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The Invention of Radical Reactions. Part XXXI.[1] Diphenylsilane: A Reagent for Deoxygenation of Alcohols *via* Their Thiocarbonyl Derivatives, Deamination *via* Isonitriles, and Dehalogenation of Bromo- and Iodo- Compounds by Radical Chain Chemistry

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Abstract: Various thionocarbonates and xanthates of alcohols and *bis*-xanthates of *vic*-diols are readily deoxygenated to the corresponding hydrocarbons or olefins, while bromides and iodides are dehalogenated with diphenylphenylsilane in good yield.

INTRODUCTION

Tributyltin hydride played an almost exclusive role as a hydrogen atom source in the early years of radical chemistry.[2] The tin-hydrogen bond is sufficiently weak and the tributyltin radical is a useful carrier of the radical chain. However, it is not always easy to remove traces of toxic tin compounds from the reaction mixtures and this problem complicates the work-up. Therefore, the search for alternative hydrogen atom transfer agents that would also produce efficient chain-carrying radicals has started relatively early.

The weakness of a given heteroatom hydrogen bond is not always desired for hydrides used in radical chain reactions. A too weak heteroatom - hydrogen bond reduces shelf and transport stability and the hydrides may become non-selective, quenching every radical in a hydrogen atom transfer process.

Silanes are good alternatives to organotin hydrides in radical chemistry.[3] The silicon-hydrogen bond is relatively weak in some silanes and the silicon - heteroatom bonds that are formed in the radical chain process are relatively strong. Depending on the substituents, silanes offer a wide range of silicon - hydrogen bond strength, providing - in principle - alternatives when choosing hydride reagents for various radical chain reactions.[4]

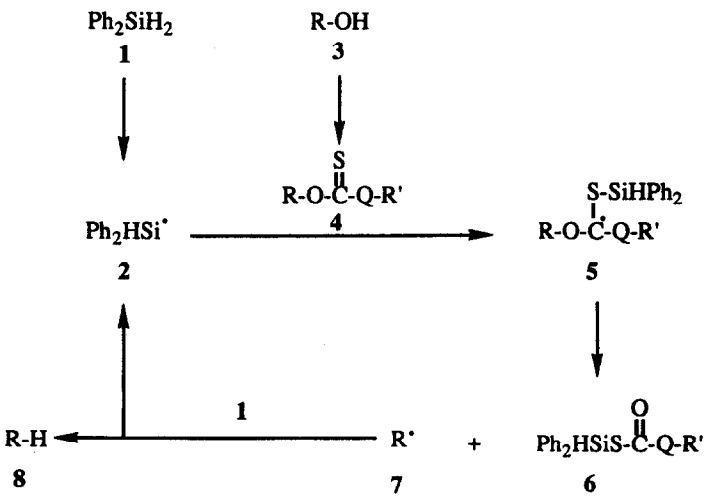
Tris(trimethylsilyl)silane was reported[5] to reduce carbon tetrachloride in 1965. More recently, however, several novel applications have been found for this known[6] silane. These include the use of tris(trimethylsilyl)silane instead of tributyltin hydride in radical reactions.[7] The silicon-hydrogen bond in tris(trimethylsilyl)silane is much weaker than in unsubstituted silane (SiH_4). Thus, the bond dissociation energy is reduced to 331 kJ/mol in tris(trimethylsilyl)silane from 376 kJ/mol (the bond dissociation energy of silane). The bond dissociation energy of tris(timethylsilyl)silane is still higher than that of tributyltin hydride

(308 kJ/mol).[8] However, this difference causes no problems in the application of tris(trimethylsily)silane in radical chemistry. Typical substrates are iodides, bromides, chlorides, secondary selenides and thioethers, isocyanides, acid chlorides, thionoesters and sulfides. The reactivity of these substrates towards tris(trimethylsilyl)silane decreases in the order: iodide > xanthate > bromide > selenide > isocyanide = nitro >sulfide ≈ chloride ≈ acid chloride.[9] The advantages of tris(trimethylsilyl)silane over tin hydrides are that the silane is less toxic and the work-up is much easier than that of the tin hydride reactions. However, tris(trimethylsilyl)silane is expensive and has a relatively high molecular weight.

Tris(alkylthio)silanes,[10] the trisilane 1,1,1,2,3,3,3-heptamethyltrisilane,[11] and silanethiols[12] have also been used in radical reactions. Simple trialkylsilanes generally have a relatively strong silicon-hydrogen bond. Therefore, these compounds require higher reaction temperatures for effective transformation. Thus, tri(n-propyl)silane has been used for the reduction of chlorocarbonates, initiated with t-butylperoxide in a sealed tube at 140°C.[13] Milder reaction conditions are sufficient when thiols are employed as mediators with alkylsilanes in elegant radical reactions.[14]

RESULTS AND DISCUSSION

The Si-H bond dissociation energies of phenyl substituted silanes are between the bond dissociation energy of tris(trimethylsilyl)silane and that of silane. Although the silicon-hydrogen bond is relatively strong in these silanes, it still allows homolytic cleavage and, hence, application in radical chemistry using normal laboratory conditions. We have demonstrated that phenyl substituted silanes[15-19] can be used in radical reactions instead of tributyltin hydride or tris(trimethylsilyl)silane. Thus, the Barton-McCombie reaction[20] can be done with various silanes (Scheme 1).



Scheme 1

We have found that diphenylsilane is a good hydrogen atom source and the diphenylsilyl radical generated from it is a chain carrier in radical deoxygenation of alcohols and dehalogenation of various organic halides.[21] In most cases the use of diphenylsilane allows high yielding transformation of xanthates,

thionocarbonates, iodides and bromides to the corresponding hydrocarbons. Primary amines can be deaminated in radical reaction with diphenylsilane *via* the corresponding isonitriles. The relatively short radical chains, however, require repeated initiation of the radical reaction.

Deoxygenation of Secondary and Primary Alcohols

The reactivity of diphenylsilane was examined with thiocarbonate derivatives of cyclododecanol **4a**, **4b**, and **4c**. Treatment of *O*-cyclododecyl S-methyl dithiocarbonate **4a** with diphenylsilane **1** (1.1 eq), triethylborane (1.1 eq), and oxygen (1.1 eq) in dry benzene under argon at room temperature afforded 81% of cyclododecane **8a** (Table 1, entry 1). The reaction without triethylborane gave no cyclododecane (entry 2). This shows that the reaction is initiated by ethyl radicals and follows a radical mechanism. The phenyl thionocarbonate of cyclododecanol **4b** was also reduced to cyclododecane **8a** in high yield (88%) under these reaction conditions (entry 3). The reaction was optimized to use a catalytic amount of triethylborane (0.2 eq) and oxygen (0.2 eq) (entries 4 and 5). When 0.6 eq of diphenylsilane was used, the yield of cyclododecane was only 61%, and 32% of the starting material **4c** was recovered (entry 6). This shows that the silicon-hydrogen bond in the transformation product **6**, formed from diphenylsilane in the first radical cycle (Scheme 1) is not as reactive as the Si-H bonds of diphenylsilane.

Table 1 Deoxygenation of thiocarbonates of cyclododecanol with Ph_2SiH_2 and Et_3B-O_2 as initiator at room temperature (Reaction time: 10 min).

Entry	Substrate	Ph_2SiH_2 (eq)	Et_3B (eq)	O_2 (eq)	RH (%)[a]
1	**4a**	1.1	1.1	1.1	81
2	**4a**	1.1	0	1.1	0
3	**4b**	1.1	1.1	1.1	88
4	**4b**	1.1	0.2	0.2	91
5	**4c**	1.1	0.2	0.2	96
6	**4c**	0.6	0.2	0.2	61 (32)[b]

[a] Analyzed by GC. [b]Starting material (analyzed by ^1H NMR).

