the system as its alkene adduct. The rate coefficient for addition of Bu^{t}S$^{\bullet}$ to oct-1-ene has been determined[27] recently to be 1.9×10^6 dm^3 mol^{-1} s^{-1} at 25 °C and the rate coefficient for abstraction of hydrogen from the silane by RS$^{\bullet}$ is very unlikely to be significantly greater than this value. However, thiyl radical addition to alkenes is readily reversible. In accord with this explanation, increasing the silane concentration at constant thiol concentration leads to greater yields of reduction products (entries 8 and 9).

The thiol concentration will decrease during a reaction, because of its consumption by overall addition to the double bond and perhaps because of its reaction with the Et_3SiBr formed in the reduction. It is thus not easy to relate the [methylcyclopentane]:[hexene] ratios to the rate coefficient for abstraction of hydrogen from the thiol by the hex-5-enyl radical. Certainly the product ratios are generally in accord with the value of *ca.* 1×10^7 dm^3 mol^{-1} s^{-1} at 50 °C for alkanethiols reported by Newcomb and his co-workers.[3,28]

Disappointingly, in terms of total yield, triphenylsilanethiol is evidently no better than the alkanethiols as a catalyst for the reduction of 6-bromohex-1-ene (entries 6 and 8). However, as a hydrogen-atom donor to the hex-5-enyl radical it is apparently more efficient than the alkanethiols, either because the mean concentration of the silanethiol during reaction is larger or possibly because the rate coefficient for hydrogen abstraction from the silanethiol is greater.

The lack of competing hydrosilylation of the C=C group accords with the much greater reactivity of $Et_3Si^{\bullet}$ towards the bromine atom in primary alkyl bromides[29] than towards addition to the double bond in a terminal alkene.[30]

Reduction of Ethyl 4-Bromobutanoate.—The compatibility of the ester function was examined by subjecting ethyl 4-bromobutanoate to silane reduction [reaction (11)]. Without thiol catalyst, with two molar equivalents of Et_3SiH and 2 mol% DLP in refluxing cyclohexane, only 4% of ethyl butanoate was obtained after heating for 1 h; 95% of the bromoester remained.

In the additional presence of t-$C_{12}H_{25}SH$ (2 mol%), the yield of ethyl butanoate increased to 70%. Under the same conditions with 2 mol% thiol, essentially quantitative reduction of ethyl

$$BrCH_2(CH_2)_2CO_2Et + Et_3SiH \longrightarrow Me(CH_2)_2CO_2Et + Et_3SiBr \quad (11)$$

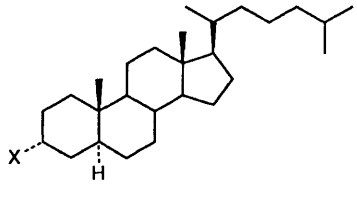
bromobutanoate was achieved with 4 molar equivalents of Et_3SiH (97% yield) or Pr^i_3SiH (98% yield). Tri-isopropylisilane might prove to be the reagent of choice if other functionality which is sensitive to less hindered trialkylbromosilanes is present in the molecule.

Reduction by Phosphine–Boranes.—Although simple alkyl radicals abstract hydrogen only very slowly from the B–H group in $Bu_3P{\rightarrow}BH_3$ or $Bu_3P{\rightarrow}BH_2Ph$, the more electrophilic α-alkoxycarbonylalkyl radicals abstract hydrogen more rapidly.[31] In the hope that hydrogen abstraction by alkyl radicals might be subject to polarity reversal catalysis, we briefly examined the effect of thiols on the reactions of the phosphine–boranes with 1-bromooctane.

With $Bu_3P{\rightarrow}BH_3$ under the usual conditions (2 mol equiv. of phosphine–borane, 2 mol% DLP, cyclohexane solvent, 1 h reflux), a 9% yield of octane was obtained and 90% of the bromide remained. When 2 mol% t-$C_{12}H_{25}SH$ was also present, the yield increased only marginally to 11%. With $Bu_3P{\rightarrow}BH_2Ph$ under similar conditions in the presence of 2 mol% thiol, the yield of octane was still only 17%.

These initial results are promising, but clearly more reactive borane hydrogen-donors and/or more effective catalysts need to be found before these reducing agents can offer a viable alternative to the tin or silicon hydrides.

