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STEREOCHEMICAL ASPECTS OF CATALYTIC SILOXYMETHYLATION OF VARIOUS OXYGEN-CONTAINING COMPOUNDS WITH HYDROSILANES AND CARBON MONOXIDE IN THE PRESENCE OF DICOBALT OCTACARBONYL

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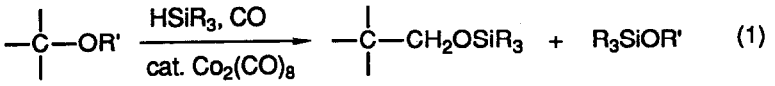
Abstract: Siloxymethylation of oxygen-containing compounds by a new catalytic reaction, $HSiR_3/CO/Co_2(CO)_8$, is described with emphasis laid on stereoselectivity. In the catalytic reaction, the carbon-oxygen bond in the substrates is cleaved and displaced by a trialkylsiloxymethyl group. The siloxymethylation takes place with inversion, racemization, or retention at the reaction sites, depending on the structure of the substrates.

Introduction

In the course of our studies on the $HSiR_3/CO/Co_2(CO)_8$ catalytic reaction,[1] we found that incorporation of carbon monoxide into a variety of oxygen-containing compounds took place under exceptionally mild reaction conditions (ambient temperature and atmospheric pressure of CO). The overall process of the catalytic reaction is introduction of a trialkylsiloxymethyl group into the carbon atom at the site where carbon-oxygen bond is cleaved (eq 1). For the catalytic siloxymethylation to take place at mild reaction conditions, the substrate must be reactive enough toward the key catalytic species $R_3SiCo(CO)_4$[1] at room temperature.

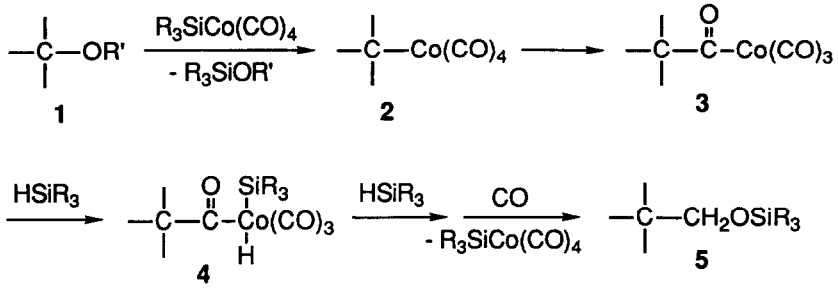


(1)

We have already found that oxiranes,[2] oxetanes,[3] five-membered cyclic ethers,[4] β-lactones,[5] glycosyl acetates,[6] acetals,[7] benzylic acetates,[8] and orthoesters[9] are sufficiently reactive to participate in this reaction. In this paper we wish to describe and discuss the stereochemical course of the catalytic siloxymethylation with representative examples. The stereochemistry of the carbon-carbon bond forming reaction has been found to vary from inversion to racemization, with retention in a special case, depending on the structure of the oxygen-containing compounds used as the substrates.

Results and Discussion

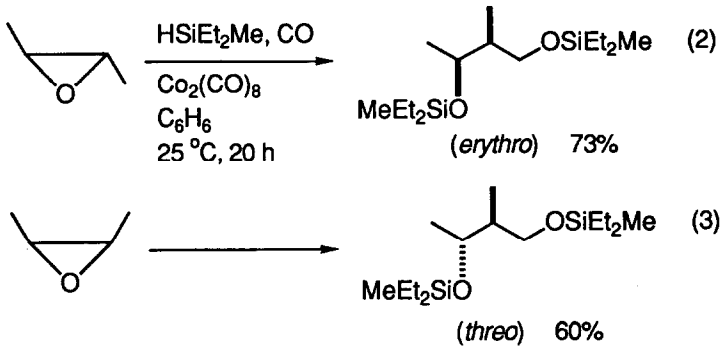
The catalytic siloxymethylation (eq 1) is believed to proceed as outlined in Scheme I. The reaction of oxygen-containing compounds **1** with the key catalyst species $R_3SiCo(CO)_4$[1,10] results in the formation of a carbon-cobalt bond in **2**. The formation of a carbon-transition metal bond is essential for incorporation of carbon monoxide. Migratory insertion of CO in **2** to give **3** followed by oxidative addition of a hydrosilane would afford **4**. Subsequent steps from **4** to the product **5** are still mechanistically not clear. The stereochemical relationship between the starting material **1** and the final product **5** must be determined in the process from **1** to **2** since the migratory insertion of CO in alkylmetal complexes like **2** to acylmetal complexes like **3** has been known to proceed with retention of configuration at the migrating carbon atom.[11]



