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The Invention of Radical Reactions. Part XXIX. Radical Mono- and Dideoxygenations with Silanes[1]

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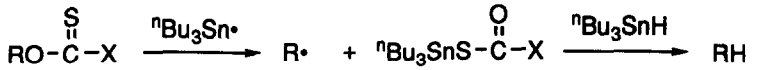
Abstract: Thionocarbonates and xanthates of primary and secondary alcohols, as well as *bis*-xanthates of *vic*-diols are readily deoxygenated to the corresponding hydrocarbons or olefins with phenylsilane, triphenylsilane, and triethylsilane in good yield.

INTRODUCTION

Deoxygenation of alcohols is an important process in organic synthesis, especially in the area of natural product chemistry. Free radical deoxygenation methodology of thiocarbonyl derivatives has been conducted on a variety of related systems (**1** : X = methylthio,[2] phenyl,[2] imidazolyl,[2] phenoxy,[3] methoxy,[4] 4-methylphenoxy,[5] pentafluorophenoxy,[6] 2,4,6-trichlorophenoxy,[6] and 4-fluorophenoxy[7]) with tri-*n*-butyltin hydride (Barton-McCombie reaction).[2] This method is compatible with sensitive functional groups and ring systems in various biomolecules. The Barton-McCombie reaction was originally developed for the deoxygenation of secondary alcohols.[2] Later, this was applied for the deoxygenation of primary,[8] or tertiary alcohols[9] and dideoxygenation of *vic*-diols.[10] Many applications of these methods have been reported in the chemical literature.[11a]



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These transformations of various natural products can bring about useful changes in the bioactivity and new properties, not found in the parent molecules (dideoxy and dideoxy-didehydro nucleosides, deoxygenated and deaminated antibiotics, etc.). This possibility makes free radical chain deoxygenations and other radical chain-based functional group transformations important and useful reactions.

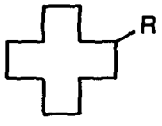
However, organotin compounds are toxic and expensive, and are difficult to remove completely from the desired products.[11b] The most often used tri-n-butyltin hydride is unstable (transport and shelf-stability is insufficient). Therefore, various attempts have been made to overcome these problems.[11b] The use of silicon hydrides seems to be attractive because of the relatively low molecular weight and elimination of toxicity and waste problems.

Various silanes, especially *tris*(trimethylsilyl)silane, have replaced tri-*n*-butyltin hydride effectively.[12] Although simple alkylsilanes have a relatively strong Si-H bond, these compounds can still be used in radical deoxygenation reactions. Jackson and coworkers reduced primary and secondary chloroformates at 140 °C in a sealed tube using $(^{n}Pr)_3SiH$-$(^{t}BuO)_2$.[13] Recently, Roberts and coworkers described the use of triethylsilane in the radical deoxygenations by polarity reversal catalysis.[14] This paper gives a full account of our work[15] on the radical deoxygenation of alcohols using phenylsilane, triphenylsilane, or triethylsilane.

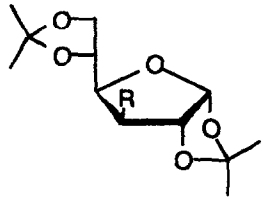
RESULTS AND DISCUSSION

Phenylsilane

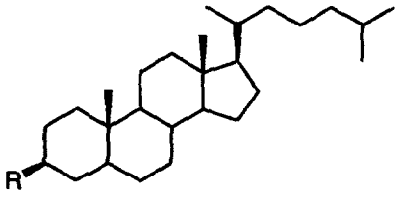
Various secondary and primary alcohols were deoxygenated by phenylsilane in refluxing toluene in the presence of AIBN (azobisisobutyronitrile) or benzoyl peroxide to furnish the corresponding deoxy products in high yield (Table 1).