Isolation of Products.—Triethylbromosilane yields Et_3SiOH and $Et_3SiOSiEt_3$ upon hydrolysis and the siloxane sometimes presented a problem during product isolation, because it was difficult to separate chromatographically from hydrocarbons. To overcome this difficulty, thiourea was added to the reaction mixture after reduction. The mixture was stirred under reflux for a further 1 h and then filtered through silica; all volatiles were removed from the filtrate under reduced pressure and the hydrocarbon product was isolated from the residue by flash chromatography on silica. Using this technique, octadecane (89%) and 5α-cholestane **2** (86%) were isolated after reduction of 1-bromooctadecane and 3α-bromo-5α-cholestane **1**, respectively, with triethylsilane in refluxing cyclohexane in the presence of 2 mol% t-dodecanethiol.



1 X = Br
2 X = H

Reduction of Dialkyl Sulphides.—Triethylsilyl radicals,[32] like trialkylstannyl radicals,[2] react with dialkyl sulphides to bring about displacement of an alkyl radical from sulphur [reaction (12)]. Hence, R_2S should be reduced to RH by Et_3SiH in a radical chain reaction catalysed by thiols. Up to two molar equivalents of RH might be obtained from R_2S if $Et_3Si^{\bullet}$ also

$$Et_3Si^{\bullet} + R_2S \longrightarrow Et_3SiSR + R^{\bullet} \quad (12)$$

displaces $R^{\bullet}$ from Et_3SiSR. Reaction (12) is subject to steric retardation if R is bulky, but tertiary alkyl groups can be cleaved readily from sulphur in R^tSMe. In the absence of steric effects, the ease of cleavage should increase in the order $Me < R^p < R^s < R^t$.

Satisfactory yields of octane were obtained from dioctyl sulphide using either TBHN as initiator in refluxing hexane or DTBPC in cyclohexane at 115 °C; the results are collected in Table 5. Interestingly, with dioctyl sulphide the yield of octane using either initiator was *lower* in the presence of t-dodecanethiol than in its absence (entries 2 and 3, 7 and 8). We suggest that a thiol (possibly triethylsilanethiol[33] Et_3SiSH), which may be a more effective promoter than t-$C_{12}H_{25}SH$, is generated *in situ* and that this functions as polarity reversal catalyst in the absence of added t-dodecanethiol. However, when the secondary cyclohexyl group is attached to sulphur, production of cyclohexane is promoted in the presence of t-dodecanethiol (entries 4 and 5, 10 and 11). With DLP, AIBN or DBCPD at appropriate temperatures, with or without t-dodecanethiol catalyst, negligible yields of octane were obtained.

Reduction of Xanthates.—Homolytic deoxygenation of alcohols is an important tool in organic synthesis, particularly in the carbohydrate and natural product fields. Deoxygenation can be accomplished by treatment of various thiocarbonyl derivatives (**3**; X = *inter alia* SMe, Ph, or 1-imidazolyl) with tributylstannane,[34] following the pioneering work of Barton and McCombie.[35] *O*-Alkyl *S*-methyl dithiocarbonates (xanthates)

$$Bu_3SnH + \underset{\mathbf{3}}{ROC(S)X} \longrightarrow RH + Bu_3SnSC(O)X \quad (13)$$

(**3**; X = SMe) are readily prepared from primary and secondary alcohols and the radical chain reactions of these derivatives with tributylstannane[35,36] proceed by the mechanism shown in reactions (14) and (15), followed by hydrogen abstraction by $R^{\bullet}$ from the tin hydride [reaction (2)].[37,38]*

$$Bu_3Sn^{\bullet} + ROC(S)Me \rightleftharpoons \underset{\mathbf{4}}{RO\dot{C}(SSnBu_3)SMe} \quad (14)$$

$$RO\dot{C}(SSnBu_3)SMe \longrightarrow R^{\bullet} + Bu_3SnSC(O)SMe \quad (15)$$

