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The Invention of Radical Reactions. Part XXI. Simple Methods for the Radical Deoxygenation of Primary Alcohols[1].

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Abstract: *Novel radical-chain deoxygenations of primary alcohols are described. The alcohols are acylated with the reagents pentafluorophenyl chlorothionoformate, 2,4,6-trichlorophenyl chlorothionoformate and 4-fluorophenyl chlorothionoformate and the intermediate thionocarbonates are deoxygenated with tributyltin hydride, triphenylsilane, diphenylsilane or phenylsilane in high-yielding reactions.*

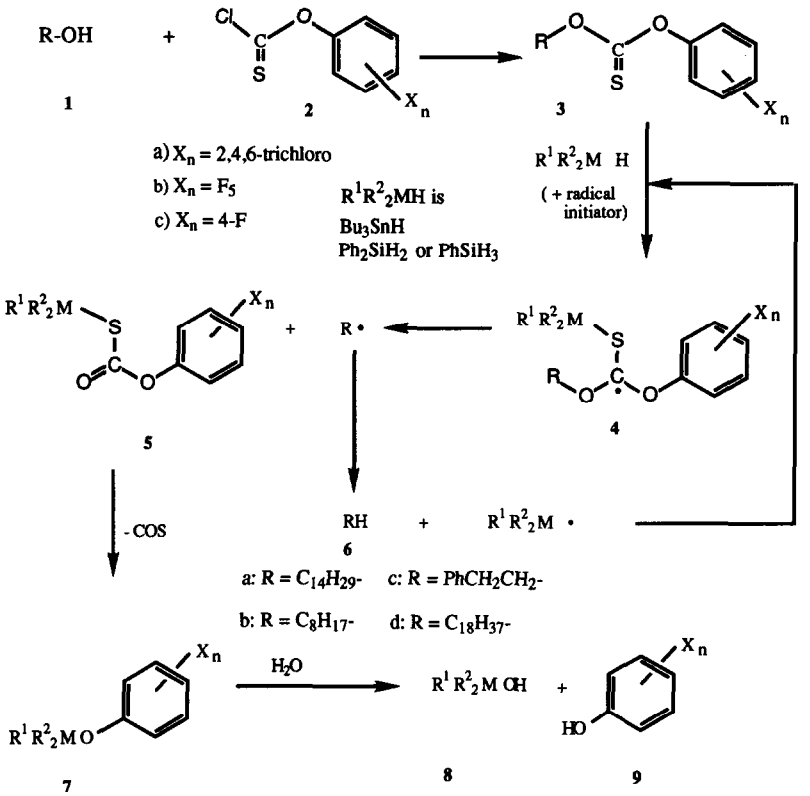
Introduction

The radical-induced deoxygenation of alcohols is an important reaction in modern synthetic chemistry[2]. The original method of Barton and McCombie for secondary alcohols[3] has later been extended to primary[4] and tertiary alcohols[5]. We have shown recently, that secondary alcohols can easily be deoxygenated in a one-pot procedure by using pentafluorophenyl chlorothionoformate or the corresponding 2,4,6-trichlorophenyl derivative[6]. More recently we have extended this method by using 4-fluorophenyl chlorothionoformate as the acylating agent and diphenylsilane as the hydrogen source and chain carrier[7]. The ease of the deoxygenation of pentafluorophenoxy thiocarbonyl and 2,4,6-trichlorophenoxy thiocarbonyl derivatives of secondary alcohols prompted us to study the use of these and related reagents for the radical-induced deoxygenation of primary alcohols. We have also extended our systematic studies on radical chain carriers and hydrogen atom sources to other silanes[8,9].

Results and discussion

Acylation of the primary alcohols (**1**, Scheme 1, Table 1) was carried out in benzene or toluene with or without N-hydroxysuccinimide as a catalyst. Dry pyridine was used as acid scavenger. The intermediate thionocarbonates **3** can either be isolated or transformed directly to the corresponding hydrocarbons. Deoxygenation occurs easily in boiling benzene or toluene and the hydrocarbons are obtained in 80-100 % yield.

Thus, the model tetradecanol **1a** was acylated in toluene in the presence of dry pyridine and N-hydroxysuccinimide with pentafluorophenyl chlorothionoformate **2a**. The acylation was complete in 5 minutes at room temperature. The pyridinium chloride was then removed by filtration and the thionocarbonate (**3a**, R = $C_{14}H_{29}$) deoxygenated with tributyltin hydride/azobisisobutyronitrile at 110°C under nitrogen or argon.



Scheme 1

The deoxygenation step is also very fast (5 min. in the case of **3a**). There was no spontaneous decomposition. Without the initiator no thermolysis or photolysis (tungsten light) of the intermediate thionocarbonates was seen. We found that the deoxygenation took place also in boiling benzene. Thus, using pentafluorophenyl thionocarbonate, the one-pot procedure gave rise to the formation of 90% tetradecane in boiling benzene (20 min.). In contrast, the reported yield of the interesting tributyltin hydride - Et_3B deoxygenation[10] of the tetradecanol methyl xanthate was 18% (at room temperature). The data in Table 1 show that we have developed fast, simple, high-yielding procedures for the radical chain deoxygenation of primary alcohols.

It is assumable that the mechanism of this deoxygenation is similar in the case of tributyltin hydride and various silanes. Thus, fragmentation of the adduct radical **4** (Scheme 1) gives the carbon radical R• and

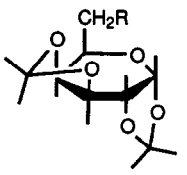
thionocarbonate **5**. The carbon radical then reacts with the hydrogen atom donor $R^1R^2{}_2MH$ furnishing the hydrocarbon **6** and the chain carrier radical $R^1R^2{}_2M\cdot$ whereas **5** is unstable and decomposes to the phenolate **7** and carbonyl sulfide. Subsequent hydrolysis (upon work-up or standing) gives rise to the formation of hydroxy compound **8** and the corresponding substituted phenol **9**. When the hydrogen atom source is a silane, hydrolysis takes place easily and the phenol **9** can be recycled to make the chlorothionocarbonate **2** with thiophosgene. The end-products make the isolation of the hydrocarbon **6** in the reaction with silanes easier than in the case of the use of tributyltin hydride.