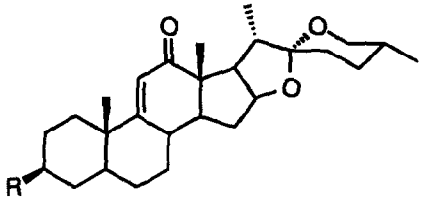
2a : R = O(C=S)SMe
2b : R = H



3a : R = O(C=S)SMe
3b : R = O(C=S)OC_6H_4-4-F
3c : R = H
3d : R = D



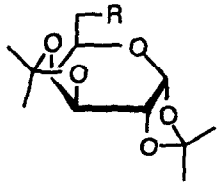
4a : R = O(C=S)OC_6H_4-4-F
4b : R = H



5a : R = O(C=S)OC_6H_4-4-F
5b : R = H

$CH_3(CH_2)_{16}CH_2$-R

6a : R = O(C=S)OC_6H_4-4-F
6b : R = H



7a : R = O(C=S)OC_6H_4-4-F
7b : R = H

Thus, when a mixture of a xanthate **2a** and phenylsilane was treated with AIBN (0.2 equiv portionwise) until the reaction was finished, the corresponding deoxy compound **2b** was obtained in quantitative yield (entry 1). Likewise the xanthate **3a** also gave a high yield. The attempted reaction without phenylsilane gave no deoxy product (entry 3).

Table 1. Deoxygenation of thionocarbonates and xanthates of various alcohols with $PhSiH_3$ in refluxing toluene.

Entry	Substrate	Product	$PhSiH_3$ (equiv)	Initiator (equiv)[a]	Time (min)	Yield (%)
1	**2a**	**2b**	5	A (0.6)	60	100[b]
2	**3a**	**3c**	2	A (2.0)	200	90[c]
3	**3a**	**3c**	0	A (2.0)	200	0
4	**3a**	**3c**	2	B (1.0)	100	96[c]
5	**3b**	**3c**	2	B (0.8)	80	100[c]
6	**3b**	**3c**	0	B (0.8)	80	26 (74)[d]
7	**4a**	**4b**	2	B (0.8)	80	87[e]
8	**5a**	**5b**	2	A (0.8)	80	85[b]
9	**6a**	**6b**	2	A (1.0)	100	100[c]
10	**7a**	**7b**	2	A (0.8)	80	88[e](95)[c]

A : AIBN B : Benzoyl peroxide

[a]AIBN or benzoyl peroxide were added portionwise in 0.2 equiv portions until the reaction was complete. [b]Analyzed by GC. [c]Analyzed by ^1H NMR.

[d] Starting material (analyzed by ^1H NMR). [e] Yield of the isolated product.

This indicates that the hydrogen that quenched the carbon radical in this process must have come from the Si-H bond in phenylsilane. Benzoyl peroxide is a more efficient radical initiator in the reaction than AIBN (entry 2, 4). The reaction of **3b** with benzoyl peroxide alone could afford the deoxy product, although it was not efficient (entry 6). In this case, the hydrogen atom originated from the solvent.

To test the possibility whether the hydrogen that quenches the carbon radical, formed by the fragmentation of the adduct radical originates from the solvent, the deoxygenation of **3a** was performed with phenylsilane and benzoyl peroxide in refluxing toluene-d_8. The relative amount of **3c** and **3d** was measured by the intensity of *m/e* 129 ($M^+ - CH_3$) and 130 (($M^+ - CH_3$) + 1) in the GC-MS. In this reaction, **3d** was obtained in 13.5% yield. This shows that there is little deuterium incorporation into the deoxy product. The

other way to prove the source of hydrogen in the reaction was using $PhSiD_3$ instead of $PhSiH_3$. Thus, the thionocarbonate **3b** was treated with $PhSiD_3$ and benzoyl peroxide in refluxing toluene. Due to the stronger silicon-deuterium bond, the reaction was not very efficient giving 50% of the deoxy product and recovery (50%) of the starting material. The amount of the deuterium labelled **3d** in this reaction was 90% (of the 50% deoxy product). This finding indicates that the hydrogen source is mainly phenylsilane.

Triphenylsilane

The bond dissociation energy of the silicon-hydrogen bond in triphenylsilane is relatively weak (~83 kcal mol^{-1}).[16] We have found that triphenylsilane can be used as a good hydrogen atom source in radical deoxygenation of alcohols. The deoxygenation of secondary and primary alcohols with triphenylsilane in the presence of benzoyl peroxide furnished the corresponding deoxy products in high yields (Table 2). The reaction of a xanthate **2a** with triphenylsilane can be initiated with triethylborane-oxygen at room temperature giving 73% of **2b** (entry 1).