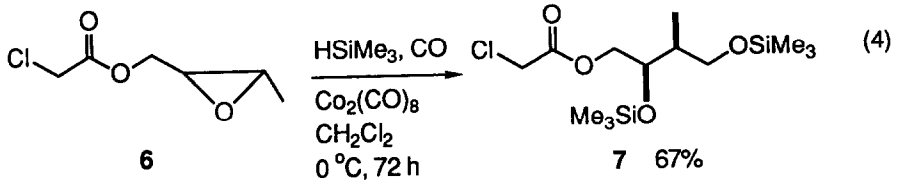
Scheme I. Simplified Mechanism of the Catalytic Siloxymethylation

We have examined the stereochemical course of the catalytic siloxymethylation of various oxygen-containing compounds. Among these, the results of the catalytic reactions of oxiranes,[2] cyclic orthoesters,[9] benzylic acetates,[8] and glycosyl acetates[6] were most informative. Because these four substrates are suitable for the examination of stereochemistry of siloxymethylation and also are readily available, these are presented below according to the type of stereochemical outcome.[1,2]

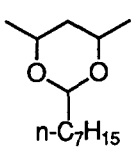
Inversion. The reaction of *trans*- (racemic) and *cis*-2-butene oxides with $HSiEt_2Me$ (3 equiv) and CO (1 atm) in the presence of $Co_2(CO)_8$ (0.04 equiv) in C_6H_6 at 25 °C for 20 h gave *erythro*- and *threo*-2-methylbutane-1,3-diol disilyl ethers, respectively (eqs 2 and 3). The reaction is stereospecific with inversion of configuration of the carbon atom at the reaction sites.



An epoxide of a substituted allylic alcohol derivative **6** (racemic) underwent highly regio- and stereoselective ring opening to give a 1,3,4-triol derivative **7** in 67% yield along with a regioisomer (not shown) in 3% yield (eq 4). The use of the chloroacetyl group was essential to attaining the observed high regioselectivity (96:4).[13] The use of acetyl or benzoyl protective groups resulted in lower selectivity (78:22) in both cases. While the stereochemistry of the minor regioisomer has not been determined, the established structure of the product **7** indicated that the reaction proceeded with inversion of configuration.



In recent years, much attention has been focused on remarkable levels of stereoselection on Lewis acid promoted, nucleophilic displacement of chiral dioxolane and dioxane acetals derived from optically active 2,3-butanediol and 2,4-pentanediols.[14] Attempted siloxymethylation of an acetal **8** derived from 2,4-pentanediol (1:1 mixture of R*R* and R*S*) resulted in no reaction in benzene ($CO/HSiMe_3/Co_2(CO)_8$, C_6H_6, 25 °C, 7 h). Reduction was observed in dichloromethane ($CO/HSiMe_3/Co_2(CO)_8$, CH_2Cl_2, 25 °C, 20 h) to give **9** in 49% yield. Also, 1,3-dioxan-4-one **10** prepared from (*R*)-3-hydroxybutyric acid,[15] which is known to be useful for asymmetric alkylation, did not undergo catalytic siloxymethylation efficiently but mainly resulted in reduction to afford **11** (53% yield).



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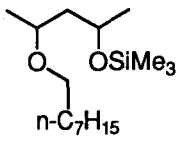

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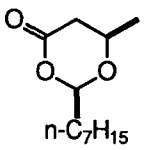

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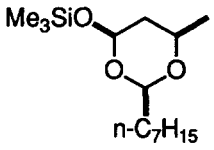
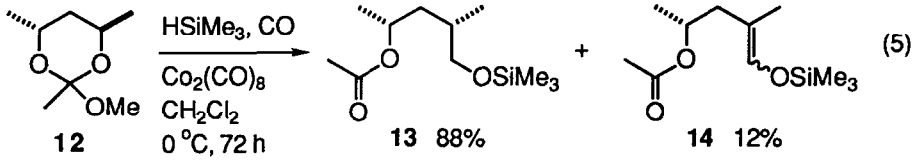