Table 1. Deoxygenation of Primary Alcohols

Compound No.	R	Acylation Time (min.)	Yield (%)	Solvent	Reagent[b]	Deoxygenation Time (min.)	Yield (%)	Solvent	Reagent[b]	Overall yield
1a	$CH_3(CH_2)_{12}CH_2$-	240	89	PhMe	B	-	-	-	-	-
1a		5	-	PhMe	B	5	95	PhMe	D	95[c,d]
1a		10	-	PhH	B	20	90	PhH	D	90[c,d,e]
1b	$CH_3(CH_2)_6CH_2$-	10	-	PhMe	B	15	97	PhMe	D	97[c,d]
1c	$PhCH_2CH_2$-	330	97	PhMe	A	10	100	PhMe	D	97[c,d]
1c		120	79	PhH	C	30	80	PhH	E	63[c]
1d	$CH_3(CH_2)_{16}CH_2$-	18	97	PhMe	B	12	86[f]	PhMe	D	83
1d		120	89.5	PhH	C	30	87	PhH	E	78[c]

a: preparative yield, b: A: 2,4,6-trichlorophenyl chlorothionoformate, B: pentafluorophenyl chlorothionoformate, C: 4-fluorophenyl chlorothionoformate, D: tributyltin hydride, E: Diphenylsilane. c: overall yield, measured by glc, d: one-pot procedure, e: 10% alcohol was also measured, f: 5 eq. tributyltin hydride was used in this experiment.

The use of these reagents has also been demonstrated in the deoxygenation of carbohydrates. Diisopropylidene galactose **10a** (Aldrich) was acylated with 2,4,6-trichlorophenyl chlorothionoformate in benzene in the presence of N-hydroxysuccinimide as acylation catalyst. The thionocarbonate derivative **10b** was isolated by column chromatography (90%) and reduced in boiling toluene with tributyltin hydride/azobisisobutyronitrile (80 min.). The product **10d** was isolated by column chromatography on silica and proved to be identical with an authentic sample prepared independently (91%)[11].



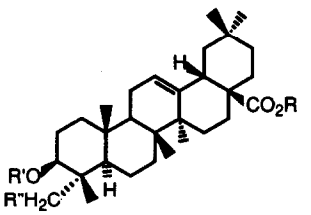
10a R = -OH

10b R = -OC=S(O-2,4,6-Cl_3Ph)

10c R = -OC=S(O-4-F-Ph)

10d R = -H

The novel reagent 4-fluorophenyl chlorothionoformate **2c** has also been used to transform the primary alcohols **1c** and **1d** to their thionocarbonates **3b** and **3d**, respectively. These compounds have been deoxygenated by using diphenylsilane as hydrogen atom donor and radical chain carrier[7]. The novel thionocarbonate **10c** was easily deoxygenated with phenylsilane giving **10d** in 88% preparative yield. In order to demonstrate the use of silanes in the most difficult case of the deoxygenation of a primary neopentyl alcohol, we have chosen hederagenin **11a**. Thus **11a** was transformed to its methyl ester **11b** with diazomethane and then the known selective method[4] was employed to make the xanthate **11c** only from the primary alcohol in 78.5% yield. This compound was then deoxygenated with diphenylsilane + benzoyl peroxide in boiling toluene under argon to give 48.5% of **11d**[13] after chromatography on a silica column. Phenylsilane gave similar results (55% yield). The relatively moderate yield may have been related to the presence of the free secondary hydroxyl group. To test this **11c** was acetylated (Ac_2O/Pyridine, 85% isolated) to give **11e**. This compound was then deoxygenated with phenylsilane + benzoyl peroxide in boiling toluene to give **11f**[14] but the yield was not much better (56% isolated on silica column). Therefore we decided to increase the temperature. When heated in boiling o-xylene at 150°C under argon with diphenylsilane and benzoyl peroxide **11e** gave the deoxygenated product **11f** in a better yield (75% isolated). Deoxygenation of the benzoate **11g** gave **11h** in an even higher yield (91% with Ph_2SiH_2 and 87% with Ph_3SiH). However, the deoxygenation with $PhSiH_3$ was less satisfactory (40%).



11a: R = R' = H, R" = OH

11b: R = Me, R' = H, R" = OH

11c: R = Me, R' = H, R" = OCS_2Me

11d: R = Me, R' = H, R" = H

11e: R = Me, R' = Ac, R" = OCS_2Me

11f: R = Me, R' = Ac, R" = H

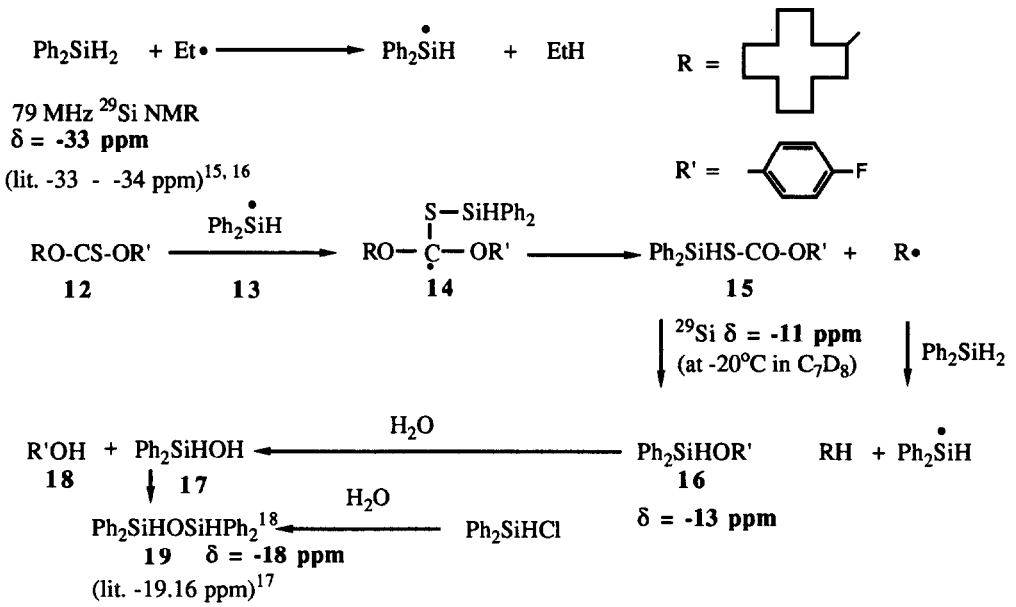
11g: R = Me, R' = PhC=O, R" = OCS_2Me

11h: R = Me, R' = PhC=O, R" = H

^{29}Si NMR studies revealed that the deoxygenation reaction with diphenylsilane follows the same pathway (Scheme 2) found earlier for the tributyltin hydride reaction[6c]. For these ^{29}Si NMR studies a secondary alcohol thionocarbonate (cyclododecanol 4-fluorophenyl thionocarbonate[12]) was used as a model compound but there is no mechanistic difference in the radical deoxygenation of thiocarbonyl derivatives of various alcohols.