Table 2. Deoxygenation of thionocarbonates of alcohols with Ph_3SiH in refluxing toluene.

Entry	Substrate	Ph_3SiH (equiv)	Benzoyl peroxide (equiv)[a]	Time (min)	RH (%)
1	**2a**	1.5	-[b]	60	73[c]
2	**3a**	2	1.6	160	95[d]
3	**3b**	2	2.6	260	89[d]
4	**5a**	3	2.2	220	83[e]
5	**7a**	2	2.2	220	88[d]

[a] Benzoyl peroxide was added portionwise (in 0.2 mol equiv portions) until the reaction was complete. [b] Et_3B was used as initiator with O_2 (both 1.6 equiv) in C_6H_6 at room temperature. [c] Analyzed by GC. [d] Analyzed by ^1H NMR. [e] Isolated product.

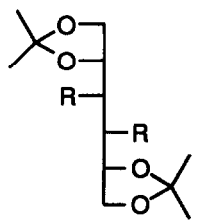
Triethylsilane

Although the silicon-hydrogen bond in triethylsilane is quite strong (90.1 kcal mol^{-1}),[17] we found that it can still be used in radical deoxygenation process. Roberts and coworkers[14] reported the use of triethylsilane in the radical deoxygenation *at elevated temperatures* by polarity reversal catalysis. The treatment of thionocarbonate **3b** with triethylsilane, *t*-$C_{12}H_{25}$-SH,[11a] and Et_3B-O_2 as initiator *at room temperature* gave no reduction product.

As expected, the deoxygenation of xanthate **2a** with triethylsilane (2 equiv) and AIBN (4 equiv) in refluxing toluene gave no sign of the deoxy product. However, the reaction of thionocarbonate **3b** with triethylsilane (10 equiv) and benzoyl peroxide (0.8 equiv) in refluxing toluene gave 45% of the deoxy product **3c** and 55% of the starting material **3b**. This shows the possibility of using triethylsilane as hydrogen atom source if the amount of the silane is increased. Thus, deoxygenation of the thionocarbonate **3b** was carried out

in refluxing triethylsilane with benzoyl peroxide to give 96% of the deoxy product **3c** (Table 3, entry 1). The same reaction was performed with only 0.2 mol equiv of benzoyl peroxide in refluxing triethylsilane for 12 hr giving 12% of the deoxy product **3b** and the recovery of 76% of the starting material **3c** (entry 2). This shows that the chain length of the reaction is very short, and that repeated addition of an initiator is important. The deoxygenation of various primary and secondary alcohols gave high yields of the deoxy products under these conditions (entry 3-5). The same method can also be used to transform *bis*-xanthates into olefins. For example, the *bis*-xanthates **8** and **10** were transformed to the corresponding olefins **9** and **11** in 82% and 100% yield, respectively (entry 6, 7).

The source of hydrogen for the deoxygenation reactions has been determined to be the triethylsilane by deuterium labeling experiments. The deoxygenation of the thionocarbonate **3b** in refluxing Et_3SiD in the presence of benzoyl peroxide gave a 68.8% yield of **3d** by GC-MS. These observations show that the hydrogen in this reaction comes mainly from the silicon-hydrogen bond in triethylsilane.



R = O(C=S)SMe

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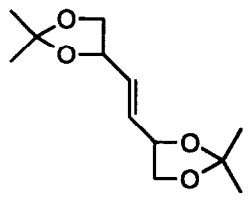

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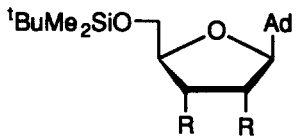
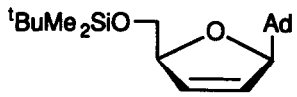