11

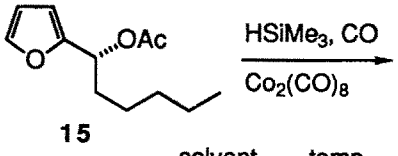
Interestingly, however, a cyclic orthoester of 2,4-pentanediol **12** (enantiomerically pure *R,R*) was found to react in the $HSiMe_3/CO/Co_2(CO)_8$ catalytic system to yield **13** as the result of siloxymethylation with inversion (eq 5). An enol silyl ether **14** was also formed as a by-product.[16] Methyl trimethylsilyl ether (not shown) was another product.



12 **13** 88% **14** 12% (5)

Racemization. Racemization at the reaction site takes place to a large extent in the catalytic siloxymethylation of secondary furfuryl acetates. Enantiomerically pure (*R*)-α-pentyl-2-furfuryl acetate **15**[17] underwent siloxymethylation in good chemical yield (eq 6). The acetoxy group in **15** was removed as Me_3SiOAc. An activating group such as the furyl group is necessary since unactivated acetates (e.g., 2-heptyl acetate) did not react at all under these conditions. The faster reaction of **15** in CH_2Cl_2 enabled the use of a lower temperature (0 °C) but the stereoselectivity became even lower. Changing the side chain in **15** to a methyl group (n-C_5H_{11} to CH_3) to diminish the steric congestion around the reaction site did not improve the

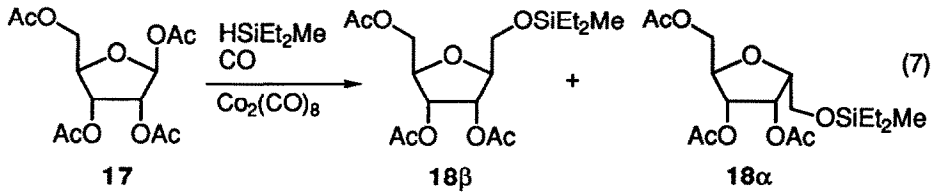
stereoselectivity (in C_6H_6, 25 °C, 16 h, 79% yield with 12% ee). These results imply that the transition state in these cases may possess carbocationic character (*vide infra*).



15 16 (6)

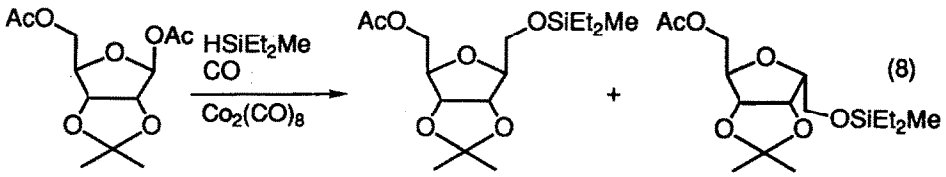
solvent	temp	time	yield (% ee)
C_6H_6	25 °C	15 h	93% (13% ee)
n-C_6H_{14}	25 °C	2 day	91% (12% ee)
n-C_6H_{14}	15 °C	3 day	89% (18% ee)
CH_2Cl_2	0 °C	2 day	93% (3% ee)

Apparent Retention. In some $Co_2(CO)_8$-catalyzed reactions of glycosyl acetates with $HSiR_3$ and CO, the acetoxy group was replaced by a siloxymethyl group from the same side as the acetoxy group originally was attached. This net