Trialkylsilyl radicals also add rapidly to sulphur in thiocarbonyl compounds[39] and addition of $R_3Si^{\bullet}$ is likely to be much less readily reversible than the corresponding addition of $R_3Sn^{\bullet}$, because the Si–S bond is probably appreciably stronger than the Sn–S bond.[40] *O*-Alkyl *S*-methyl dithiocarbonates derived from ROH should therefore react with triethylsilane by a radical chain pathway to yield the deoxy alcohol RH, provided that the adduct **5** undergoes β-scission at a similar rate to its tin-containing counterpart **4** and that hydrogen-atom transfer to $R^{\bullet}$ is sufficiently rapid [reactions (16) and (17)].

$$Et_3Si^{\bullet} + ROC(S)Me \longrightarrow \underset{\mathbf{5}}{RO\dot{C}(SSiEt_3)SMe} \quad (16)$$

$$RO\dot{C}(SSiEt_3)SMe \longrightarrow R^{\bullet} + Et_3SiSC(O)SMe \quad (17)$$

Hence, it should prove possible to use triethylsilane as a replacement for tributylstannane in the Barton–McCombie reaction, in the presence of a thiol to catalyse hydrogen-atom transfer from the silane to $R^{\bullet}$. As for the reduction of alkyl halides described above, aliphatic solvents should be preferred in order to avoid addition of silyl radicals to aromatic rings.

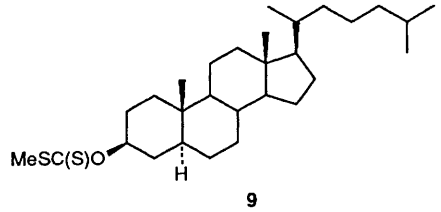
* Under the normal reaction conditions, $Bu_3SnSC(O)SMe$ decomposes *in situ* to Bu_3SnMe and COS.

Table 5 Reduction of dialkyl sulphides by triethylsilane

Entry	Dialkyl sulphide	Mol%[a] t-dodecanethiol	Initiator[b] (mol%)[a]	Solvent	Reaction conditions	Alkane product (mol%)[a]
1	$(n\text{-}C_8H_{17})_2S$	None	None	Hexane	Reflux, 1 h	Octane (0)
2		None	TBHN (5)			Octane (98)
3		2	TBHN (5)			Octane (79)
4	cyclo-$C_6H_{11}SMe$	None	TBHN (2)			Cyclohexane (16)
5		2	TBHN (2)			Cyclohexane (59)
6		2	TBHN (5)			Cyclohexane (89)
7	$(n\text{-}C_8H_{17})_2S$	None	DTBPC(2)	Cyclohexane	Sealed tube 115 °C, 2 h	Octane (123)
8		2	DTBPC(2)			Octane (96)
9	$n\text{-}C_{10}H_{21}SMe$	None	DTBPC(2)			Decane (75)
10	cyclo-$C_6H_{11}SMe$	None	DTBPC(2)	Decane		Cyclohexane (43)
11		2	DTBPC(2)			Cyclohexane (96)

[a] Mol% based on dialkyl sulphide. [b] TBHN = di-t-butyl hyponitrite, DTBPC = 1,1-di-t-butylperoxycyclohexane.

ROC(S)SMe
6 R = 2-octyl
7 R = 1-octyl
8 R = 1-octadecyl



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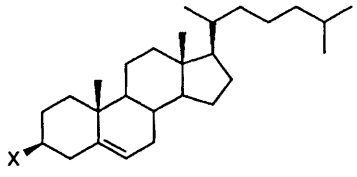
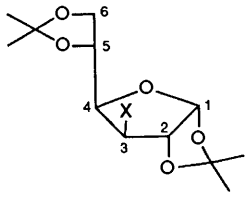


10 X = OC(S)SMe
11 X = H



12 X = OH
13 X = OC(S)SMe
14 X = H

Table 6 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 **6**	0	2	1	0
2		2	0	1	63
3		2	2	1	92
4	1-Octyl **7**	0	2	1	0
5		2	0	1	46
6		2	2	1	63
7		5	2	4	82

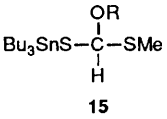
[a] 1,1-Di-t-butylperoxycyclohexane (DTBPC). [b] Based on xanthate.

Six representative xanthates **6**–**10** and **13** were chosen for study in this work and hydrocarbon products were either isolated or determined quantitatively by GLC analysis.