1,2;5,6-Di-*O*-isopropylidene-α-D-glucofuranose was chosen for the deoxygenation because the compound has been a typical substrate for the Barton-McCombie reaction using tri-*n*-butyltin hydride. The deoxygenation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose with diphenylsilane, triethylborane, and air at room temperature *via* its 4-fluorophenyl thionocarbonate[22] **4g** gave the deoxy product **8c** in a 94% yield after purification on a silica gel column (entry 3). The yield of the deoxy product by this method is comparable to those reported previously, using tri-*n*-butyltin hydride (75-85%).[20, 23] The deoxygenation of

Δ^9-hecogenin *via* its 4-fluorophenyl thionocarbonate **4h** gave the deoxy product **8d** in 83% yield (entry 4). This shows that the reaction can be performed in the presence of α,β-unsaturated ketones and ketals.

Deoxygenation of primary alcohols gave low yields of the deoxy products at room temperature. Mainly, the corresponding thioformates were formed (entries 5, 7). This problem was solved by carrying out the reaction at higher temperature (80 °C). Thus, the deoxygenation of phenethyl alcohol and octadecanol *via* 4-fluorophenyl thionocarbonates **4i** and **4k** gave 80% and 87% of the corresponding hydrocarbons **8e** and **8f**, respectively (entries 6, 8).

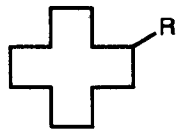
Since the 4-fluorophenyl thionocarbonate derivative gave the best yield of the corresponding hydrocarbons, various substrates were made to investigate the reactivity of the novel deoxygenation system. The 4-fluorophenyl thionocarbonate derivatives are new and the precursor, 4-fluorophenol, is inexpensive. The treatment of the 4-fluorophenyl thionocarbonate of cholestanol **4d** with diphenylsilane, triethylborane, and oxygen at room temperature gave 82% of cholestane **8b** along with 8% of the thioformate **4e** after

Table 2 Deoxygenation of thiocarbonates of various alcohols with Ph_2SiH_2 (1.1 eq) and Et_3B-O_2 as initiator.

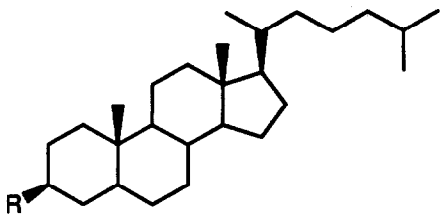
Entry	Substrate	Et_3B (eq)	O_2 (eq)	Temp (°C)	Time (min)	RH (%)
1	**4d**	0.25	0.25	25	30	82 (8)[a]
2	**4d**	0.25	0.25	80	30	93
3	**4g**	1.1	1.1	25	40	94
4	**4h**	0.25	0.25	25	30	83
5	**4i**	0.25	0.25	25	30	19[b](79)[a]
6	**4i**	0.25	0.25	80	30	80[b](12)[a]
7	**4k**	0.25	0.25	25	30	38[b](39)[a]
8	**4k**	0.25	0.25	80	30	87[b]

[a] Thioformate derivative. [b] Analyzed by GC.

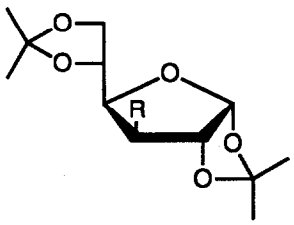
purification by column chromatography on silica gel (Table 2, entry 1). The formation of the thioformate **4e** is probably the result of the ineffectiveness of fragmentation of the radical intermediate **5**. Increasing the reaction temperature to 80 °C raised the yield of cholestane **8b** to 93% without the formation of the thioformate **4e** (entry 2). The hydrocarbon can be purified by column chromatography on silica gel. Hydrocarbons can not easily be purified by column chromatography on silica gel after using tin hydrides because of the presence of non-polar tin compounds.



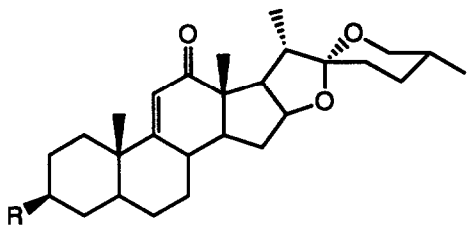
4a : R = O(C=S)SMe
4b : R = O(C=S)OPh
4c : R = O(C=S)OC$_6$H$_4$-4-F
8a : R = H



4d: R = O(C=S)OC$_6$H$_4$-4-F
4e: R = O(C=S)H
9: R = O(C=O)Ph
10: R = O(C=O)OEt
11: R = OMe
12: R = OCH$_2$SH
8b: R = H



4f : R = O(C=S)SMe
4g : R = O(C=S)OC$_6$H$_4$-4-F
8c : R = H



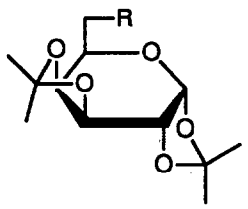
4h : R = O(C=S)OC$_6$H$_4$-4-F
8d : R = H

PhCH$_2$CH$_2$—R

4i : R = O(C=S)OC$_6$H$_4$-4-F
4j : R = O(C=S)H
8e : R = H

CH$_3$(CH$_2$)$_{16}$CH$_2$—R

4k : R = O(C=S)OC$_6$H$_4$-4-F
4l : R = O(C=S)H
8f : R = H



4m : R = O(C=S)OC$_6$H$_4$-4-F
8g : R = H

The reactivity of diphenylsilane toward other functional groups was also examined. Cholestanol benzoate **9** and cholestanyl ethyl carbonate **10** did not react under these conditions.[19] Cholestanyl thioformate **4e** gave the corresponding thiol **12** in 85% yield, that originates from 1,2-addition to the thiocarbonyl group and some methyl ether **11** (8%).

A comparison was made between diphenylsilane and *tris*(trimethylsilyl)silane. *Tris*(trimethylsilyl)silane also works well at room temperature using Et_3B-O_2 as initiator. The yields obtained with either silane are comparable. However, at present, diphenylsilane is about 30 times cheaper (mole for mole) than *tris*(trimethylsilyl)silane.

Et_3B-O_2 as an initiator is not suitable for large scale work. Therefore, thermal initiators were introduced. α,α'-Azo*bis*isobutyronitrile (AIBN) is a good substitute for thermal generation of radicals. The deoxygenation of the *S*-methyl dithiocarbonate of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **4f** with diphenylsilane in refluxing toluene or dioxane in the presence of AIBN gave the deoxy product **8c** in 90-92% yield (Table 3, entries 1, 2). Also, cholestanyl 4-fluorophenyl thionocarbonate **4d** with diphenylsilane and AIBN in refluxing dioxane afforded cholestane **8b** in 85% yield (entry 3).

Table 3 Deoxygenation of thiocarbonates of secondary alcohols with Ph_2SiH_2 (2 eq) and AIBN.

Entry	Substrate	AIBN (eq)[a]	Solvent (refluxing)	Time (min)	RH (%)
1	**4f**	2.0	toluene	200	92
2	**4f**	2.0	dioxane	200	90
3	**4d**	2.6	dioxane	390	85

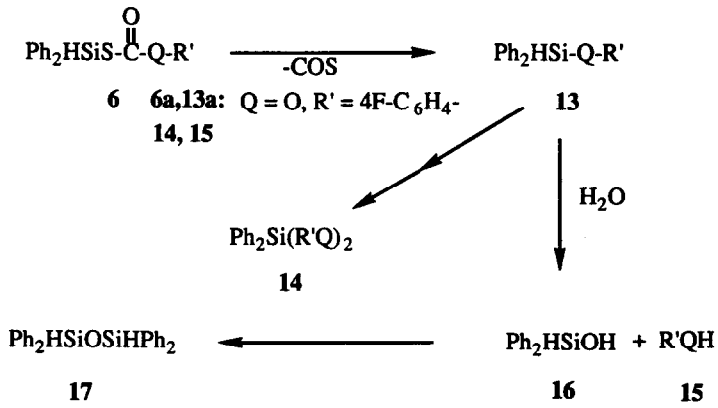
[a]The AIBN was added portionwise (0.2 eq portions) until the reaction was completed.