R = O(C=S)SMe

10



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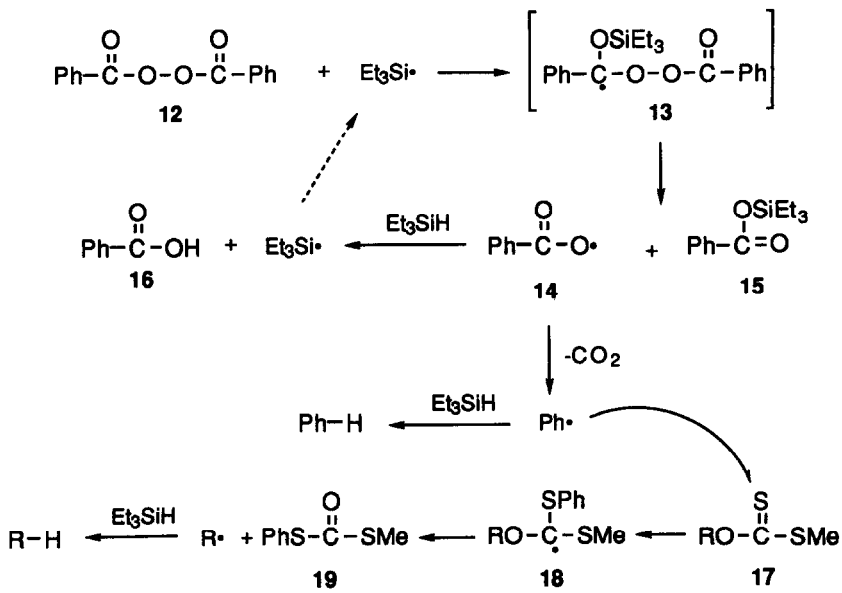
Product analysis of the deoxygenation of the thionocarbonate **3b** with triethylsilane and benzoyl peroxide showed 94% of the deoxy product **3c**, triethylsilyl benzoate **15** (65%), 4-fluorophenol (42%), and 4-fluorophenoxytriethylsilane (21%). The formation of 4-fluorophenoxy triethylsilane indicates that the radical reaction follows at least in part the usual pathway similar to the one found in the case of the radical deoxygenation with tri-*n*-butyltin hydride[18] and diphenylsilane.[7b] The presence of triethylsilyl benzoate indicates that benzoyl peroxide is not only the source of the initiator, but also a trap for the triethylsilyl radicals. This finding explains the observation that relatively large amounts of benzoyl peroxide are needed to ensure useful levels of conversion to the deoxygenated product.

Table 3. Deoxygenation of thionocarbonates of alcohols and *vic*-diols with Et_3SiH as solvent and benzoyl peroxide as initiator.

Entry	Substrate	Product	Initiator (equiv)[a]	Time (min)	Yield (%)
1	**3b**	**3c**	1.0	150	96[b]
2	**3b**	**3c**	0.2	12 hr	12 (76)[c]
3	**3a**	**3c**	1.0	150	89[b]
4	**4a**	**4b**	0.6	90	93[d]
5	**7a**	**7b**	0.8	120	96[b]
6	**8**	**9**	0.8	120	82[d]
7	**10**	**11**	0.6	90	100[b]

[a] Benzoyl peroxide was added portionwise in 0.2 equiv portions until the reaction was complete. [b]Analyzed by ^{1}H NMR. [c]Starting material (analyzed by ^{1}H NMR). [d] Yield of the isolated product.



Scheme 1

Benzoyl peroxide with boiling triethylsilane gave benzene (30%), triethylsilyl benzoate **15** (31%), and benzoic acid **16** (43%) (determined by ^{1}H NMR) in accordance with Scheme 1. A triethylsilyl radical reacts with benzoyl peroxide **12** to give radical intermediate **13**, which then fragments to a benzoyloxy radical **14** and triethylsilyl benzoate **15**. This radical can abstract a hydrogen from triethylsilane, or decompose to give a phenyl radical and carbon dioxide. In the presence of a xanthate **17**, reaction of the phenyl radical with the thiocarbonyl group of **17** can also be expected as a competing minor pathway for the deoxygenation. Indeed, the carbonate **19** was observed (6%) in the deoxygenation of **3a**.

The reduction of thionocarbonate **3b** was attempted with commercially available silanes, *tris*(dimethylamino)silane and triethoxysilane, initiated with Et_3B-O_2 or AIBN. However, no reaction was observed. On the other hand, when triethoxysilane was used as a solvent in the deoxygenation of xanthate **3a** with benzoyl peroxide, a yield 70% of the deoxy product **3c** was obtained.