A series of pilot experiments with 1- and 2-octyl xanthates was carried out in sealed tubes at 115 °C. The reaction mixtures consisted of the xanthate (2.5 mmol), triethylsilane (5.0 mmol) and decane (0.250 g) in cyclohexane (3.8 cm^3), together with DTBPC initiator and t-dodecanethiol catalyst. The yields of octane were determined by GLC analysis (using the decane as internal standard) and the results are summarised in Table 6.

In view of the results obtained from the reduction of 1-bromooctane at 115 °C (Table 3, entries 20–22), unexpectedly high yields of octane were produced from both primary and secondary octyl xanthates in the absence of thiol catalyst (entries 2 and 5). It seems likely that SH-containing compounds (*e.g.* Et_3SiSH) are generated *in situ* by side reactions, perhaps requiring the intervention of traces of adventitious moisture, and that these thiols act as polarity reversal catalysts for abstraction of hydrogen from the silane by R$^\bullet$. It is clear that simple primary and secondary alcohols can be efficiently deoxygenated by the reaction of the derived *S*-methyl xanthates with triethylsilane in the presence of thiols.

Neither xanthate gave any octane in the absence of initiator (Table 6, entries 1 and 4), confirming the radical chain nature of the reduction. These latter results also highlight the importance of the initiation step of any chain process and indicate that the unexpectedly[34] efficient tin hydride-mediated reductions of primary[41] and secondary[42] alkyl xanthates which have been reported may be explained in terms of inefficient initiation under normal[35,36] 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. In particular, no added initiator was present in tin hydride-mediated reductions of 1-octadecyl xanthate[36] which required very high reaction temperatures before satisfactory yields were obtained. We note that the same product **15** will result from heterolytic addition of the Sn–H bond across the C=S group as from the radical chain reaction between Bu_3SnH and the xanthate, when the intermediate radical **4** is captured by the tin hydride *before* it undergoes β-scission [reaction (15)].



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In the next series of experiments, trialkylsilane reductions of the *O*-alkyl *S*-methyl dithiocarbonates **8**–**10** derived from octadecan-1-ol, 5α-cholestan-β-ol and cholesterol, respectively, were carried out in flasks under atmospheric pressure of argon. The xanthate (2–2.5 mmol) and triethyl- or tripropyl-silane (2–8 mol equiv.), together with thiol catalyst and dicumyl peroxide (DCP) or di-t-butyl peroxide (DTBP) initiator, were heated in a hydrocarbon solvent (6–7.5 cm^3).* After removal of all volatile material (40 °C, 0.1 Torr†), the octadecane, 5α-cholestane **2** or

* At 126 °C (the boiling point of octane) the half-life of DCP (*ca.* 3 h) is shorter and more convenient than that of DTBP (*ca.* 10 h);[11] DCP is also involatile and easy to handle. However, excess DTBP is easily removed after reaction and under certain conditions DCP might possibly give phenol, which would be undesirable.

† 1 Torr ≈ 1 mmHg.

Table 7 Reduction of *O*-alkyl *S*-methyl dithiocarbonates ROC(S)SMe by trialkylsilanes[a]

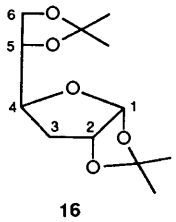
Entry	Xanthate	Solvent	Initiator[b]	t-$C_{12}H_{25}SH$ (mol%)[c]	Reaction conditions	Isolated Yield of RH (%)
1		Octane	DCP	0	Reflux, 4 h	60
2		Octane	DCP	2	Reflux, 4 h	70
3[d]	**8**	Octane	DCP	2	Reflux, 4 h	80
4[e]		Decane	DCP	2	140 °C, 2 h	79
5[e]		*m*-Xylene	DCP	2	140 °C, 2 h	45
6		Octane	DCP	0	Reflux, 2 h	49
7	**9**	Octane	DCP	2	Reflux, 2 h	72
8[d]		Octane	DCP	2	Reflux, 4 h	85
9		Octane	DTBP	2	Reflux, 4 h	94
10[f]		Octane	DCP	2[g]	Reflux, 8 h	63
11[f]	**10**	Octane	DTBP	2[g]	Reflux, 8 h	66
12[f]		Octane	DTBP	2[h]	Reflux, 4 h	52
13[d]	**13**	Octane	DTBP	2	Reflux, 6 h	60
14[i]		Octane	DTBP	2	Reflux, 8 h	70