Mechanism

An analysis of the reduction of cyclododecyl 4-fluorophenyl thionocarbonate **4c** with diphenylsilane (1.1 eq), triethylborane (0.2 eq) and oxygen (0.2 eq) in benzene-d_6 at room temperature gave diphenyl(4-fluorophenoxy)silane **13** (60%), diphenyldi(4-fluorophenoxy)silane **14** (~10%), and 4-fluorophenol (**15** (Q = O) (20%), which was formed by the hydrolysis of diphenyl(4-fluorophenoxy)silane **13**. The small amount of diphenyldi(4-fluorophenoxy)silane formed implies that only one silicon-hydrogen bond of diphenylsilane is used as a hydrogen source in this radical chain reaction. The formation of diphenyl(4-fluorophenoxy)silane indicates that the mechanism follows the pathway that is observed in the case of tri-*n*-butyltin hydride.[20, 25]

Further studies on the mechanism by ^{29}Si NMR revealed that the deoxygenation reaction with diphenylsilane follows the same pathway[17] found earlier for the tri-*n*-butyltin hydride reactions. For these ^{29}Si NMR studies the thionocarbonate of a secondary alcohol, **4c** was used as a model compound. The low temperature ^{29}Si NMR experiment was possible because the triethylborane/air system can be used to generate ethyl radicals at low temperature. It was assumed that silicon containing intermediate **6a** (Q = O, R' = 4F-C_6H_4-) would be stable enough at lower temperature (-20 °C or below) to be detected in the low temperature ^{29}Si NMR experiment before it eliminates COS giving **13** (Scheme 2). As expected, a new signal attributed to a silicon-containg intermediate **6a** appeared in the ^{29}Si NMR spectrum (-11 ppm, at -20 °C). It is worth to note that upon being warmed up to 20 °C, this intermediate was transformed to **13** with a peak at -13 ppm in

the ^{29}Si NMR. The ^{29}Si NMR signal of the silicon-containing intermediate (at -11 ppm) did not even appear. Hydrolysis of **13** gave **17** as an end-product with a ^{29}Si NMR peak at -18 ppm as well as 4-fluorophenol **15**. From the above observations and additional NMR measurements it is clear that the radical chain deoxygenation of alcohols follows the same mechanistic pathway with silicon[17] and tin hydrides.[25]



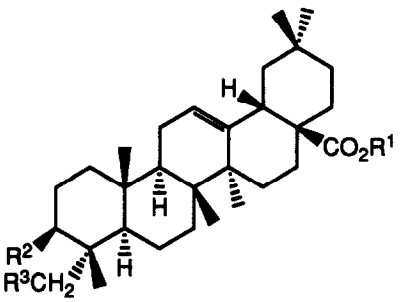
Scheme 2

The possibility of trapping diphenylsilyl radicals by aromatic solvents was also examined. The reaction of diphenylsilane with benzoyl peroxide (0.6 eq) in refluxing toluene gave less than 5% of the product that originates from the addition of diphenylsilyl radical to toluene. This shows that the trapping of diphenylsilyl radicals by aromatic solvents is a minor reaction pathway, and in the presence of highly reactive thiocarbonyl substrates this reaction cannot play any significant role.

Deoxygenation of a Primary Neopentyl Alcohol

Hederagenin **18** is a good substrate for the study of the radical chain deoxygenation of a primary neopentyl alcohol.[17] Hederagenin methyl ester **19** was therefore prepared and transformed[20a] to the corresponding monoxanthate **20.** Only the primary alcohol was transformed to the xanthate in 79% yield. Xanthate **20** was then reacted with diphenylsilane, catalyzed with benzoyl peroxide, in refluxing toluene under an atmosphere of argon to **21** (51%) after purification by silica gel column chromatography (Table 4, entry 1). We assumed that the 51% yield was caused by the unprotected hydroxy group. In order to avoid any reaction of the free alcohol with diphenylsilane, the xanthate **20** was first *O*-acetylated to the corresponding fully protected compound **22.** This xanthate was reacted with diphenylsilane and benzoyl peroxide in refluxing chlorobenzene to give 73% of the deoxy product **23** (Table 4, entry 2). A similar result was obtained in performing the reaction in refluxing *o*-xylene (entry 3). The deoxygenation of the benzoate **24** gave **25** in an

even higher yield (91%) (entry 4). It is assumable, that the silyl compound **26** could give similar or better results for the synthesis of the corresponding deoxygenated derivative **27**.



18 :	$R^1 = H$	$R^2 = OH$	$R^3 = OH$
19 :	$R^1 = CH_3$	$R^2 = OH$	$R^3 = OH$
20 :	$R^1 = CH_3$	$R^2 = OH$	$R^3 = O(C{=}S)SMe$
21 :	$R^1 = CH_3$	$R^2 = OH$	$R^3 = H$
22 :	$R^1 = CH_3$	$R^2 = OAc$	$R^3 = O(C{=}S)SMe$
23 :	$R^1 = CH_3$	$R^2 = OAc$	$R^3 = H$
24 :	$R^1 = CH_3$	$R^2 = OBz$	$R^3 = O(C{=}S)SMe$
25 :	$R^1 = CH_3$	$R^2 = OBz$	$R^3 = H$
26 :	$R^1 = CH_3$	$R^2 = OSiMe_3$	$R^3 = O(C{=}S)SMe$
27 :	$R^1 = CH_3$	$R^2 = OSiMe_3$	$R^3 = H$

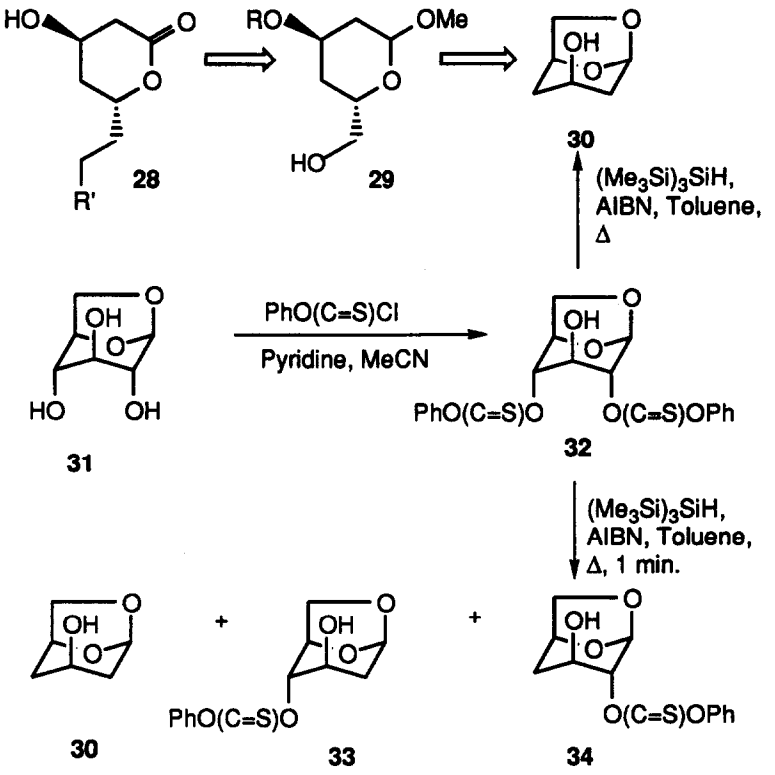
Table 4 Deoxygenation of hederagenin derivatives with Ph_2SiH_2 and benzoyl peroxide.

Entry	Substrate	Product	Ph_2SiH_2 (eq)	Benzoyl peroxide (eq)[a]	Solvent (refluxing)	Time (min)	RH (%)
1	**20**	**21**	2	1.4	toluene	140	51
2	**22**	**23**	5	1.0	chloro-benzene	100	73
3	**22**	**23**	5	1.0	*o*-xylene	100	76
4	**24**	**25**	5	1.0	*o*-xylene	100	91

[a]Benzoyl peroxide was added portionwise (0.2 eq at a time) until the reaction was complete.