The low temperature ^{29}Si NMR experiment was possible because the triethylborane/air system can be used to generate ethyl radicals at low temperatures[10, 6c]. We assumed that intermediate **15** would be stable enough at -30 or -20°C to enable us to detect it in the low temperature ^{29}Si NMR experiment before it loses COS and gives **16**. Indeed, the build-up of **15** can be observed in the ^{29}Si NMR spectrum at -20°C (δ_{Si} = -11 ppm). Allowing

the reaction mixture to warm up to 20°C this compound (**15**) decomposes to **16** (δ_{Si} = -13 ppm). Without cooling the reaction mixture before and during the reaction, the ^{29}Si NMR peak related to **15** (at δ_{Si} = -11 ppm) cannot be observed. In the latter case diphenylsilane is transformed to **16** (obviously *via* the unstable **15**). Upon hydrolysis **16** gives **19** as an endproduct (δ_{Si} = -18 ppm). These findings corroborate the initial assumption that the silicon pathway is very similar to the tin pathway[6c] in the radical deoxygenation of alcohols.



Scheme 2

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. UV-VIS spectra were recorded on a Beckman DU-7 spectrometer. Specific rotations were determined on a Jasco Model DIP-360 digital polarimeter. ^{1}H, ^{13}C and ^{29}Si NMR spectra were determined for solutions in deuterochloroform (unless specified otherwise) with TMS internal reference on Varian Gemini 200, Varian XL 200E, Varian XL 200 or Varian XL 400 instruments. 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 EI or FAB mode. FAB spectra

were obtained neat or in glycerol matrix. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Solvents were used either as purchased or dried and purified by standard methodology under dry, pure argon. Other reference compounds and starting materials were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

2,4,6-Trichlorophenyl chlorothionoformate **2a.**

Thiophosgene (11.5 g, 7.62 ml, 0.1 mol) was dissolved in dry dichloromethane (60 ml) in a 250 ml round bottom flask equipped with a thermometer, reflux condenser and addition funnel and cooled in an ice bath to 0°C. 2,4,6-Trichlorophenol (19.75 g, 0.1 mol) was dissolved in 20% NaOH solution (22.5 ml), diluted to 90 ml with water and transferred into the addition funnel. The cold solution of the thiophosgene was then stirred with a magnetic stirrer and treated dropwise with the sodium trichlorophenolate solution. After the addition the reaction mixture was stirred for a further 1 hr at 0°C and separated. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuum. Crystals were separated from the brown oil by filtration. The crystalline compound is a small amount of the by-product, bis(2,4,6-trichlorophenyl) thionocarbonate (mp: 166-8°C). The oil (21-24 g, 75-87%) is sufficiently pure for the next step. For optimal yields it is essential that the starting phenol be very pure. Commercial 2,4,6-trichlorophenol (Aldrich, 98%) was recrystallized prior to use. Fractional distillation (72°C/0.12 mm) gave the pure **2a** (78%). IR (neat) 1564, 1445, 1235, 1138, 1020, 862, 820 cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 7.40(s, 2Ar-H); ^{13}C NMR ($CDCl_3$, ppm, δ, TMS): 129 (2C, C3; C5), 129.1 (2C, C2; C6), 133.4 (1C, C4), 145.7 (1C, C1), 191.9 (C=S).

The bis(2,4,6-trichlorophenyl)thionocarbonate is a byproduct: IR: (CH_2Cl_2) 1571, 1447, 1387, 1284, 1181, 1127, 858, 820, 752 cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 7.43 (s, 4Ar-H); ^{13}C NMR ($CDCl_3$, ppm, δ, TMS): 129.0 (4C, C3; C5; C3'; C5'), 129.7 (4C, C2; C6; C2'; C6'), 133.1 (2C, C4; C4'), 144.6 (2C, C1, C1'), 187.1 (C=S); (Found: C, 35.79; H, 0.95; Cl, 48.61; S, 7.36. Calcd for $C_{13}H_4Cl_6O_2S$: C, 35.73; H, 0.92; Cl, 48.69; S, 7.34%).

Pentafluorophenyl chlorothionoformate **2b.**

Thiophosgene (2.3 g, 1.53 ml, 20 mmol) was dissolved in dry chloroform (12 ml) in a 50 ml 3-neck round bottom flask equipped with a thermometer, reflux condenser and addition funnel and cooled in an ice bath to 0°C. Pentafluorophenol (3.6812 g, 20 mmol) was then dissolved in aqueous sodium hydroxide solution (16.1 ml 5% solution) and transferred into the addition funnel. The cold solution of the thiophosgene was then stirred with a magnetic stirrer and treated dropwise with the sodium pentafluorophenolate solution. After the addition the reaction mixture was stirred for a further 1 h at 0°C and separated. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuum. The oily chlorothionoformate (4.1-4.7 g, 78-90%) is sufficiently pure for the acylation step. Rf: 0.74 (CH_2Cl_2 : Et_2O 10:1), IR (CH_2Cl_2): 1522, 1211, 1039, 1002, 784 cm^{-1}; ^1H NMR: no protons; ^{13}C NMR: 129, 136, 138, 141.5, 144 (C-F multiplets), 154 (C-O), 183.5 (s, 1C, C=S); m/e 262 (M^+,^{35}Cl, 2.1%), 227 (M^+- Cl, 19.2%). When the reaction was carried out at room temperature (54 mmol scale), the title product was obtained in 97% (>95% pure by NMR).

4-fluorophenyl chlorothionoformate **2c.**

The 4-fluorophenol (10g, 89.2 mmol) was dissolved in a concentrated aqueous solution of NaOH or KOH and then diluted with water (90 ml). This solution was added dropwise to a stirred solution of thiophosgene (7.5 ml, 98.1 mmol) in chloroform (75 ml) at room temperature (1 hr). The reaction mixture was stirred for further 3 hr. The organic layer was then removed and washed first with saturated $NaHCO_3$ solution, two times with water and finally brine. The solution was dried over anhydrous $MgSO_4$ and the solvent and unreacted thiophosgene were evaporated together at reduced pressure (40°C/aspirator). The thionocarbonate byproduct was precipitated with hexanes. Filtration and evaporation provided the product in high yield. Isolated yield 83.5%, (74 mmol; > 95% purity by ^1H NMR). Bp 58°C/0.58 mm; IR (neat film): 1490, 1217, 1161, 1009, 831 cm^{-1}; ^1H NMR: ($CDCl_3$, ppm, δ, TMS) 7.10 (s, 2H, H2; H6), 7.11 (d, 2H, H3; H5, $^3J_{H-F}$ = 6.6 Hz); ^{13}C NMR: 116.6 (d, 2C, C3; C5, $^2J_{C-F}$ = 23.9 Hz), 122.7 (d, 2C, C2; C6, $^3J_{C-F}$ = 9.0 Hz), 150.3 (d, 1C, C1, $^4J_{C-F}$ = 3.0 Hz), 161.0 (d, 1C, C4, $^1J_{C-F}$ = 247.1 Hz), 185.5 (s, 1C, C=S); m/e 192 (M^+, ^{37}Cl), 190 (M^+, ^{35}Cl), 155 (M^+-Cl), 127, 95, 79. High resolution: found: 189.9651. Calcd for C_7H_4ClFOS: 189.9655.