[a] Two molar equivalents of triethylsilane unless noted otherwise. [b] DCP = dicumyl peroxide (4 mol%), DTBP = di-t-butyl peroxide (20 mol%). [c] Based on xanthate. [d] Four molar equivalents of Et_3SiH. [e] Two molar equivalents of Pr^n_3SiH. [f] Eight molar equivalents of Et_3SiH. [g] A further 1 mol% t-$C_{12}H_{25}SH$ in octane (0.5 cm^3) was added after 2 h and again after 5 h. [h] The catalyst was Ph_3SiSH. A further 1 mol% of this thiol in octane (0.5 cm^3) was added after 1 h and again after 2.5 h. [i] Four molar equivalents of Pr^n_3SiH.

cholest-5-ene **11** was isolated from the residue by flash chromatography on silica using hexane eluant. These experiments are summarised in Table 7.

Aromatic solvents are, as expected, less suitable than aliphatic ones. Octadecyl xanthate and tripropylislane in decane solvent at 140 °C (entry 4) gives a good yield of octadecane, while in *m*-xylene under otherwise identical conditions with efficient initiation (entry 5) the yield was lower, a significant amount of the xanthate remained unreacted and by-products (including at least one aromatic compound) were formed. Good yields of cholest-5-ene could be obtained from the xanthate **10** by using eight molar equivalents of triethylsilane, extending the reflux time, and adding extra thiol catalyst at intervals during the reaction (entries 10–12). The presence of the C=C group is thus not a major problem, although it does lead to reduced yields compared with those obtained from the saturated counterpart **9**. Triphenylsilanethiol is not a markedly more efficient catalyst than t-dodecanethiol.

To further assess the usefulness of the silane–thiol couple as a replacement for Bu_3SnH in the Barton–McCombie reaction, we carried out the deoxygenation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **12**. This particular secondary alcohol was chosen because reactions of the derived xanthate[35,43] **13** and of other thiocarbonyl derivatives[44] of **12** with tributylstannane have been investigated previously and the full procedure for deoxygenation *via* the xanthate has been described in detail and is available for comparison with the silane-mediated route. The yields (entries 13 and 14) of deoxy-product **14**, isolated by flash



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chromatography (silica, diethyl ether–hexane eluant), were comparable with those reported previously[35,43] using Bu_3SnH (75–80%). A small amount of a crystalline substance was isolated along with **14** from the silane-mediated reduction of **13**. This substance turned out to be an isomer of **14**, which was identified as 3-deoxy-1,2:5,6-di-*O*-isopropylidene-β-L-lyxo-hexofuranose **16** by comparison of its melting point and ^1H NMR spectrum with the properties reported by Stick *et al.*[45] for the D-enantiomer. Evidently **13** and/or **14** undergoes radical-induced epimerisation at C-5 under the reaction conditions. Regioselective epimerisation can be understood because epimerisation at C-1 or C-2 would give a less stable *trans*-fused bicyclic structure, while molecular models show that 4-H is sterically shielded by isopropylidene-methyl groups. It seems likely that thiyl radicals can abstract hydrogen from the *O*-activated tertiary 5-H bond in **13** or **14** to give a carbon radical which would subsequently abstract hydrogen to give back the original molecule or its C-5 epimer.

This result highlights a potential problem with thiol-catalysed reductions using R_3SiH. If hydrogen-atom abstraction by RS$^\bullet$ from the reactant or reduced product occurs in competition with abstraction from the silane, isomeric products could be formed. This would be a particular drawback with sensitive molecules which contain a number of asymmetric centres. A way around this difficulty, while retaining the positive aspects of thiol catalysis, would be to use a more reactive hydrogen-atom donor than R_3SiH. Possible donors would be pentamethyldisilane[12] ($Me_3SiSiMe_2H$) or diphenylsilane[46] (Ph_2SiH_2), both of which contain more available hydrogen than does tris(trimethylsilyl)silane.[23] After this research was completed, we became aware of work by Barton *et al.*[46,47] on the deoxygenation of alcohols by reduction of their thiocarbonyl derivatives with tin[47] and silicon[46] hydrides. These authors concluded that xanthate reduction by diphenylsilane gives satisfactory yields of hydrocarbon products[46] and that unless effective initiation was provided in the tin hydride mediated reduction, a heterolytic process could intervene,[47] as we propose here.