Dideoxygenations of 1,3-Diol Derivatives

Mevinic acids and their analogues are potent inhibitors of HMG-CoA reductase for the treatment of severe hypercholesterolaemia.[27, 28] Most of the retrosyntheses for the preparation of HMG-CoA reductase inhibitors use a chiral synthon **28**. Thus, it is interesting to transform 1,6-anhydro-D-glucose **31** into **28**, which can then be converted to synthon **29** easily.[29]

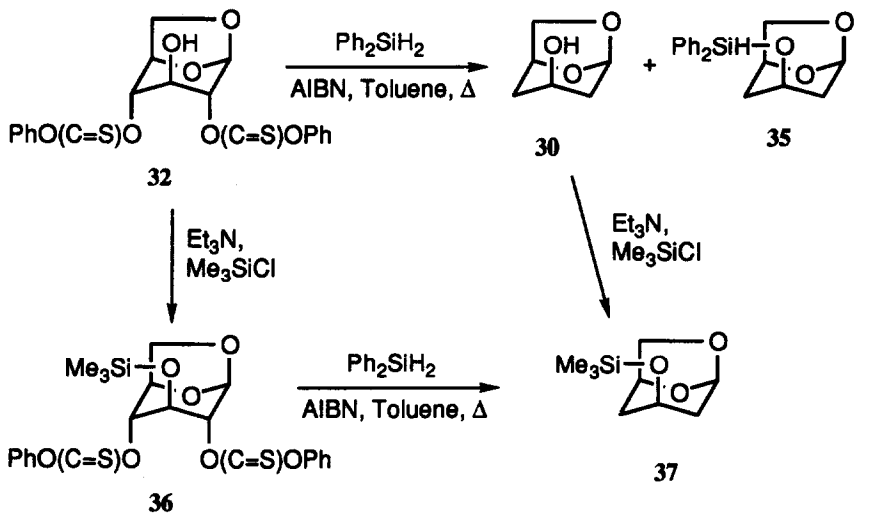


Scheme 3

In a recent paper, the dideoxygenation of 1,6-anhydro-D-glucose was described with tri-*n*-butyltin hydride (60%), diphenylsilane (46%), and *tris*(trimethylsilyl)silane (86%).[29] We studied this 2,4-dideoxygenation reaction to try either to explain the low yield with diphenylsilane or to improve the reported data.[19] Thus, 1,6-anhydro-D-glucose **31** was reacted with phenyl chlorothionoformate in the presence of pyridine in acetonitrile at room temperature to give dithionocarbonate **32**. Treatment of the dithionocarbonate **32** with *tris*(trimethylsilyl)silane in the presence of AIBN in refluxing toluene for 30 min afforded the dideoxygenated product 2,4-dideoxy-1,6-anhydro-D-glucose **30** (Scheme 3). The yield, determined by ^{1}H NMR, was 87% similar to the reported value (86%).[29] This reaction was quenched in 1 min in another run to give a mixture of the two monodeoxy compounds **33** and **34** (57%) and the dideoxy compound **30** (38%).

There was no sign of the cyclized intermediate that was formed by the reaction of radical formed at C-2 with the thionocarbonate at C-4 intramolecularly in the deoxygenation of 3,6-anhydro-D-glucopyranoside.[30]

The reaction of the dithionocarbonate **32** with diphenylsilane in refluxing toluene, initiated by AIBN, gave 48% of 2,4-dideoxy-anhydro-D-glucose **30**, similarly to the reported yield (46%) (Scheme 4). However, the reaction mixture contained the two monodeoxy compounds **33** and **34** (28%). The use of diphenylsilane as solvent improved the yield of the dideoxy compound **30** only to 60%. Using an increased amount of the radical initiator AIBN (1.4 eq) in refluxing toluene furnished the dideoxy compound **30** in a 60% yield. An analysis of the reaction mixture by TLC showed the presence of a less polar (more mobile) carbohydrate derivative. It was assumed that this compound was the *O*-silylated derivative of **30** (**35**).

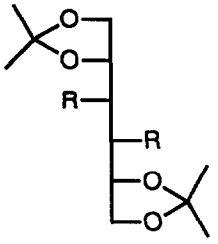


Scheme 4

Treatment of the reaction mixture with 0.3 M aqueous potassium hydroxide solution removed this spot and increased the yield of the dideoxy product **30** by 14% (to 74%). The product **30** was partly consumed in the silylation reaction. Earlier acetate and benzoate derivatives of hederagenin were used to protect the hydroxyl groups and increase the yields of deoxygenation. In this case, a trimethylsilyl protecting group was introduced after the formation of the dithionocarbonate **32**. This compound was formed in the presence of triethylamine with chlorotrimethylsilane. The silylated intermediate **36** was not isolated but transformed directly to the silylated dideoxy compound **37**. The overall yield of the silylation and radical dideoxygenation steps was 85% (determined by ^{1}H NMR). This compound, 1,6-anhydro-2,4-dideoxy-3-*O*-trimethylsilyl-D-glucose **37** was also prepared from the dideoxy compound **30** by silylation with chlorotrimethylsilane in the presence of triethylamine. This finding indicates that diphenylsilane can give the same yield as *tris*(trimethylsilyl)silane in the radical chain deoxygenation reactions.

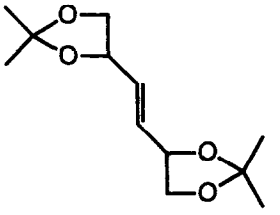
Dideoxygenations of 1,2-Diol Derivatives

The application of this diphenylsilane-based radical chemistry to the inexpensive and easily formed *bis*-xanthates would be a simple radical method for the formation of olefins from 1,2-diols. The reaction of the *bis*-xanthate of 1,2:5,6-di-*O*-isopropylidene-D-mannitol **38** with diphenylsilane and Et_3B-O_2 as initiator at room temperature gave only 38% of the corresponding olefin **39** (Table 5, entry 1).



38

R = O(C=S)SMe



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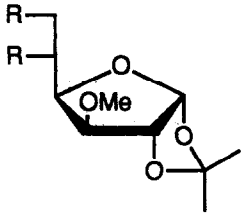
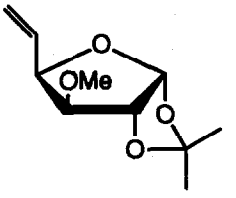
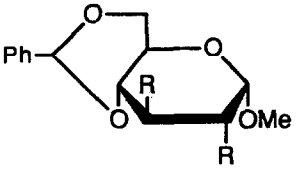


R = O(C=S)SMe

40

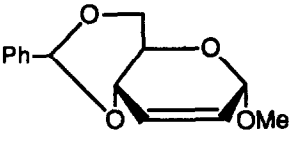


41



R = O(C=S)SMe

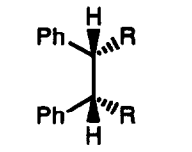
42



43

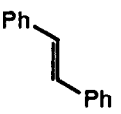
The olefin **39** was obtained only in moderate yield (60-66%), when the reaction was performed in refluxing benzene or toluene (entry 2, 3). There was an unexpected side product. It was assumed that the compounds

were derived from the addition of triethylborane derivatives to the olefin. The treatment of the *bis*-xanthate of 1,2:5,6-di-*O*-isopropylidene-D-mannitol **38** with diphenylsilane in refluxing toluene in the presence of AIBN gave a quantitative yield of olefin (entry 4). Using 1.1 mol eq of diphenylsilane also gave the olefin **39** in high yield, although more radical initiator was required to complete the reaction (entry 5).