Bis(4-fluorophenyl)thionocarbonate.

Isolated from the crude **2c**; white crystalline solid insoluble in hexanes. Crystallization (twice from CH_2Cl_2/hexanes) gave the pure compound (5.2%) mp 167.0°C; ^1H NMR: 7.13 (d, 2H, H3; H5, $^3J_{H-F}$ = 4.1 Hz), 7.16 (d, 2H, H2; H4, $^4J_{H-F}$ = 1.6 Hz); ^{13}C NMR: 116.4 (d, 2C, C3; C5, $^2J_{C-F}$ = 23.9 Hz), 123.3 (d, 2C, C2; C6, $^3J_{C-F}$ = 8.5 Hz), 149.4 (s, 1C, C1), 160.8 (d, 1C, C4, ^1J = 246.1), 194.9 (s, 1C, C=S).

General Procedure for One Pot Deoxygenation of Primary Alcohols

The alcohol (0.1 mmol), the internal standard, N-hydroxysuccinimide (0.0023 g, 0.02 mmol) and the dry solvent (0.5 ml) were placed in a two-neck flask equipped with a magnetic stirrer bar. The flask was sealed with rubber septa, then dry pyridine (21 µl, 0.26 mmol) and pentafluorophenyl chlorothionoformate (25 µl, 0.15 mmol) were injected, in sequence. The reaction mixture was stirred at room temperature, the precipitate formed was removed by reduced pressure filtration (caution was taken to prevent condensation of water vapor) and the reaction flask was washed twice with the dry solvent (0.2 ml, 0.1 ml). The filtrate was transferred to another flask fitted with a condenser wich was attached to an oil bubbler. Dry nitrogen was passed through the system to give an inert atmosphere, then the solution was brought to boil, followed by the addition of a solution of AIBN (1.6 mg, 0.01 mmol), tributyltin hydride (80 µl, 0.3 mmol) in the dry solvent (0.1 ml). Aliquots were removed every five minutes and the hydrocarbon formation measured by glc (Table 1).

The Acylation of β-Phenylethanol **1c** with 2,4,6-Trichlorophenyl chlorothionoformate **2a.**

β-Phenylethanol **1c** (0.6138 g, 5 mmol), dry pyridine (1ml, 12.3 mmol) and dry benzene (9 ml) were placed in a round bottom flask and sealed with a rubber septum. To this stirred solution was added 2,4,6-trichlorophenoxythiocarbonyl chloride. The resulting solution was stirred for five and a half hours. The solvent was removed under reduced pressure and the remaining residue was dissolved in methylene dichloride. This solution was then washed with saturated sodium hydrogen carbonate solution and brine. The organic layer was then dried with anhydrous magnesium sulphate and evaporated.

The pure β-phenylethyl (2,4,6-trichlorophenyl)thionocarbonate **3b** (1.762 g, 97% yield, oil) was obtained by column chromatography on silica (dichloromethane : ether = 10:1; Rf: 0.79); IR (solution, $CHCl_3$): 3081(w), 1742(w), 1430(m), 1298(s), 1193(s) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 7.2-7.4 (m, 7H), 4.78 (t, 2H), 3.16 (t, 2H); MS m/e: 181 (M^+-$C_6H_2Cl_3$); 241, 239 (M^+-$PhCH_2CH_2O$). FAB $(M+H)^+$ 361 ($^{35}Cl_2{}^{37}Cl$) (Found: Cl, 30.27; S, 8.54 Calc for $C_{15}H_{11}Cl_3O_2S$: Cl, 29.41; S, 8.87%).

The Acylation of β-Phenylethanol **1c** with 4-Fluorophenyl chlorothionoformate **2c.**

β-Phenylethanol **1c** (1.194 ml, 10 mmol), N-hydroxysuccinimide (0.115 g, 1 mmol), dry pyridine (2.43 ml, 30 mmol) and dry benzene (50 ml) were placed in a round bottom flask and sealed with a rubber septum. Dry nitrogen gas was passed through this stirred solution while 4-fluorophenyl chlorothionoformate was added. The resulting solution was stirred for two hours at room temperature. Dichloromethane (50 ml) was added and the solution washed with 1 M hydrochloric acid, saturated solution of sodium bicarbonate and brine. The organic layer was then dried with anhydrous magnesium sulphate, filtered and then the solvent was evaporated under reduced pressure. Hexane was then added and the resulting precipitate was removed by filtration. The hexane was evaporated and the solid was separated with column chromatography (hexane:dichloromethane 8:2; Rf: 0.2).

The pure β-phenylethyl (4-fluorophenyl)thionocarbonate **3b** (2.17 g, 79%, mp: 91-92°C) was obtained by crystallization from dichloromethane and methanol. IR (nujol): 2924(s), 1497(s), 1379(s), 1263(s), 1195(s), 840(s) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 7.35-7.04(m, 9H), 4.72(t, 2H), 3.14(t, 2H); ^{13}C NMR ($CDCl_3$, δ, ppm) 195.0, 160.6 (J_{C-F} = 245 Hz), 149.2 (J_{C-F} = 2.8 Hz), 136.8, 129.0, 128.7, 126.9, 123.5 (J_{C-F} = 8.6 Hz, 2C), 116.2 (J_{C-F} = 23.8 Hz, 2C), 74.6, 34.6, m/e: 155(M^+-OC_6H_4F, 0.2); (Found C, 64.08; H, 4.58; S, 11.50. Calc for $C_{15}H_{13}FO_2S$: C, 65.20; H, 4.74; S, 11.60%).

The Acylation of Tetradecanol **1a** with Pentafluorophenyl chlorothionoformate **2b**

Tetradecanol **1a** (0.9647 g, 4.5 mmol), dry pyridine (0.25 ml, 3mmol), dry benzene (1.75 ml) and 4-dimethylaminopyridine (0.0750 g, 0.6 mmol) were placed in a round bottom flask and the flask was then sealed with a rubber septum. To this stirred solution was added pentafluorophenyl chlorothionoformate **2b** (0.8 ml, 5 mmol). The resulting solution was stirred for four hours and then filtered. The filtrate yielded pure tetradecyl pentafluorophenyl-thionocarbonate **3a** (1.4124 g, 3.2 mmol, 71%) upon removel of the benzene under reduced pressure.