Comparison of Silanes

Several sets of competitive reactions were performed in the deoxygenation of thionocarbonate **3b** with silanes and benzoyl peroxide. These results gave the relative reactivity among silanes. Two reagents were chosen for reaction. The decrease of Si-H bond in silanes was measured by ^{1}H NMR. Between phenylsilane and diphenylsilane, phenylsilane is slightly more reactive than diphenylsilane (Table 4, entry 1). Diphenylsilane is twice as reactive as triphenylsilane (entry 2). A set of competitive reaction between phenylsilane and triphenylsilane shows that phenylsilane is twice as reactive as triphenylsilane (entry 3). However, after normalization based on the number of hydrogen atoms on the silicon, the three silanes have very similar reactivity.

Table 4. Comparative study of various silanes and tri-*n*-butyltin hydride.[a]

	Hydride consumption (%)					
Entry	Ph_3SiH	Ph_2SiH_2	$PhSiH_3$	Et_3SiH	$(Me_3Si)_3SiH$	$^nBu_3SnH$
1		44 (22)	52 (17)			
2	32	65 (33)				
3	31		65 (22)			
4		100		0		
5			0		100	
6			0			100
7					0	100

[a] The decrease of the amount of silanes was analyzed by ^{1}H NMR in the reaction with silanes and benzoyl peroxide in refluxing toluene-d_8. (Values in parenthesis represent the normalized value based on the number of Si-H bonds).

A set of competitive reactions between diphenylsilane and triethylsilane showed 100% consumption of diphenylsilane and the recovery (100%) of triethylsilane (entry 4). This indicates that diphenylsilane is much more reactive than triethylsilane. As expected, the competitive reactions between phenylsilane and *tris*(trimethylsilyl)silane or tri-*n*-butyltin hydride resulted in the 100% of recovery of phenylsilane and 100% consumption of *tris*(trimethylsilyl)silane or tri-*n*-butyltin hydride (entry 5, 6). In the competition between *tris*(trimethylsilyl)silane and tri-*n*-butyltin hydride, only tri-*n*-butyltin hydride was consumed (entry 7). Based on the data of the competitive reactions above, the order of reactivity of silanes and tri-*n*-butyltin hydride is as shown below:

$$^{n}Bu_3SnH > (Me_3Si)_3SiH > PhSiH_3 \approx Ph_2SiH_2 \approx Ph_3SiH > Et_3SiH$$

CONCLUSIONS

We have demonstrated that phenylsilane, triphenylsilane and triethylsilane are good hydrogen sources in the radical deoxygenation of primary and secondary alcohols and *vic*-diols. Although the silicon-hydrogen bonds in these silanes are quite strong compared to tri-*n*-butyltin hydride or *tris*(trimethylsilyl)silane, this problem can be solved by carefully controlling the radical initiation.

From the practical point of view, their low boiling points (phenylsilane, triethylsilane) make it easy to work-up the reaction and isolate the deoxygenated product. It is possible to recover and recycle the excess of these silanes by distillation. Compared to tri-*n*-butyltin hydride or *tris*(trimethylsilyl)silane, mole per mole, they are inexpensive. They are less toxic than tin hydrides and it is much easier to isolate the products after the radical reaction. Therefore, the use of these silanes results in improvements in free-radical deoxygenation reaction methodology.

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. ^{1}H and ^{13}C NMR spectra were determined for solutions in deuterochloroform (unless specified otherwise) with TMS internal reference on a Varian Gemini 200, or a Varian XL 200E 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.

General Procedure for Deoxygenation of Alcohols with Phenylsilane. To a solution of a thionocarbonate (0.4 mmol) in dry toluene (3 mL) was added phenylsilane (100 μL, 0.8 mmol) under argon. Then the solution was heated to reflux and treated with 150 μL portions of a solution of benzoyl peroxide in toluene (387 mg benzoyl peroxide was dissolved in 3 mL dry toluene) at 20 min intervals. The reaction was monitored by TLC. When the reaction was complete the solvent was evaporated in vacuum and the reaction mixture was analyzed by GC or NMR using internal standard, or the product was isolated by column chromatography on silica gel.