We conclude that, provided a little effort is put into optimising reaction conditions, the silane–thiol couple could often be a viable replacement for trialkylstannane in the Barton–McCombie deoxygenation of alcohols *via* the corresponding xanthates.

Experimental

NMR spectra were obtained using a Varian VXR-400 instrument (400 MHz for ^1H); the solvent was $CDCl_3$ and the internal standard was tetramethylsilane. Values for coupling constants *J* are given in Hz. Mass spectra (70 eV, electron

impact) were obtained with a VG 7070H spectrometer interfaced to a Finnigan–Incos data system. GLC analyses were performed using a Perkin-Elmer F11 instrument equipped with a flame-ionisation detector. A 4 m × 1/8″ packed column containing MS 200/200 silicone oil (10%) on Chromosorb W (80–100 mesh) was used in conjunction with suitable temperature programmes; the carrier gas was nitrogen. The detector response was calibrated using mixtures of authentic compounds.

Materials.—Di-t-butyl hyponitrite[48] (TBHN), 1-adamantanethiol,[49] triphenylsilanethiol[18a] and tributylphosphine–phenylborane[31] were prepared as described in the literature. 1,1-Di-t-butylperoxycyclohexane[50] (DTBPC) and bis(4-t-butylcyclohexyl)peroxydicarbonate[51] (DBDPD) were gifts from Interox Chemicals Ltd.; the former, as a 50% w/w solution in white oil, was used as received; the latter was recrystallised from pentane (m.p. 85–86 °C) and shown by ^{1}H NMR spectroscopy to contain *cis*-and *trans*-4-t-butylcyclohexyl groups in the ratio 44:56. (Found: C, 66.1; H, 9.9. $C_{22}H_{38}O_6$ requires C, 66.3; H, 9.6%).

1-Bromo-1-methylcyclohexane[52,53] was prepared from 1-methylcyclohexanol and aqueous HBr in the presence of lithium bromide, b.p. 56 °C at 10 Torr. (lit.,[52] b.p. 57–59 °C at 14 Torr).

3-α-Bromo-5α-cholestane[54] **1** was prepared in low yield by the reaction of 5α-cholestan-3β-ol with phosphorus tribromide in refluxing benzene[55] (Found m.p. and lit.,[56] m.p. 101–102 °C).

The *S*-methyl dithiocarbonates derived from octan-1-ol,[57] (±)-octan-2-ol,[58] and octadecan-1-ol[59] were prepared by the method of Chênevert *et al.*;[57] those derived from cholesterol[35] and from 5α-cholestan-3β-ol[60] were prepared by the method of Barton and McCombie.[35] The xanthate derived from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[61] was prepared as described by Iacono and Rasmussen.[43]

All other reagents and solvents were commercial products which were purified and dried using standard methods. Liquids were purged with argon before reaction mixtures were prepared. Typical experiments are described below.

Sealed Tube Reactions.—Reagents and solvent were introduced by weight and volume, respectively, into dry, argon-filled, cylindrical Pyrex tubes of appropriate volume fabricated with a constricted neck below a standard joint. The filled tube was transferred to the vacuum line, the contents were frozen in liquid nitrogen and the tube was then evacuated and flame-sealed at the constriction. The sample was allowed to warm to room temperature before being thoroughly mixed and then transferred to a pre-heated, thermostatted oil bath. After reaction, the tubes were cooled in an ice bath and cracked open. The reaction mixture was subjected to GLC analysis either immediately or (for alkyl halide reductions) after it had been washed with ice-cold saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3) and dried ($MgSO_4$).

In a representative run, a solution of cyclohexyl methyl sulphide (0.325 g, 2.50 mmol), triethylsilane (0.581 g, 5.00 mmol), t-dodecanethiol (10 mg, 2 mol% based on sulphide), 1,1-di-t-butylperoxycyclohexane (13 mg, 2 mol%) and octane (0.250 g, 2.19 mmol) in decane (3.57 cm^3) was heated in a sealed tube at 115 °C for 2 h. GLC analysis (octane internal standard) showed the presence of cyclohexane (2.40 mmol, 96%).