The reaction flask and the precipitate were washed with dichloromethane which was then washed with sodium bicarbonate and brine. The resulting organic layer was dried with anhydrous magnesium sulphate, the pure tetradecyl pentafluorophenyl thionocarbonate **3a** (0.349 g, 18%; total yield 89%) was recovered upon reduced pressure evaporation. Rf: 0.61 (dichloromethane: ether 10:1); IR (solution, $CHCl_3$): 2928(s), 2857(s), 1744(w), 1660(w), 1520(s), 1311(s), 1157(s), 995(s) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 4.55 (t, 2H), 1.83 (m, 2H), 1.3 (m, 22H), 0.85 (m, 3H); m/e: 257 (M^+-OC_6F_5), 197 (M^+-$OCSOC_6F_5$). FAB $(M+H)^+$ 439. (Found: S, 6.99: Calc for $C_{21}H_{29}F_5O_2S$: S, 7.28%).

The Acylation of Octadecanol **1d** with 4-Fluorophenyl chlorothionoformate **2c**.

Octadecanol **1d** (2.705 g, 10 mmol), N-hydroxysuccinimide (0.115 g, 1 mmol), dry pyridine (2.43 ml, 30 mmol), and dry benzene (100 ml) were placed in a round bottom flask and sealed with a rubber septum. Dry nitrogen gas was passed through this stirred solution while 4-fluorophenyl chlorothionoformate **2c** was added. The resulting solution was stirred for two hours at room temperature. Dichloromethane (50 ml) was added and the solution washed with 1 M hydrochloric acid, saturated solution of sodium bicarbonate and brine. The organic layer was the dried with anhydrous magnesium sulphate. The magnesium sulphate was removed, the solvent was evaporated and the pure octadecyl 4-fluorophenylthionocarbonate **3d** was obtained by recrystallization from dichloromethane and methyl alcohol (3.89 g, 88.8%, mp: 42-44°C). Rf: 0.4 (hexane:dichloromethane 8:2); IR (nujol): 2921(s), 2849(s), 1501(s), 1461(s), 1376(s), 1296(s), 1191(s), 836(s) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS): 7.02-7.12 (m, 4H), 4.52 (t, 2H J = 7 Hz), 1.93-0.742 (m, 35H); MS m/e (%): 424 (M^+, 0.5), 380 (2.0), 128 (44), 112 (100), high resolution: found: 424.2794. Calcd for $C_{25}H_{41}FO_2S$: 424.2811.

Deoxygenation of β-Phenylethyl (2,4,6-Trichlorophenyl) Thionocarbonate **3c** with Tributyltin Hydride

β-Phenylethyl (2,4,6-trichlorophenyl) thionocarbonate **3c** (0.0036 g, 0.01 mmol), the internal standard and dry toluene (0.6 ml) were placed in a flame dried two neck flask fitted with a condenser attached to a bubbler. The system was sealed with a rubber septum and flushed with nitrogen to provide an inert atmosphere. The nitrogen source was removed and the solution was stirred and brought to boil.

A solution of AIBN (0.3 mg, 0.002 mmol), tributyltin hydride (4 μl, 0.015 mmol) in dry toluene was then added to the flask. After ten minutes an aliquot was removed and the formation of ethylbenzene **6c** measured by glc (Table 1).

Deoxygenation of β-Phenylethyl (4-fluorophenyl) thionocarbonate **3b** with Diphenylsilane

β-Phenylethyl (4-fluorophenyl) thionocarbonate **3b** (0.11g, 0.4 mmol) was dissolved in dry benzene (5.0 ml) in a round bottom flask under argon. Diphenylsilane (81 μl, 0.44 mmol) and a 1 M solution of triethylborane

in hexanes (100 µl, 0.1 mmol) were added and the flask was immersed into a pre-heated oil bath. Then dry air (10.4 ml) was bubbled through the reaction mixture for 20 min with a syringe pump. The reaction mixture was kept boiling for a further 10 min. The ethylbenzene content was measured by glc using an authentic sample as reference (Table 1).

The Acylation of Octadecanol **1d** with Pentafluorophenyl chlorothionocarbonate **2b.**

Octadecanol **1d** (0.1352 g, 0.5 mmol), dry pyridine (0.0514 g, 0.65 mmol), dry toluene (0.5 ml) and N-hydroxysuccinimide (0.0057 g, 0.05 mmol) were placed in a round bottom flask and sealed with a rubber septum. To this stirred solution was added pentafluorophenyl chlorothionoformate (105 µl, 0.65 mmol). The solution was then stirred for 18 minutes.

Then the solution was filtered and washed with toluene (0.2 ml) yielding pure octadecyl pentafluorophenyl thionocarbonate **3e** (0.2107 g, 85% yield) mp:31-32°C; Rf: 0.68 (dichloromethane:hexanes 3:1); IR: ($CHCl_3$) 2927(s), 2856(m), 1519(s), 1161(s) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS) 4.55 (t, 2H), 1.85 (m, 2H), 1.27 (m, 30H), 0.87 (t, 3H); m/e: 313 (M^+-OC_6F_5); 252 (M^+-$OCSOC_6F_5$). FAB $(M+H)^+$ 497, $(M-H)^+$ 495; (Found: S, 6.34. Calc for $C_{25}H_{37}F_5O_2S$: S, 6.46%).

A further experiment was undertaken where the reaction was stirred for 14 hours. The solution was then filtered and the toluene evaporated under reduced pressure resulting in an oil. (Crude yield of octadecyl pentafluorophenylthionocarbonate **3e**: 100%). This was then purified by column chromatography on silica gel (dichloromethane : hexanes = 3:1) to give a yield of 97% of pure crystalline **3e**.

Deoxygenation of Octadecyl Pentafluorophenylthionocarbonate **3e**

Octadecyl pentafluorophenylthionocarbonate **3e** (0.0090 g, 0.02 mmol) the internal standard and dry toluene (0.3 ml) were placed in a flame dried two neck-flask connected to a condenser equipped with a bubbler and sealed with a rubber septum. The system was flushed with dry nitrogen to provide an inert atmosphere. The nitrogen source removed and the contents of the flask brought to reflux (oil bath temperature: 125°C).

To this boiling solution was added in three portions a solution of tributyltin hydride (27 µl, 0.10 mmol), AIBN, (0.0128 g, 0.8 mmol) in dry toluene (273 µl) (t = 0 min, 120 µl ; t = 3 min, 60 µl; t = 6 min, 120 µl). An aliquot was removed after a further 6 minutes and the octadecane **6d** formed measured by glc (Table 1).