General Procedure for Deoxygenation of Alcohols with Triphenylsilane. To a solution of a thionocarbonate (0.4 mmol) in dry toluene (3 mL) was added triphenylsilane (0.2 g, 0.8 mmol) under argon. Then the solution was heated to reflux and treated with 150 μL portions of a solution of benzoyl peroxide in toluene (387 mg benzoyl peroxide was dissolved in 3 mL dry toluene) at 20 min intervals. The reaction was monitored by TLC. When the reaction was complete, the solvent was evaporated in vacuum and the reaction mixture was analyzed by GC or NMR using an internal standard, or the product was isolated and purified by column chromatography on silica gel.

Deoxygenation of 2a with Triphenylsilane, Triethylborane and Oxygen. To a mixture of **2a** (135 mg, 0.40 mmol), triphenylsilane (115 mg, 0.44 mmol) and triethylborane (440 μL, 0.44 mmol, 1 M solution in hexane) in dry benzene (5 mL) under argon was injected dry air (20 mL) for 20 min by a syringe pump and then the reaction was stirred for an additional 10 min. After evaporation of the solvent the residue was analyzed by GC using naphthalene as an internal standard.

General Procedure for Deoxygenation of Alcohols and Olefination of *vic*-Diols with Triethylsilane. To a thionocarbonate (0.4 mmol) was added triethylsilane (3 mL, 18.8 mmol) under argon. Then the solution was heated to reflux and then treated with benzoyl peroxide (19.4 mg, 0.08 mmol) at 30 min intervals. The reaction was monitored by TLC. When the reaction was complete the solvent was evaporated in vacuum and the reaction mixture was analyzed by GC or NMR using an internal standard, or the product was isolated by column chromatography on silica gel.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(4-fluorophenoxy)thionocarbonyl-α-D-glucofuranose (3b). To a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2.6 g, 10 mmol), *N*-hydroxysuccinimide (115 mg, 1 mmol), and dry pyridine (2.4 mL, 30 mmol) in THF (50 mL) was added 4-fluorophenyl chlorothionoformate (3.8 g, 20 mmol, 2 equiv) dropwise at room temperature under argon. The solution was stirred for an additional 2 h. The organic layer was 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 hexane/CH_2Cl_2 (7:3) to afford 3.1 g (76%) of **3b**: mp 82-83 °C (EtOH/H_2O); $[\alpha]^{27}_D$ = -33.0° (c 1, $CHCl_3$); IR (nujol) 2929, 2859, 1497, 1459, 1379, 1261, 1209,

1077, 1017, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.36 (s, 3 H), 1.45 (s, 3 H), 1.55 (s, 3 H), 4.02-4.20 (m, 2 H), 4.25-4.40 (m, 2 H), 4.77 (d, J = 4 Hz, 1 H), 5.62 (s, 1 H), 5.97 (d, J = 4 Hz, 1 H), 7.00-7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 25.3, 26.2, 26.6, 26.9, 67.1, 72.2, 79.6, 82.8, 85.2, 105.0, 109.5, 112.5, 116.3 (d, J_{C-F} = 23.6 Hz, 2 C), 123.3 (d, J_{C-F} = 8.6 Hz, 2 C), 149.0 (d, J_{C-F} = 3.0 Hz), 160.7 (d, J_{C-F} = 245 Hz), 193.7; MS *m/e* (relative intensity) 414 (M^+, 0.2), 303 (5), 185 (20), 127 (20), 101 (100), 95 (18), 59 (19), 43 (75), 28 (48); HRMS calcd. for $C_{19}H_{23}FO_7S$ 414.1148, found 414.1140.