R = O(C=S)SMe

44



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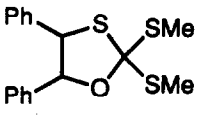
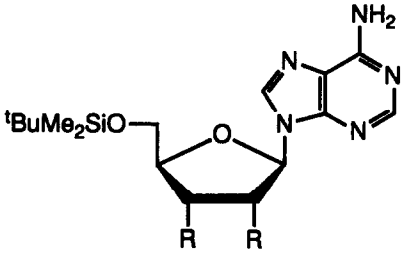
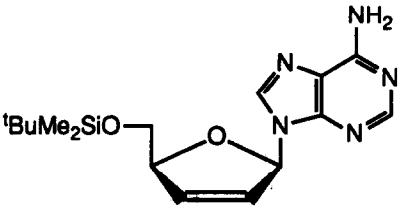


46

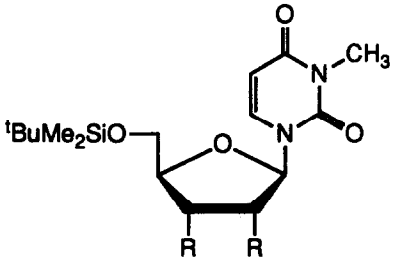


R = O(C=S)SMe

47

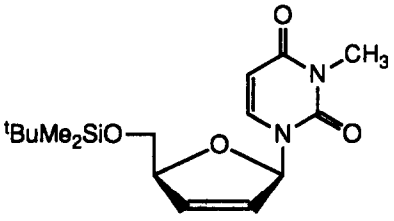


48



R = O(C=S)SMe

49



50

Table 5 Synthesis of olefins from *bis*-xanthates with Ph_2SiH_2.

Entry	Substrate	Product	Ph_2SiH_2 (eq)	Initiator (eq)[a]	Solvent (refluxing)	Time (hr)	Yield (%)
1	**38**	**39**	1.6	A (1.6)	benzene[b]	0.66	38
2	**38**	**39**	1.1	A (1.1)	benzene	0.5	66
3	**38**	**39**	1.1	A (1.1)	toluene	0.5	60
4	**38**	**39**	2.2	B (1.8)	toluene	4.5	100[c]
5	**38**	**39**	1.1	B (2.8)	toluene	28	100[c]
6	**38**	**39**	0	B (0.4)	toluene	4.0	0
7	**40**	**41**	2.2	B (1.0)	toluene	2.5	88
8	**42**	**43**	2.0	B (2.0)	toluene	5.0	94 (97)[c]
9	**42**	**43**	2.0	B (2.0)	dioxane	3.3	97[c]
10	**42**	**43**	2.0	C (1.0)	toluene	2.5	95[c]
11	**44**	**45**	2.0	B (0.4)	dioxane	1.0	63
12	**47**	**48**	2.0	B (0.8)	toluene	1.33	90 (95)[c]
13	**47**	**48**	2.0	C (0.4)	toluene	0.66	93[c]
14	**47**	**48**	0	C (0.4)	toluene	0.66	< 5[c]
15	**49**	**50**	2.0	B (0.8)	toluene	1.33	91(97)[c]

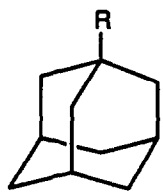
A : Et_3B with the same mol eq of O_2. B : AIBN C : Benzoyl peroxide
[a] 0.2 mol eq of AIBN or benzoyl peroxide was added portionwise until the reaction was completed. [b] Room temperature. [c] Analyzed by ^1H NMR.

There was no sign of the formation of olefin without diphenylsilane (entry 6). This shows that diphenylsilane is a radical mediator. The *bis*-xanthate **40** afforded the corresponding olefin **41** in high yield (88%) (entry 7). The deoxygenation of **42** in refluxing toluene or refluxing dioxane showed no difference in the yields of olefin **43** (entry 8, 9). Generally, benzoyl peroxide is more effective in initiating the reaction under these conditions than AIBN (entry 9, 10). The olefination of the *bis*-xanthate of *meso*-hydrobenzoin **44** afforded 63% of stilbene **45** along with the cyclized product **46** (30%), which was formed by nucleophilic attack at C-1 by 2-thiocarbonyl group.[30] The synthesis of the *bis*-xanthates of nucleosides was difficult with the NaH-CS_2-MeI method. For steric reasons, the cyclic thionocarbonates were obtained. The *bis*-xanthate of the adenosine derivative **47** was obtained with NaH-CS_2-MeI in moderate yield, while in the case of the uridine derivative, the major product was the cyclized thionocarbonate. The *bis*-xanthate of the uridine derivative, **49**, could be made using NaOH-CS_2-MeI at room temperature.[31] However, the yield was only 50%, and the 3-*N*-

methylated compound was produced. To avoid the *N*-methylation, $BrCH_2CH_2CN$ was tried for the alkylation. Although *N*-alkylation could be avoided, the yield was low. It is not easy to make *bis*-xanthates of nucleosides, but the olefination from their *bis*-xanthates works well. The reaction of the adenosine derivative **47** with diphenylsilane in refluxing toluene with AIBN or benzoyl peroxide gave high yields of the corresponding olefin **48** (entry 12, 13). The blank experiment with benzoyl peroxide, without the silane, gave only a trace amount of the olefin **48** (entry 14). Uridine derivative **49** was transformed into the corresponding olefin **50** in 91% yield after chromatography on silica gel (entry 15).

Removal of Other Functional Groups

In dehalogenation, as expected, debromination of 1-bromo-adamantane **52** with diphenylsilane and benzoyl peroxide in refluxing toluene furnished 91% of adamantane **178**, but dechlorination of 1-chloro-adamantane **53** under these conditions gave only 8% of adamantane with recovery of 1-chloro-adamantane **53** (91%) (Table 6, entry 2, 3).



51 : R = I
52 : R = Br
53 : R = Cl
54 : R = NC
55 : R = SePh
56 : R = NO_2
57 : R = H

Table 6 Reduction of various functional groups with Ph_2SiH_2 and benzoyl peroxide in refluxing toluene.

Entry	Substrate	Ph_2SiH_2 (eq)	Benzoyl peroxide (eq)[a]	Time (min)	RH (%)[b]
1	**51**	10	2	300	35 (65)[c]
2	**52**	4	1	150	91
3	**53**	2	2	300	8 (91)[c]
4	**54**	5	0.4	60	100[d]
5	**55**	5	1	100	0
6	**56**	5	1	100	0

[a] 0.2 mol eq of benzoyl peroxide was added portionwise until the reaction was completed. [b] Analyzed by GC. [c] Starting material. [d] In dioxane.

Surprisingly, attempted deiodination of 1-iodo-adamantane **51** resulted in only 35% of adamantane **57** and the recovery (65%) of 1-iodo-adamantane **51** (entry 1). The bond strength of the carbon-iodine bond is much weaker than that of the carbon-chlorine bond. Indeed, deiodination is more efficient than debromination in

using tri-*n*-butyltin hydride and *tris*(trimethylsilyl)silane. This finding can be rationalized as an equilibrium between Ad-I/Ph_2SiH• and Ph_2SiHI/Ad• due to the weakness of the silicon-iodine bond. 1-Isocyanoadamantane **54** was reduced to adamantane **57** by diphenylsilane in quantitative yield (entry 4). However, phenylselenyl and nitro groups in the C1-position of adamantane are inert to diphenylsilyl radicals (entry 5, 6).

Experimental

General Procedures and Starting Materials. Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. Specific rotations were determined on a Jasco Model DIP-360 digital polarimeter. ^1H and ^{13}C NMR spectra were determined for solutions in deuterochloroform (unless specified otherwise) with TMS internal reference on a Varian Gemini 200, a Varian XL 200E, or a VARIAN UNITY 500 spectrometer. Gas chromatography (glc) measurements were performed on a Chrompack Packard Model 439 gas chromatograph on 30 m capillary columns. Mass spectra were obtained on a VG Analytical 70S high resolution double focusing magnetic sector mass spectrometer with attached VG 11/250J data system in the electron impact (EI) mode. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F-254). Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230-400 mesh). Solvents were used either as purchased or dried and purified by standard methods under pure, dry argon. Other reference compounds and starting materials were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

Typical procedure for deoxygenation with diphenylsilane, triethylborane and oxygen: To a substrate (0.4 mmol) in dry benzene (5 mL) under argon was added diphenylsilane (0.44 mmol) and triethylborane (0.1 mmol, 1 M solution in hexane). Dry air (10.4 mL) was injected for 20 min by a syringe pump and then the reaction was stirred for 10 min. After evaporation of the solvent the residue was separated by column chromatography on silica gel.