Deoxygenation of Octadecyl 4-fluorophenylthionocarbonate **3d.**

To octadecyl 4-fluorophenylthionocarbonate **3d** (170 mg, 0.4 mmol) was added toluene (3 ml) and phenylsilane (100 µl, 0.8 mmol) under argon. The solution was brought to boil and 150 µl portions of a toluene solution of benzoyl peroxide (387 mg was dissolved in 3.0 ml dry toluene) were added in 20 min intervals until the reaction was completed (tlc). The yield was measured by glc with an internal reference. (Table 1).

Gram Scale Acylation and Deoxygenation of Octadecanol with Tributyltin hydride.

Octadecanol **1d** (1.08 g, 4 mmol), N-hydroxysuccinimide (0.046 g, 0.4 mmol) and dry toluene (10 ml) were placed in a two-neck flask equipped with a magnetic stirrer bar. The flask was sealed with rubber septa, then dry pyridine (0.42 ml, 5.2 mmol) was added. The flask was then placed into a warm bath (60°C) until the octadecanol completely dissolved (5 mins). Once this was achieved the pentafluorophenyl chlorothionoformate (0.84 ml, 5.2 mmol) was injected into the reaction flask. The reaction mixture was stirred at room temperature overnight and the precipitate formed was removed by reduced pressure filtration, the reaction flask being washed twice with dry toluene (2 ml, 2 ml).

The filtrate was then transfered to another flask fitted with a condenser which was connected to an oil bubbler. Dry nitrogen was passed through the system to give an inert atmosphere, the solution was brought to boil, followed by the addition of a solution of AIBN (0.1956 g, 1.2 mmol) tributyltin hydride (3.2 ml, 12 mmol) in dry toluene (2 ml).

After ten minutes a sample was removed and a proton nmr spectrum recorded. Deoxygenation was deemed complete from the absence of the methylene triplet at 4.5 ppm. Then the reaction mixture was cooled and the toluene removed by reduced pressure evaporation. The residue was refluxed for three hours in carbon tetrachloride (80 ml). After evaporation, iodine/ether solution was added until the iodine colour remained, the solution was then diluted with more ether (100 ml) and shaken with 10% potassium fluoride solution (70 ml), filtered and separated. This procedure was repeated until no precipitate was detected. Drying and evaporation gave the crude product which was filtered down a silica gel column to give octadecane (0.73 g, 71.8%, mp: 28°C (lit 29°C).

1,2:3,4-Di-O-isopropylidene-D-galactopyranose-6-(2,4,6-trichlorophenyl) thionocarbonate **10b**

1,2:3,4-Di-O-isopropylidine-D-galactopyranose **10a** (1.31 g, 5 mmol) (Aldrich) was dissolved in dry benzene (20 ml). N-Hydroxysuccinimide (100 mg, 0.87 mmol) and dry pyridine (1.0 ml) were added. This mixture was treated with 2,4,6-trichlorophenyl chlorothionoformate **2a** (1.79 g, 1.3 eq). The reaction mixture was stirred at room temperature for 3 h, evaporated, dissolved in dichloromethane, washed with water, sodium hydrogen carbonate solution, dried over anhydrous $MgSO_4$ and evaporated. The pure product **10b** was isolated by chromatography on a silica column. Yield: 2.25 g (90%, glass). Slowly crystallizes; mp: 83-85°C. Rf: 0.87 dichloromethane.$[\alpha]_D^{26}$ -30.5° (C 2.0, $CHCl_3$); IR (CH_2Cl_2): 2988, 1257, 1190, 1133, 1071 cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS) 7.37 (s, 2H, Ar), 5.54 (d, 1H, J=4.88 Hz), 4.81 (dd, 1H, J_1=11.35 Hz, J_2=4.0 Hz), 4.62 (m, 2H), 4.2-4.37 (m, 3H), 1.49 (s, 3H, Me), 1.45 (s, 3H, Me), 1.33 (s, 3H, Me), 1.31 (s, 3H, Me); ^{13}C NMR ($CDCl_3$, ppm, δ, TMS) 191.91 (C=S), 145.20 (q, ArO), 132.90 (q, Ar), 130.32 (2q, ortho-Ar), 129.23 (2m CH, Ar), 110.27, 109.35 ($2sp^3q$, O-CMe_2O), 96.73 (1-CH), 74.02 (CH_2), 71.45, 71.20, 70.80, 65.85 (4 ring-CH), 26.58, 26.43, 25.40, 24.94 (4 CH_3 groups) (assignment based on CDEPT experiment). The shifts of the aromatic carbons are in agreement with the calculated values. MS: m/e 483, 485 $(M\text{-}Me)^+$. (Found m/e for $(M\text{-}Me)^+$; 486.9765, $C_{18}H_{18}{}^{35}Cl^{37}Cl_2O_7S$ requires 486.9780; 484.9797, $C_{18}H_{18}{}^{35}Cl_2{}^{37}ClO_7S$ requires

484.9809; 482.9825, $C_{18}H_{18}{}^{35}Cl_3O_7S$ requires 482.9839. (Found: C, 45.54; H, 4.17; Cl, 21.41; S, 6.39. Calcd for $C_{19}H_{21}Cl_3O_7S$: C, 45.66; H, 4.24; Cl, 21.28; S, 6.42%).

1,2:3,4-Di-O-isopropylidene-D-galactopyranose-6-(4-fluorophenyl) thionocarbonate **10c**

1,2:3,4-Di-O-isopropylidene-D-galactopyranose (3.57 g, 13.7 mmol) and N-hydroxysuccinimide (0.16 g, 1.37 mmol) were dissolved in freshly distilled dry tetrahydrofuran (50 ml) and dry pyridine (3.3 ml, 41 mmol) under dry argon. To this solution 4-fluorophenyl chlorothionocarbonate (5.2 g, 27.4 mmol) was added and the reaction mixture was stirred for 1 h at 25°C. Then the reaction mixture was diluted with methylene dichloride (200 ml) and the organic layer was washed with cold 1 M aqueous hydrogen chloride solution, saturated sodium hydrogen carbonate solution and brine and dried over anhydrous magnesium sulfate. Then the solvent was removed in vacuum and the product was isolated by column chromatography (hexanes: methylene dichloride = 8 : 2 in gradient to pure methylene dichloride). The title product was isolated as an oil (4.50 g, 79%). IR ($CDCl_3$): 2990, 2935, 1497, 1376, 1293, 1252, 1193, 1070, 1005 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 7.02-7.12 (m, 4 Ar-H), 5.58 (d, J = 4.96 Hz, 1H), 4.56-4.8 (m, 3H), 4.20-4.40 (m, 3H), 1.54 (s, 3H), 1.48 (s, 3H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, ppm, δ, TMS) 195.0 (C=S), 160.6 (d, 1C, C1, $^1J_{C\text{-}F}$ = 243.9 Hz), 149.2 (d, 1C, C1,$^4J_{C\text{-}F}$ = 2.9 Hz), 123.4 (d, 2C, C2; C6, $^3J_{C\text{-}F}$ = 8.6 Hz), 116.2 (d, 2C, C3, C5, $^2J_{C\text{-}F}$ = 23.5 Hz), 109.8, 108.9, 96.3, 73.7, 71.0, 70.7, 70.4, 65.5, 26.1, 26.0, 24.9, 24.5.