***O*-Cholestan-3β–yl-*O'*-(4-fluorophenyl)thionocarbonate (4a).** To a solution of 3β-cholestanol (5.0 g, 12.9 mmol), *N*-hydroxysuccinimide (0.15 g, 1.3 mmol) and dry pyridine (3.1 mL, 35.6 mmol) was added 4-fluorophenyl chlorothionoformate (6.3 g, 33.4 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 evaporation, the crude product was purified by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (8 : 2) to afford 6.0 g (86%) of **4a**: mp 132-133 °C ($MeOH/CH_2Cl_2$); $[\alpha]^{26}_D$ = +1.3° (c 1, $CHCl_3$); IR (nujol) 2928, 2857, 1497, 1462, 1375, 1295, 1180, 1003, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65 (s, 3 H), 0.80-2.12 (m, 43 H), 5.08-5.25 (m, 1 H), 7.02-7.10 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 12.2, 18.7, 21.3, 22.6, 22.9, 23.9, 24.2, 26.7, 28.0, 28.3, 28.6, 32.0, 33.1, 35.5, 35.8, 36.2, 36.6, 39.5, 40.0, 42.6, 44.6, 54.2, 56.2, 56.4, 84.6, 116.2 (d, J_{C-F} = 23.6 Hz, 2 C), 123.6 (d, J_{C-F} = 8.55 Hz, 2 C), 149.1 (d, J_{C-F} = 2.85 Hz), 160.6 (d, J_{C-F} = 243.8 Hz), 194.4; MS *m/e* (relative intensity) 370 (M^+, 45), 355 (15), 316 (19), 257 (15), 218 (11), 217 (22), 214 (23), 203 (12), 161 (14), 149 (15), 147 (15), 135 (12), 121 (14), 119 (11), 112 (100), 109 (20), 95 (31) 81 (34), 60 (56), 43 (35), 28 (70). Anal. Calcd for $C_{34}H_{51}FO_2S$: C, 75.23; H, 9.47; S, 5.91. Found: C, 75.33; H, 9.44; S, 5.97.

Cholestane (4b). Isolated by column chromatography on silica gel (eluent; hexane), this gave a mp 78-79 °C (lit.[19] 78-80 °C); $[\alpha]^{26}_D$ = +25.0° (c 1, $CHCl_3$) (lit.[19] +25.8°); ^1H NMR ($CDCl_3$) δ 0.46-2.06 (m, 48 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 12.2, 18.7, 20.8, 22.2, 22.6, 22.8, 23.9, 24.2, 26.9, 28.0, 29.1, 29.1, 32.2, 35.5, 35.8, 36.2, 36.2, 36.7, 39.5, 40.1, 42.6, 47.0, 54.8, 56.3, 56.6; MS *m/e* (relative intensity) 372 (M^+, 30), 371(M^+ - 1, 98), 355 (24), 316 (17), 261 (32), 215 (69), 149 (44), 135 (40), 121 (45), 109 (64), 95 (100), 81 (98), 67 (60), 55 (77), 43 (66).

***O*-(Δ⁹-Hecogenin-3β-yl)-*O'*-(4-fluorophenyl)thionocarbonate (5a).** To a solution of Δ⁹-hecogenin (3 g, 7 mmol), *N*-hydroxysuccinimide (0.7 g, 0.08 mmol) and dry pyridine (2.8 mL, 35 mmol) in benzene (30 mL) was added 4-fluorophenyl chlorothionoformate (4 g, 21 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. The precipitate was removed by filtration. After evaporation of the solvent the crude product was purified by column chromatography on silica gel eluting with $CHCl_3$ to afford 3.3 g (80%) of **5a**: mp 210-212 °C ($MeOH/CH_2Cl_2$); $[\alpha]^{25}_D$ = -6.4° (c 1.1, $CHCl_3$); IR (nujol) 2935, 2859, 1587, 1459, 1375, 1268, 1201, 1160, 1062, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77-2.60 (m, 34 H), 3.29-3.55 (m, 2 H), 4.38 (q, J = 8.18 Hz, 1 H), 5.05-5.25 (m, 1 H), 5.69 (d, J = 1.6 Hz, 1 H), 7.02-7.12

(m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 15.0, 17.1, 18.4, 26.5, 27.5, 28.8, 30.2, 31.3, 31.5, 32.3, 32.8, 34.4, 36.8, 39.2, 42.3, 42.5, 51.0, 52.3, 53.7, 66.9, 79.7, 83.1, 109.4, 116.2 (d, $J_{C\text{-}F}$ = 23.6 Hz, 2 C), 120.2, 123.5 (d, $J_{C\text{-}F}$ = 8.6 Hz, 2 C), 149.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 160.6 (d, $J_{C\text{-}F}$ = 244 Hz) 170.1, 194.3, 204.7; MS *m/e* (relative intensity) 583 (M^+ + 1, 3), 582 (M^+, 7), 410 (100), 338 (100), 297 (100), 281 (100), 244 (100), 229 (100), 188 (100), 139 (100); HRMS calcd. for $C_{34}H_{43}FO_5S$ 582.2815, found 582.2839.