Typical procedure for the dideoxygenation: To a solution of the starting dixanthate (0.4 mmol) in dry toluene (3 mL), diphenylsilane (147 μL, 0.8 mmol) was added under argon. Then the solution was brought to the boil and treated with 300 μL portions of a solution of AIBN in toluene at 30 min intervals (262.4 mg AIBN was dissolved in 6.0 ml dry toluene). The reaction was monitored by TLC. When the reaction was complete the solvent was evaporated in vacuum and the olefin was isolated by column chromatography on silica gel.

***O*-Cyclododecyl-*S*-methyl xanthate 4a.**[32] To a solution of cyclododecyl alcohol (3.68 g, 20 mmol) in THF (40 mL) was added *n*-butyllithium (12.5 mL, 1.6 M in THF, 20 mmol) at 0°C under N_2. The solution was stirred for 30 min at 0 °C before the addition of CS_2 (1.24 mL, 21 mmol). The mixture was then stirred at room temperature for 4 h followed by the addition of MeI (1.3 mL, 21 mmol). The final solution was sitrred for 1 h at room temperature. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$ and brine sucessively. After drying over anhydrous $MgSO_4$ and evaporation of the solvent, the residue was crystallized from CH_2Cl_2-EtOH to give 3.37 g (62 %) of the xanthate: mp 47-49 °C ($EtOH/CH_2Cl_2$) (lit., 48-48.5 °C); IR ($CHCl_3$) 2940, 2860, 1210, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20-1.45 (m, 18 H), 1.60-1.90 (m, 4 H), 2.50 (s, 3 H, SMe), 5.85-5.90 (m, 1 H); ^{13}C NMR (C_6D_6) δ 18.7, 21.4 (2 C), 23.6 (2 C), 23.8 (2 C), 23.9, 24.2 (2 C), 29.1 (2 C), 82.7, 216.2; MS *m/e* (relative intensity) 227 (M^+ -SMe, 0.2), 183 (0.9), 166 (70), 111 (31), 97 (61), 83

(68), 69 (75), 55 (100), 41 (77), 28 (84). Anal. Calcd for $C_{14}H_{26}OS_2$: C, 61.26; H, 9.55; S, 23.36. Found: C, 61.11; H, 9.57; S, 23.32 %.

***O*-Cyclododecyl-*O'*-phenylthionocarbonate 4b.** To a solution of cyclododecyl alcohol (0.92 g, 5 mmol) and dry pyridine (15 mL, 19 mmol) in dry CH_2Cl_2 (30 mL) was added phenyl chlorothionoformate (1.0 mL, 5.5 mmol) under N_2. Then the solution was stirred for 2 h at room temperature. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. After filtration and concentration in vacuum the residue was crystallized from EtOH to give 0.98 g (61 %) of the thionocarbonate: mp 60-62 °C (EtOH); IR (CH_2Cl_2) 2938, 2863, 1489, 1256, 1199 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25-1.60 (m, 18 H), 1.64-2.00 (m, 4 H), 5.45-5.58 (m, 1 H), 7.04-7.18 (m, 2 H), 7.20-7.30 (m, 1 H), 7.32-7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (2 C), 23.1 (2 C), 23.3 (2 C), 23.6, 23.9 (2 C), 28.5 (2 C), 83.9, 122.0 (2 C), 126.3, 129.3 (2 C), 153.3, 194.6; MS *m/e* (relative intensity) 166 (M^+ - OC(S)OPh, 56), 94 (83), 82 (55), 69 (58), 55 (100), 41 (84). Anal. calcd for $C_{19}H_{28}O_2S$: C, 71.21; H, 8.81; S, 10.00. Found: C, 71.16; H, 8.83; S, 9.90 %.

***O*-Cyclododecyl-*O'*-(4-fluorophenyl)thionocarbonate 4c.** To a solution of cyclododecyl alcohol (3.7 g, 20 mmol), *N*-hydroxysuccinimide (0.23 g, 2 mmol) and dry pyridine (4.1 mL, 50 mmol) was added 4-fluorophenyl chlorothionoformate (7.56 g, 40 mmol) dropwise at room temperature under argon. The solution was stirred for an additional hour. The organic layer was then washed with 1 M HCl, saturated $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. After filtration and concentration the thionocarbonate byproduct was precipitated by the addition of hexane. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with *n*-hexane to afford 4.37 g (65 %) of the thionocarbonate: 47-49 °C ($EtOH/CH_2Cl_2$); IR ($CDCl_3$) 2936, 1497, 1289, 1186, 1144, 994, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20-1.55 (m, 18 H), 1.60-2.00 (m, 4 H), 5.43-5.55 (m, 1 H), 7.02-7.11 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (2 C), 23.2 (2 C), 23.4 (2 C), 23.6, 23.9 (2 C), 28.6 (2 C), 84.2, 116.1 (d, $J_{C\text{-}F}$ = 23.5 Hz, 2 C), 123.5 (d, $J_{C\text{-}F}$ = 8.5 Hz, 2 C), 149.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 160.5 (d, $J_{C\text{-}F}$ = 244 Hz), 194.6; MS *m/e* (relative intensity) 166 (57), 112 (70), 97 (44), 83 (55), 69 (62), 55 (100), 41 (77). Anal. calcd for $C_{19}H_{27}FO_2S$: C, 67.42; H, 8.04; S, 9.47. Found: C, 67.39; H, 8.10; S, 9.37 %.

***O*-Cholestanyl thionoformate 4e.**[20] Column chromatography on silica gel (eluent; hexane): mp 106-107 °C (lit.[20], 104-105 °C); $[\alpha]^{26}_D$ = -69.4 ° (lit., $[\alpha]^{22}_D$ = -69.6°); IR (nujol) 2928, 1462, 1379, 1243 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57-2.06 (m, 46 H), 5.34-5.58 (m, 1 H), 9.71 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 12.2, 18.7, 21.2, 22.6, 22.8, 23.8, 24.2, 26.6, 28.0, 28.2, 28.6, 31.9, 33.0, 34.4, 35.5, 35.8, 36.2, 36.6, 39.5, 39.9, 42.6, 44.5, 54.2, 56.2, 56.4, 79.9, 206.2; MS *m/e* (relative intensity) 433 (M^+ + 1, 0.2), 432 (M^+, 1), 387 (1), 371 (100), 355 (7), 316 (7), 275 (5), 261 (7), 245 (10), 217 (14), 203 (13), 163 (20), 149 (25), 109 (37), 95 (55), 81 (45), 55 (40), 43 (36), 28 (54).

***O*-β-Phenethylthionoformate 4j.** Column chromatography on silica gel (eluent; hexane : CH_2Cl_2, 7 : 3): oil; IR (nujol) 3066, 3031, 2954, 1496, 1452, 1383, 1242, 1001, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.13 (t, *J* = 7 Hz, 2 H), 4.75 (t, *J* = 7 Hz, 2 H), 7.08-7.49 (m, 5 H), 9.73 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 34.3, 70.7, 126.8, 128.7 (2 C), 128.9 (2 C), 137.2, 206.6; MS *m/e* (relative intensity) 166 (M^+, 0.3), 122 (10), 105 (100), 91 (85), 77 (56), 65 (24).

***O*-1-Octadecylthionoformate 4l.** Column chromatography on silica gel (eluent; hexane : CH_2Cl_2, 7 : 3): mp 30-32 °C; IR (neat) 2923, 2852, 1463, 1383, 1240, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70-1.95 (m, 35 H), 4.51 (t, *J* = 7 Hz, 2 H), 9.76 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.1, 26.3, 28.4, 29.7,29.8, 29.9, 30.0, 30.1 (9 C), 32.4,

71.1, 207.0; MS *m/e* (relative intensity) 125 (15), 111 (14), 97 (28), 83 (31), 69 (33), 57 (96), 43 (67). Anal. calcd. for $C_{19}H_{38}OS$: C, 72.55; H, 12.18; S, 10.19. Found: C, 72.62; H, 12.13; S, 10.08 %.