1,2:3,4-Di-O-isopropylidene-α-D-fucose[11] (**10d**)

The thionocarbonate **10b** (0.5482 g, 1.097 mmol) was dissolved in dry toluene and heated to 111°C. Tributyltin hydride (400 ul, 1.5 mmol) and AIBN (30 mg) was added into the stirred reaction mixture in one portion. The heating was continued for 80 min and then the solvent was evaporated. TLC showed the absence of the UV-active thionocarbonate. The pure title product was isolated by column chromatography using hexane:ether (10:1) eluent. The pure **10d** (324 mg, 91%) is a colourless oil which slowly solidifies (mp 34-35.5°C)[n]. $[\alpha]_D^{27}$ -60.0° (C 2.0, $CHCl_3$); lit. $[\alpha]_D^{19}$: -52°, $[\alpha]_D^{19}$: -62° (without solvent)[11]. Rf: 0.66 (CH_2Cl_2:Et_2O = 10:1); IR (CH_2Cl_2) 3000, 2940, 2920, 1382, 1215, 1075, 1008 cm^{-1}; ^1H NMR ($CDCl_3$, ppm, δ, TMS) 5.49 (d, 1H, H-1, $J_{1,2}$=5.0 Hz), 4.56 (dd, 1H, H-3, $J_{3,2}$=2.3 Hz, $J_{3,4}$=7.63 Hz), 4.27 (dd, 1H, H-2, $J_{2,1}$=5.0 Hz, $J_{2,3}$=2.3 Hz), 4.04 (dd, 1H, H-4, $J_{4,3}$=7.63 Hz, $J_{4,5}$=1.82 Hz), 3.88 (dq, 1H, H-5, $J_{5,4}$=1.882 Hz), 1.55, 1.50 (2s, 2x3H, CMe_2), 1.30 (d, 3H, (CH)-Me). EI MS: m/e 245 $(M+H)^+$, 229 $(M\text{-}Me)^+$.

Deoxygenation of 1,2:3,4-Di-O-isopropylidene-D-galactopyranose-6-(4-fluorophenyl) thionocarbonate **10c** with Phenylsilane.

To a solution of **10c** (300 mg, 0.72 mmol) in dry toluene (3.0 ml) phenylsilane (157 µl, 1.45 mmol) was added under argon. The reaction mixture was then brought to boil and treated with portions (248 µl, 0.2 eq.) of a

toluene solution of benzoyl peroxide at 20 min intervals (387 mg benzoyl peroxide was dissolved in 3.0 ml dry toluene). The boiling was continued until the reaction was completed. Then the reaction mixture was evaporated and the residue was separated by column chromatography on silica (hexanes: EtOAc = 8 : 2). Evaporation of the selected fractions gave the deoxygenated product **10d** (0.155 g, 88%), identical with the authentic sample.

Mono-xanthate of hederagenin methyl ester (**11c**)[4]

Hederagenin methyl ester **11b** (200 mg, 0.42 mmol)[4] was dissolved in N,N-dimethylformamide (2 ml) under argon. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.25 ml, 1.68 mmol) and carbon disulfide (2 ml, 33.25 mmol) were then added and the solution was stirred for 20 min at 20°C. Methyl iodide (4 ml, 64.25 mmoles) was added and the reaction mixture was stirred for a further 20 min. at 20°C. The reaction mixture was then washed with 1M HCl solution, saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum and the residue was separated by column chromatography (silica column, CH_2Cl_2 eluent). Evaporation of the selected fractions gave the title product (0.19 g, 78.5%), m.p. 173-174°C (lit.[4] m.p. 173-175°C). IR ($CDCl_3$) 3487, 2947, 1718, 1455, 1380, 1229, 1066, 964 cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm, TMS) 5.25 - 5.35 (m, 1H), 4.75 (d, J = 11.3 Hz, 1H), 4.34 (d, J = 11.3 Hz, 1H), 3.62 (s, 3H), 3.62-3.47 (m, 1H), 2.70 - 2.92 (m, 1H), 2.57 (s, 3H), 0.70 - 2.00 (m, 41 H); ^{13}C NMR ($CDCl_3$, δ, ppm, TMS) 215.8 (C=S), 178.2, 143.7, 122.2, 75.6, 72.0, 51.5, 48.2, 47.8, 46.7, 45.8, 42.7, 41.6, 41.3, 39.2, 38.2, 36.8, 33.8, 33.1, 32.3, (2C), 30.6, 27.6, 26.3, 25.7, 23.6, 23.3, 23.0, 18.7, 18.3, 16.8, 15.7, 11.8.

O-Acetylation of **11c**. Synthesis of **11e**. The xanthate **11c** (0.32 g, 0.56 mmol) was stirred with acetic anhydride (3 ml) and pyridine (3 ml) under argon for 8 hrs at 20°C. The solvent was then evaporated and the residue was crystallized from ethyl alcohol. First crop: 0.3034 g (85.5%), m.p. 166-167°C. IR ($CHCl_3$) 3155, 2949, 1247, 114, 1084 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 5.25 - 5.35 (m, 1H), 4.82 (dd, J = 5.5 Hz, 11.3 Hz, 1H), 4.38 (d, J = 11.4 Hz, 1H), 4.22 (d, J = 11.4 Hz, 1H), 3.62 (s, 3H), 2.70 - 2.95 (m, 1H), 2.56 (s, 3H), 2.03 (s, 3H), 0.74 - 2.00 (m, 40 H); ^{13}C NMR ($CDCl_3$, δ, ppm, TMS) 215, 178.3, 170.5, 143.8, 122.1, 74.8, 74.6, 51.2, 48.3, 47.8, 46.7, 45.8, 41.6, 41.3 (2C), 39.2, 37.8, 36.8, 33.8, 33.1, 32.3, 32.3, 30.7, 27.6, 25.7, 23.6, 23.4, 23.0, 22.9, 21.3, 18.6, 18.1, 16.8, 15.7, 12.9; (Found: C, 67.91; H, 8.81; S, 10.29. Calcd for $C_{35}H_{54}O_5S_2$: C, 67.92; H, 8.80; S, 10.36%).