3-Deoxy-Δ^9-hecogenin (5b). Isolated by column chromatography on silica gel (eluent; hexane : EtOAc, 9 : 1), mp 177-179 °C; $[\alpha]^{26}_D$ = -6° (c 0.5, $CHCl_3$); IR (nujol) 2928, 1664, 1587, 1459, 1372, 1184, 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.77-2.60 (m, 3 H), 3.28-3.55 (m, 2 H), 4.38 (q, *J* = 8.68, 1 H), 5.69 (d, *J* = 1.82 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 13.8, 15.2, 17.3, 18.2, 22.2, 26.5, 28.2, 29.2, 29.3, 30.6, 31.9, 32.0, 32.7, 36.6, 36.9, 39.9, 43.2, 44.8, 51.3, 52.8, 54.8, 67.1, 80.2, 109.4, 120.2, 170.6, 203.5; MS *m/e* (relative intensity) 412 (M^+, 8), 384 (5), 340 (10), 298 (32), 274 (20), 231 (17), 190 (18), 139 (100), 121 (20); HRMS calcd. for $C_{27}H_{40}O_3$ 412.2977, found 412.2989.

Di-*O*-isopropylidene-α-D-fucose (7b). Isolated by column chromatography on silica gel (eluent; hexane: EtOAc, 8 : 2) giving 155 mg (88%) of **7b**: (oil), $[\alpha]^{27}_D$ = -60.0° (c 2, $CHCl_3$) (lit.[20] -52°); IR ($CDCl_3$) 2988, 1379, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, *J* = 6 Hz, 3 H), 1.33 (s, 3 H), 1.36 (s, 3 H), 1.47 (s, 3 H), 1.53 (s, 3 H), 3.93 (dt, *J* = 2, 6 Hz , 1 H), 4.09 (dd, *J* = 2, 8 Hz, 1 H), 4.30 (dd, *J* = 2, 6 Hz, 1 H), 4.60 (dd, *J* = 2, 8 Hz, 1 H), 5.53 (d, *J* = 6Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.8, 24.3, 24.8, 26.0 (2 C), 63.4, 70.3, 70.9, 73.4, 96.5, 108.2, 108.8; MS *m/e* (relative intensity) 229 (31), 113 (28), 100 (43), 83 (38), 59 (36), 43 (100).

1,2:5,6-Di-*O*-isopropylidene-hex-3-(*E*)-ene-D-*threo*-1,2:5,6-tetraol (9). After column chromatography on silica gel (eluent; hexane : EtOAc, 7 : 3), mp 80-81 °C (lit.[11b] 80-81 °C); $[\alpha]^{27}_D$ = +57.7° (c 0.45, $CHCl_3$) (lit.[21] +56.7°); IR ($CHCl_3$) 2930, 1456, 1375, 1059 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 6 H), 1 43 (s, 6 H), 3.59 (dd, *J* = 8, 8 Hz, 2 H), 4.10 (dd, *J* = 8, 8 Hz, 2 H), 4.47-4.53 (m, 2 H), 5.80 (dd, *J* = 1.9, 3.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.3 (2 C), 27.1 (2 C), 69.8 (2 C), 76.5 (2 C), 109.9 (2 C), 131.3 (2 C); MS *m/e* (relative intensity) 228 (M^+, 0.3), 213 (100), 170 (34), 95 (71), 72 (100), 43 (100).

Synthesis of triethylsilyl benzoate (15). To a solution of benzoic acid (2.6 g, 20.9 mmol) and pyridine (2.4 mL, 29.8 mmol) in benzene (30 mL) under argon was added triethylchlorosilane (4.6 mL, 27.1 mmol) dropwise. The reaction mixture was then stirred for 10 h. After filtration the solvent was evaporated. The residue was distilled under reduced pressure to give 3.5 g (72 %) of **15**:[21] bp 94 °C/0.6 mmHg; IR ($CDCl_3$) 2961, 2880, 1687, 1453, 1317, 1294, 1119, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70-1.05 (m, 15 H), 7.30-8.05 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 4.6 (3 C), 6.6 (3 C), 128.3 (2 C), 130.1 (2 C), 131.4, 132.9, 166.6; MS *m/e* (relative intensity) 236 (M^+, 0.1), 135 (100), 105 (100), 77 (100).

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