Open Flask Reactions.—Reagents and solvent (8–15 cm^3) were introduced by weight and volume, respectively, into a dry, argon-filled round-bottomed flask equipped with a magnetic stirrer bar and, with argon flowing downwards through it, a condenser was attached. The flask was immersed in a pre-heated, thermostatted oil bath (80, 100 or 140 °C for hexane, cyclohexane, or octane solvents, respectively) and the contents was stirred under reflux under argon. The mixture was allowed to cool to room temperature, washed in saturated aqueous sodium hydrogen carbonate and dried before being subjected to GLC analysis.

In a representative run, a solution of 1-bromooctane (0.965 g, 5.00 mmol), triethylsilane (1.16 g, 10.00 mmol), t-dodecanethiol (23.6 × 10^{-3} cm^3, 2 mol% based on bromide), dilauroyl peroxide (40 mg, 2 mol%) and decane (0.510 g, 3.58 mmol) in cyclohexane (15 cm^3) was heated under reflux for 1 h. The mixture was allowed to cool to room temperature, washed with saturated aqueous $NaHCO_3$ (2 × 15 cm^3) and dried ($MgSO_4$); GLC analysis (decane internal standard) showed the presence of octane (4.85 mmol, 97%).

TLC was carried out using aluminium sheets pre-coated with Silica Gel 60 F_{254} (Merck 5554) and Silica Gel 60 (Merck 9385, particle size 0.040–0.063 mm) was also used for column chromatography. In TLC work the plates were generally developed by immersion in a 10% w/v solution of phosphomolybdic acid in methanol or spraying with a 5% v/v solution of sulphuric acid in ethanol and then heating the plate with a hot-air blower. Experimental methods and work-up procedures for product isolation are described below for representative reactions.

Octadecane from 1-Bromooctadecane.—A solution in cyclohexane (15 cm^3) containing 1-bromooctadecane (1.67 g, 5.0 mmol), triethylsilane (1.16 g, 10.0 mmol), dilauroyl peroxide (40 mg, 2 mol%) and t-dodecanethiol (23.6 × 10^{-3} cm^3, 2 mol%) was stirred magnetically and heated under reflux for 1 h under an atmosphere of argon. Finely powdered thiourea (0.76 g, 10.0 mmol), which had been dried at 40 °C/1 Torr for 1 h, was added to the cooled solution and the mixture was then stirred and heated under reflux for a further 1 h. Most of the volatile material was removed under reduced pressure and the resulting slurry was subjected to flash chromatography on silica (50 g), eluting with hexane (b.p. 67–70 °C). Octadecane (1.13 g, 89%) was obtained as a colourless crystalline solid, m.p. 29–30 °C; δ_C (^{1}H decoupled) 14.2, 22.7, 29.4, 29.7 and 32.0.

5α-Cholestane from Cholestanyl Xanthate **9**.—A solution in octane (6.0 cm^3) containing cholestanyl xanthate (0.958 g, 2.0 mmol), triethylsilane (0.930 g, 8.0 mmol), dicumyl peroxide (26 mg, 4 mol%) and t-dodecanethiol (9.4 × 10^{-3} cm^3, 2 mol%) was stirred magnetically and heated under reflux (bath temperature 140 °C) for 4 h under argon. The reaction mixture was allowed to cool and the octane and excess silane were removed under reduced pressure using a rotary evaporator. The residue was subjected to flash chromatography on silica (50 g), eluting with hexane, to give 5α-cholestane (0.64 g, 86%), m.p. 80–81 °C (lit.,[35] m.p. 78.5–79.5 °C). The ^{1}H NMR spectrum was indistinguishable from that of an authentic sample. δ_C(^{1}H decoupled) 12.1, 12.2, 18.7, 20.8, 22.2, 22.6, 22.8, 23.8, 24.2, 26.9, 28.0, 28.3, 29.1 (2 peaks), 32.2, 35.6, 35.8, 36.2, 38.7, 39.5, 40.1, 42.6, 47.1, 54.8, 56.3 and 56.7.