The following compounds have already been reported in the literature. We have characterized them by standard techniques and comparison of the data observed with the reported values.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl-α-D-glucofuranose 4f.[33]

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 8c.[34]

***O*-Cholestanyl-*O'*-methylenethiol 12.**[35]

***O*-Cholestanyl benzoate 9.**[36]

***O*-Cholestanyl-*O'*-ethylcarbonate 10.**[37]

1,2:5,6-di-*O*-isopropylidene-3,4-bis-*O*-[(S-methylthio)-thiocarbonyl]-D-mannitol 38.[38]

1,2-*O*-Isopropylidene-3-*O*-methyl-5,6-bis-*O*-[(methylthio)-thiocarbonyl)]-α-D-glucose 40.[39]

5,6-Dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylohex-5-enofuranose 41.[40]

Methyl 4,6-*O*-benzylidene-2,3-bis-*O*-[(*S*-methylthio)thiocarbonyl]-α-D-glucopyranoside 42.[33]

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-erythro-hex-2-eno-pyranoside 43.[38]

(*meso*)-1,2-Bis-[(*S*-methylthio)thiocarbonyloxy]-1,2-diphenylethane 44.[38]

5'-*O*-(*tert*-Butyldimethylsilyl)adenosine.[31] A solution of adenosine (2 g, 7.48 mmol), *t*-butylchlorodimethylsilane (1.4 g, 9 mmol), DMAP (0.14 g, 1.12 mmol) and triethylamine (2.1 mL, 15 mmol) in DMF (40 mL) was stirred at room temperature for 20 h. After filtration the solvent was evaporated in vacuum. The residue was then purified by column chromatography on silica gel eluting with $CHCl_3$/MeOH (10 : 1) to give 2 g (70 %) of the desired product: ^{1}H NMR (DMSO-d_6) δ 0.02 (s, 6 H), 0.84 (s, 9 H), 3.34 (br, 1 H), 3.68-3.98 (m, 3 H), 4.10-4.22 (m, 1 H), 4.45-4.60 (m, 1 H), 5.20 (d, J = 6 Hz, 1 H), 5.54 (d, J = 6 Hz, 1 H), 5.89 (d, J = 4 Hz, 1 H), 7.29 (br, 2 H), 8.13 (s, 1 H), 8.27 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ -5.4 (2 C), 18.1, 25.8 (2 C), 62.9, 69.9, 73.8, 84.4, 87.4, 119.0, 139.0, 149.4, 152.7, 156.1.

5'-*O*-(*tert*-Butyldimethylsilyl)-2',3'-bis-*O*-[(methylthio)-thiocarbonyl]adenosine 47.[31] To a solution of the diol (1 g, 2.62 mmol) and CS_2 (0.8 mL, 13.10 mmol) in DMSO (15 mL) was added 5 N NaOH (1.2 mL) dropwise. Before the addition of MeI (0.82 mL, 13.1 mmol) the reaction was stirred at room temperature for 2 h. The solution was stirred after the addition of MeI for 2 h. After evaporation of the solvent in vacuum the reaction mixture was diluted with EtOAc and washed with water and dried over anhydrous $MgSO_4$. The title compound was then purified by column chromatography on silica gel eluting with EtOAc to give 1 g (68 %) of the desired product: mp 161-162 °C (benzene/ hexane) (lit.[31], 164-165 °C); $[\alpha]^{26}_D$= -70° (c 1, $CHCl_3$); IR ($CHCl_3$) 3519, 3411, 3015, 2957, 1630, 1584, 1469, 1420, 1194, 1095, 1076, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.95 (s, 9 H), 2.51 (s, 3 H), 2.59 (s, 3 H), 3.89-4.10 (m, 2 H), 4.48-4.52 (m, 1 H), 5.72 (br, 2 H), 6.35-6.62 (m, 3 H), 8.20 (s, 1 H), 8.36 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.5, -5.3, 18.4, 19.3 (2 C), 26.0 (3 C), 63.2, 78.8, 80.8, 84.4 (2 C), 119.5, 138.2, 150.1, 153.3, 155.7, 214.2, 214.6; MS *m/e* (relative intensity) 504 (M^+ - *t*-butyl, 31), 396 (3), 290 (5), 91 (100).

5'-O-(*tert*-Butyldimethylsilyl)-2',3'-didehydro-2',3'-dideoxyadenosine 48.[31] Column chromatography on silica gel (eluent; $CHCl_3$: MeOH, 10 : 0.5): mp 128-130 °C (lit., 117-121 °C); $[\alpha]^{26}_D$ = -44° (c 1, $CHCl_3$); IR ($CHCl_3$) 3485, 3410, 3017, 2958, 1629, 1583, 1468, 1414, 1363, 1204, 1137, 1086, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6 H), 0.92 (s, 9 H), 3.84-3.88 (m, 2 H), 4.96-5.16 (m, 1 H), 5.76-5.87 (br, 2 H), 6.06-6.21 (m, 1 H), 6.38-6.46 (m, 1 H), 7.11-7.16 (m, 1 H), 8.13 (s, 1 H), 8.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.5, -5.4, 18.5, 25.9 (3

C), 64.8, 87.7, 88.2, 119.4, 125.5, 134.5, 139.2, 149.6, 152.7, 155.4; MS *m/e* (relative intensity) 290 (M^+ - *t*-butyl, 6), 155 (100), 135 (31), 81 (89).

5'-O-(*tert*-Butyldimethylsilyl)uridine.[31] A solution of uridine (3 g, 12.3 mmol), *t*-butyldimethylchlorosilane (2.22 g, 14.76 mmol), DMAP (30 mg, 0.25 mmol) and triethylamine (3.4 mL, 24.6 mmol) in DMF (60 mL) was stirred at room temperature for 20 h. After filteration of precipitate the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel eluting with EtOAc to give 3.41 g (77 %) of the desired product: mp 137-139 °C (CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$) δ 0.12 (s, 6 H), 0.92 (s, 9 H), 1.27 (br, 2 H), 2.62-2.92 (br, 1 H), 3.72-4.32 (m, 6 H), 5.63 (d, J = 8 Hz, 1 H), 5.90-5.94 (m, 1 H), 8.05 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.6, -5.5, 18.1, 25.8 (3 C), 62.6, 69.5, 73.8, 84.1, 88.0, 101.5, 140.2, 150.6, 163.0.

5'-*O*-(*tert*-Butyldimethylsilyl)-2',3'-bis-*O*-[(methylthio)-thiocarbonyl]-N^3-methyluridine 49.[31] To a solution of the diol (0.5 g, 1.4 mmol) and CS_2 (1.68 mL, 27.9 mmol) in DMSO (5 mL) was added 5 N NaOH (2.23 mL) dropwise. Before the addition of MeI (1.74 mL, 27.9 mmol) the reaction mixture was stirred at room temperature for 2 h. The solution was stirred after the addition of MeI for 2 h. After evaporation of the solvent the reaction mixture was diluted with EtOAc and washed with water and dried over anhydrous $MgSO_4$. The title compound was then purified by column chromatography on silica gel eluting with EtOAc/hexane (3 : 7) to give 0.31 g (40 %) of the dixanthate: mp 75-78 °C (EtOH/H_2O); $[\alpha]^{25}_D$ = -44° (c 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.17 (s, 3 H), 0.95 (s, 9 H), 2.57 (s, 3 H), 2.60 (s, 3 H), 3.33 (s, 3 H), 3.87-4.07 (m, 2 H), 4.44-4.47 (m, 1 H), 5.80 (d, H = 8 Hz, 1 H), 6.03-6.11 (m, 1 H), 6.31-6.36 (m, 1 H), 6.60 (d, J = 8 Hz, 1 H), 7.84 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.7, -5.4, 18.3, 19.2, 19.3, 25.9 (3 C), 27.8, 63.2, 78.8, 79.9, 84.1, 86.1, 102.7, 137.3, 151.1, 162.5, 214.4, 214.6.