Deoxygenation of **11e** with diphenylsilane. The mono-xanthate acetate **11e** was dissolved in o-xylene (1.0 ml) under argon. The solution was then heated to 150°C and diphenyl silane (149 μl, 0.8 mmol) was added. At every 20 min 60 μl aliquots of a solution of benzoyl peroxide (0.129 g/ 1 ml o-xylene) were added up to 1.8 eq. The solvent was evaporated in vacuum and the residue was separated on a silica column (eluent: hexanes : CH_2Cl_2 = 3 : 7). Evaporation of the appropriate fractions gave the deoxy product **11f**[14] (62 mg, 75%), m.p. 220-222°C, lit.[14] m.p. 220-221°C). IR ($CDCl_3$) 2949, 1717, 1452, 1275, 1112, 964 cm-1; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 5.25 - 5.35 (m, 1H), 4.45-4.55 (m, 1H), 3.62 (s, 3H), 2.05 (s, 3H), 0.70 - 2.00 (m, 44 H); ^{13}C NMR ($CDCl_3$, δ, ppm, TMS) 178.3, 171.0, 143.8, 122.2, 80.9, 55.3, 51.5, 47.5, 46.7, 45.8, 41.6, 41.2, 39.2,

38.1, 37.6, 36.9, 33.8, 33.1, 32.6, 32.3, 30.7, 28.0, 27.6, 25.9, 23.6, 23.5, 23.4, 23.0, 21.3, 18.2, 16.8, 16.7, 15.3.

Benzoylation of **11c**. The xanthate **11c** (1.0 g, 1.74 mmol) was stirred with benzoyl chloride (0.4 ml) and dry pyridine (5 ml) under argon for 10 hrs at 20°C. The solvent was then evaporated in vacuum and the residue was dissolved in methylene chloride (100 ml). This solution was washed with 1 M HCl solution, saturated aqueous $NaHCO_3$ solution and brine and dried over anhydrous $MgSO_4$. The methylene chloride was evaporated in vacuum and the residue was then crystallized from ethyl alcohol to give the benzoate **11g**. First crop: 1.1 g (93%), m.p. 180-181°C. IR ($CDCl_3$) 2949, 1717, 1452, 1275, 1112, 1069, 964 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 7.97-8.09 (m, 2H), 7.35-7.60 (m, 3H), 5.28 - 5.35 (m, 1H), 5.05-5.18 (m, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.22 (d, J = 11.5 Hz, 1H), 3.62 (s, 3H), 2.80-2.95 (m, 1H), 2.55 (s, 3H), 0.75 - 2.05 (m, 40 H); ^{13}C NMR ($CDCl_3$, δ, ppm, TMS) 215.2, 178.2, 165.8, 143.8, 132.9, 130.6, 129.5 (2C), 128.3 (2C),122.1, 75.4, 74.7, 51.5, 48.4, 47.9, 46.7 (2C), 45.8, 41.7, 41.6, 41.3, 39.3, 37.9, 36.9, 33.9, 33.1, 32.3, 30.7 (2C), 27.6, 25.8, 23.6, 23.4, 23.0, 18.7, 18.2, 16.9, 15.7, 13.2. (Found: C, 70.45; H, 8.30; S, 9.51. Calcd. for $C_{40}H_{56}O_5S_2$: C, 70.54; H, 8.29; S, 9.42%).

Deoxygenation of **11g** with diphenylsilane. The mono-xanthate benzoate **11g** (0.408 g, 0.6 mmol) was dissolved in dry o-xylene (3.0 ml) under argon. The solution was then heated to 150°C and diphenylsilane (550 µl, 3.0 mmol) was added. At every 20 min 225 µl aliquots (0.2 eq. to the substrate) of a solution of benzoyl peroxide (0.3872 g/ 3 ml o-xylene) were added (5 times). The solvent was evaporated in vacuum and the residue was separated on a silica column (eluent: hexanes : CH_2Cl_2 = 1 : 1). Evaporation of the appropriate fractions gave the deoxy product **11h** (313 mg, 91%), m.p. 268-269°C (from ethyl alcohol). IR ($CDCl_3$) 2950, 1705, 1453, 1277, 1116 cm-1; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 8.00-8.10 (m, 2H), 7.40-7.60 (m, 3H), 5.27 - 5.35 (m, 1H), 4.69-4.80 (m, 1H), 3.63 (s, 3H), 2.80-2.95 (m, 1H), 0.70 - 2.10 (m, 43 H); ^{13}C NMR ($CDCl_3$, δ, ppm, TMS) 178.3, 166.2, 143.8, 132.7, 130.9, 129.5 (2C), 128.3 (2C), 122.3, 81.5, 55.3, 51.5, 47.5, 46.7, 45.8, 41.6, 41.3, 39.3, 38.1 (2C), 37.0, 33.8, 33.1, 32.6, 32.4, 30.7, 28.2, 27.9, 25.9, 23.6, 23.5, 23.4, 23.0, 18.2, 17.0, 16.8, 15.4. (Found: C, 79.34; H, 9.52. Calcd. for $C_{38}H_{54}O_4$: C, 79.40; H, 9.47%).

Deoxygenation of **11g** with triphenylsilane. The mono-xanthate benzoate **11g** (0.272 g, 0.4 mmol) and triphenylsilane (0.52 g, 2.0 mmol) were dissolved in dry o-xylene (2.0 ml) under argon. The solution was then heated to 150°C. At every 20 min 150 µl aliquots of a solution of benzoyl peroxide (0.258 g/ 2 ml o-xylene) were added dropwise (5 times). The solvent was evaporated in vacuum and the residue was separated on a silica column (eluent: hexanes : CH_2Cl_2 = 1 : 1). Evaporation of the appropriate fractions gave the deoxy product **11h** (200 mg, 87%), m.p. 268-269°C (from ethyl alcohol).

Deoxygenation of **11g** with phenylsilane. The mono-xanthate benzoate **11g** (0.272 g, 0.4 mmol) was dissolved in dry o-xylene (2.0 ml) under argon. The solution was then heated to 115°C. Phenylsilane (0.25 ml, 2 mmol) was then added. At every 20 min 150 µl aliquots of a solution of benzoyl peroxide (0.258 g/ 2 ml o-xylene) were added dropwise (3 times). This was followed by phenylsilane (0.25 ml, 2 mmol) and two more 150 µl portions of the benzoyl peroxide solution. The solvent was evaporated in vacuum and the residue was separated on a silica column (eluent: hexanes : CH_2Cl_2 = 1 : 1). Evaporation of the appropriate fractions gave the deoxy product **11h** (90 mg, 40%), m.p. 268-269°C (from ethyl alcohol).

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