Cholest-5-ene from Cholesteryl Xanthate **10**.—A solution in octane (3.5 cm^3) containing cholesteryl xanthate (0.500 g, 1.04 mmol), tripropylsilane (1.33 g, 8.39 mmol), dicumyl peroxide (13.6 mg, 2 mol%) and t-dodecanethiol (4.9 × 10^{-3} cm^3, 2 mol%) was stirred magnetically and heated under reflux (bath temperature 140 °C) for 8 h under argon. Two further additions, each of t-dodecanethiol (4.9 × 10^{-3} cm^3) in octane (0.5 cm^3) were made by syringe after 2 h and 5 h. The reaction mixture was allowed to cool and the octane and excess silane were removed under reduced pressure (0.05 Torr) at 40 °C. The residue was subjected to flash chromatography on silica (50 g), eluting with hexane, to give cholest-5-ene (0.24 g, 62%), m.p. 91–92.5 °C (lit.,[35] m.p. 90–92 °C). The ^{1}H NMR spectrum was indistinguishable from that of an authentic sample. δ_C(^{1}H decoupled) 11.9, 18.7, 19.5, 20.8, 22.6, 22.9, 23.8, 24.3, 28.0, 28.1,

28.3, 31.8, 31.9, 32.9, 35.8, 37.5, 36.2, 39.5, 39.9 (2 peaks), 42.3, 50.6, 56.2, 56.9, 119.0 and 143.7.

3-Deoxy-1,2:5,6-di-O-isopropylidene-α-D-ribo-hexofuranose **14** *from the Xanthate* **13**.—A solution in octane (25 cm^3) containing the xanthate **13** (3.50 g, 9.94 mmol), tripropylsilane (12.61 g, 80.0 mmol), di-t-butyl peroxide (0.29 g, 20 mol%) and t-dodecanethiol (47×10^{-3} cm^3, 2 mol%) was stirred magnetically and heated under reflux (bath temperature 140 °C) for 8 h under argon. The mixture was allowed to cool and the octane and excess silane were removed under reduced pressure (0.1 Torr) at 35 °C. The residual oil was subjected to flash chromatography on silica (90 g), eluting with hexane containing increasing amounts of diethyl ether (up to 50% v/v), to give **14** (1.71 g, 70%). The product could be distilled to give a colourless syrup, b.p. 75 °C at 0.05 Torr (lit.,[43] b.p. 72–73 °C at 0.2 Torr). (Found: C, 58.9; H, 8.3. $C_{12}H_{20}O_5$ requires: C, 59.0; H, 8.3%). δ_H 1.32 (3 H, s), 1.36 (3 H, s), 1.43 (3 H, s), 1.52 (3 H, s), 1.74–1.81 (1 H, m), 2.19 (1 H, dd), 3.30 (1 H, m), 4.13 (3 H, m), 4.77 (1 H, t) and 5.82 (1 H, d); δ_C(^{1}H decoupled) 25.1, 26.1, 26.4, 26.7, 35.1, 67.1, 76.7, 78.6, 80.4, 105.5, 109.6 and 111.3. The mass spectrum showed $(M - Me)^+$ at (*m*/*z*) 229.

A small amount of crystalline solid (m.p. 58–59 °C) was eluted from the column shortly after **14**. Analysis for C and H gave values which were the same as those for **14**, within experimental error, and the mass spectrum was similar to that of **14** with the most massive ion at (*m*/*z*) 229. δ_H 1.32 (3 H, s), 1.37 (3 H, s), 1.43 (3 H, s), 1.52 (3 H, s), 1.72 (1 H, ddd, *J* 13.3, 10.7, 4.9), 2.02 (1 H, dd, *J* 4.5, 13.3), 3.79 (1 H, dd, *J* 8.3, 7.0), 4.03 (1 H, dd, *J* 8.3, 6.6), 4.11–4.16 (1 H, m), 4.26 (1 H, ddd, *J* 10.7, *ca.* 4.7, *ca.* 4.7), 4.75 (1 H, dd, *J ca.* 4.3, *ca.* 4.3) and 5.84 (1 H, d, *J* 3.7). Chemical considerations (see Results and Discussion section) suggested that the crystalline substance might be 3-deoxy-1,2:5,6-di-*O*-isopropylidene-β-L-*lyxo*-hexofuranose **16**. The D-enantiomer[45] is reported to melt at 57–58 °C and its ^{1}H NMR spectrum has been analysed completely.[45] The ^{1}H NMR spectrum of the crystalline material was essentially the same as that reported for the D-enantiomer.

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