5'-*O*-(*tert*-Butyldimethylsilyl)-2',3'-didehydro-2',3'-dideoxy-N^3-methyluridine 50.[31]

1-Iodo-adamantane 51.[41]

***N*-1-Adamantyl formamide.** A solution of 1-adamantanamine (2g, 13.2 mmol), ethyl formate (25 ml) and DMSO (10 mL) was heated at 100 °C in a sealed tube for 24 h. After evaporation of the ethyl formate the residue was poured onto an ice-water mixture. The solid was isolated by filtration and dried over P_2O_5 to give 2 g of the crude product. The formamide was used without further purification.

1-Adamantyl isocyanide 54.[42] To a solution of the amide (2 g, 11.17 mmol) and phosphoroyl chloride (3.12 mL, 33.52 mmol) in CH_2Cl_2 (20 mL) at - 40 °C was added triethylamine (14 mL, 100.56 mmol). The reaction mixture was then stirred at room temperature for 24 h. Then the solution was poured onto an ice-water mixture. The organic layer was separated, washed with saturated $NaHCO_3$ and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give 1.2 g (47 %, from the amine) of the isocyanide: mp 186-188 °C (sealed tube, from CH_2Cl_2/EtOH) (lit., 179-180 °C); IR (nujol) 2853, 2122, 1458, 1375, 1076 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (br, s, 6 H), 2.03 (br, s, 6 H), 2.10 (br, s, 3 H); ^{13}C NMR ($CDCl_3$) δ 28.5 (3 C), 35.3 (3 C), 43.4 (3 C), 54.0 (t, J_{C-N} = 5.5 Hz), 151.5 (t, J_{C-N} = 5.0 Hz).

1-Phenylseleno-adamantane 55. A solution of the *O*-(1-adamantoyl) derivative of *N*-hydroxy-2-thiopyridone (0.79 g, 2.84 mmol) and diphenyl diselenide (1.77 g, 5.68 mmol) in CH_2Cl_2 (30 mL) under argon was irradiated with a tungsten lamp for 2 h. After evaporation of the solvent the residue was purified by column chromatography on silica gel eluting with CH_2Cl_2. The fraction containing the title product was treated with an ethanolic solution of $NaBH_4$ and washed with saturated $NaHCO_3$ and dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent the residue was crystallized from MeOH to give 0.3 g (36 %) of the

desired product: mp 42-45 °C (lit.); ^{1}H NMR ($CDCl_3$) δ 1.65 (br, s, 7 H), 2.00 (br, s, 8 H), 7.30-7.70 (m, 5 H); MS *m/e* (relative intensity) 292 (M^+, 5), 135 (M^+-SePh, 100).

1-Nitro-adamantane 56.[43]

Synthesis of dithionocarbonate 32. To a solution of 1,6-anhydro-β-D-glucose (400 mg, 2.5 mmol) and dry pyridine (2 mL, 25.2 mmol) in acetonitrile (6 mL) was added phenyl chlorothionoformate (750 μL, 5.4 mmol) dropwise at room temperature under argon. The solution was stirred for 2 h. The organic layer was then washed with H_2O and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to afford 710 mg (67%) of the thionocarbonate **32**: mp 126-127 °C (hexane-diethyl ether) (lit.[29] 116-119 °C); $[\alpha]^{25}_D$ = -51.7° (c 1.2, $CHCl_3$) (lit.[29] -50°); IR ($CDCl_3$) 3596, 1276, 1224 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.20-2.75 (br, 1 H), 3.88 (dd, *J* = 6, 6 Hz, 1 H), 4.22-4.35 (m, 2 H), 4.91-5.01 (m, 1 H), 5.09-5.15 (m, 1 H), 5.20-5.25 (m, 1 H), 5.77 (s, 1 H), 7.00-7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 66.1, 68.9, 73.8, 80.4, 81.6, 99.4, 121.7 (4 C), 126.8 (2 C), 129.6 (4 C), 153.3 (2 C), 194.3 (2 C).

Deoxygenation of 32 with with *tris*(trimethylsilyl)silane. A solution of **32** (87 mg, 0.20 mmol), *tris*(trimethylsilyl)silane (136 μL, 0.44 mmol), and AIBN (1.6 mg, 5 mmol %) in toluene (1.5 mL) under argon was heated to reflux for 1 h. After evaporation of the solvent the residue was analyzed by ^{1}H NMR to give 87% of **30**.

Deoxygenation of 32 with diphenylsilane. A solution of **32** (174 mg, 0.4 mmol) and diphenylsilane (294 μL, 1.6 mmol) in toluene (1 mL) under argon was treated with 150 μL of AIBN solution (262 mg AIBN in 3 mL dioxane) seven times at every 20 min during reflux. After evaporation of the solvent the residue was separated by column chromatography on silica gel eluting with hexane/EtOAc (6 : 4) to give 32 mg (60%) of **30** and a non-polar side product. The side product was treated with 0.3 N KOH for 5 h at room temperature. After washing with CH_2Cl_2 the aqueous layer was neutralized by 1 M HCl, and washed with CH_2Cl_2 and dried over anhydrous $MgSO_4$. After evaporation of the solvent 7.5 mg (14%) of **30** was obtained: $[\alpha]^{28}_D$ = -81.7° (c 1.2, H_2O) (lit.[44] -81°); ^{1}H NMR ($CDCl_3$) δ 1.85-2.27 (m, 5 H), 3.70-3.80 (m, 1 H), 4.00-4.10 (m, 1 H), 4.32 (d, *J* = 8 Hz, 1 H), 4.50-4.60 (m, 1 H), 5.64 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.5, 38.7, 64.1, 68.4, 72.4, 101.3.

Trapping the monothionocarbonates 33 and 34. A solution of the dithiocarbonate **32** (87 mg, 0.20 mmol), *tris*(trimethylsilyl)silane (136 μL, 0.44 mmol), and AIBN (1.6 mg, 5 mmol %) was heated to reflux for 1 min under argon. The reaction was then quenched in a dry ice-acetone bath. The product were separated by preparative TLC to afford 32 mg (57%) of the mixture of the oily monodeoxy compounds **33** and **34** (in a 1 : 1.2 ratio) and 10 mg (38%) of the dideoxy compound **30**: oil. Anal. Calcd for $C_{13}H_{14}O_5S$: C, 55.32; H, 4.96. Found: C, 54.49; H, 5.00.

Deoxygenation of 32 with diphenylsilane *via* 36. A solution of 1,6-anhydro-2,4-*bis*-*O*-phenoxythiocarbonyl-D-glucose (174 mg, 0.4 mmol), chlorotrimethylsilane (0.31 mL, 2.4 mmol), and triethylamine (0.5 mL, 3.6 mmol) in benzene (3 mL) was stirred for 1 h at room temperature. After filtration the solvent was evaporated. The residue was dissolved in toluene (1 mL) and diphenylsilane (294 μL, 1.6 mmol) was added. The reaction mixture was heated to reflux and treated under argon with 150 μL portions of AIBN solution (262 mg of AIBN in 3 mL of dioxane) five times (at every 20 min) during reflux. After evaporation of the solvent the residue was analyzed by ^{1}H NMR to give 85% of **37**.

Synthesis of 1,6-anhydro-2,4-dideoxy-3-*O*-trimethylsilyl-D-glucose 37. A solution of 1,6-anhydro-2,4-dideoxy-D-glucose **30** (40 mg, 0.31 mmol), chlorotrimethylsilane (0.31 mL, 2.4 mmol), and triethylamine (0.5 mL, 3.6 mmol) in benzene (3 mL) was stirred for 12 h at room temperature. After evaporation of the volatile compounds the residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give 37 mg (60%) of **37**: oil; $[\alpha]^{28}_D = -70°$ (c 0.6, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.62-2.23 (m, 4 H), 3.69 (dd, J = 6, 6 Hz, 1 H), 3.98-4.10 (m, 1 H), 4.38 (d, J = 6 Hz, 1 H), 4.41-4.50 (m, 1 H), 5.52 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.07, 37.6, 39.1, 63.1, 67.5, 71.7, 100.3. Anal. Calcd for $C_9H_{18}O_3Si$: C, 53.46; H, 8.91. Found: C, 53.53; H, 8.92.

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