17 18β 18α

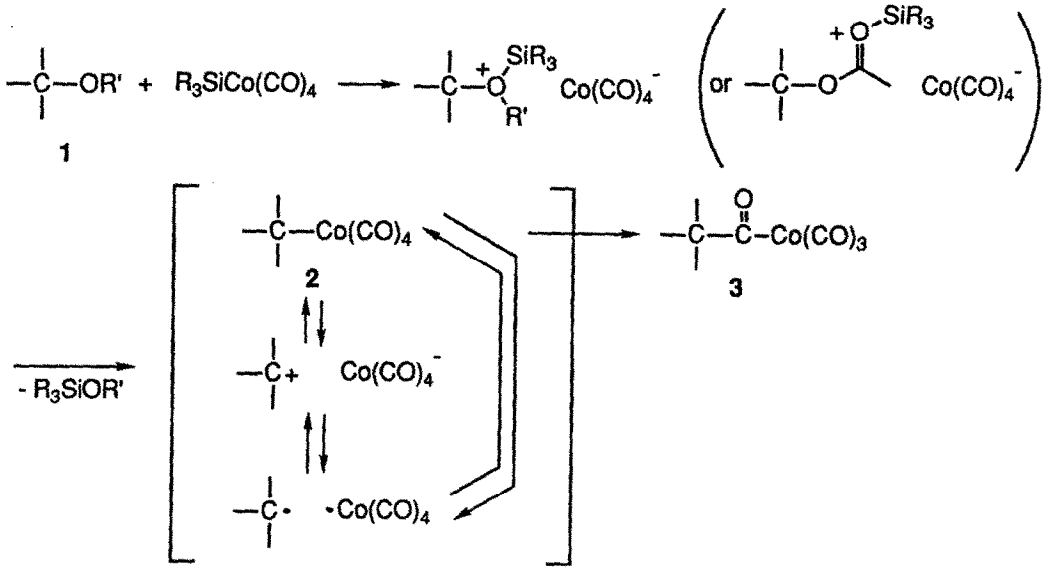
solvent	temp	time	18β	18α
C_6H_6	30 °C	3 day	23%	10%
CH_2Cl_2	30 °C	20 h	70%	5%



19 20β 20α

solvent	temp	time	20β	20α
C_6H_6	45 °C	20 h	7%	39%
CH_2Cl_2	25 °C	20 h	7%	27%

retention of configuration was observed for the substrates having an adjacent acetoxy or benzoyloxy group. The results obtained for ribose derivatives are shown in eqs 7 and 8. The major by-products (not shown) were reduction products where the anomeric acetoxy group was replaced with hydrogen.[18] For synthetic purposes, the reaction in eq 7 using CH_2Cl_2 as a solvent is most satisfactory. Under these conditions, β-tri-O-benzoylribofuranosyl acetate gave better results, i.e., a β-siloxymethylation product in 75% isolated yield. In the reaction of **19** which is similar to **17** but has no 2-acetoxy group, the β/α ratio of the product has been reversed (eq 8). Obviously, participation of the neighboring acetoxy group existing in **17** but not in **19** seems to play an important role for this type of apparent retention of stereochemistry.

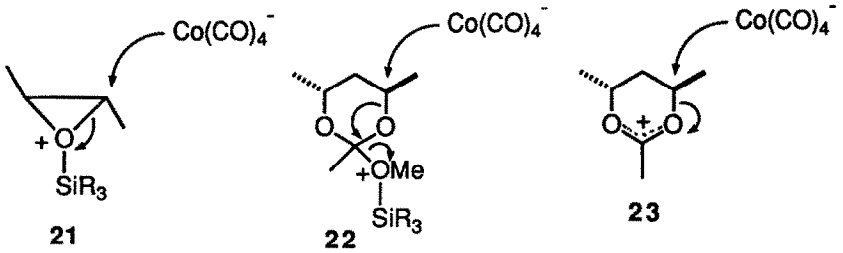


Scheme II. Proposed Mechanism Leading to Acylcobalt Complex **3**

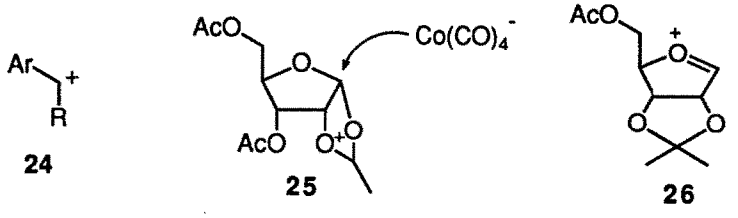
Stereodetermining Step. In the course of the catalytic siloxymethylation with $HSiR_3/CO/Co_2(CO)_8$ outlined in Scheme I, the stereochemistry of the reaction is determined in the step of the formation of an alkylcobalt complex **2** as has been mentioned before. The experimental results described above indicate that the mechanism of the formation of the carbon-cobalt bond heavily depends on the structure of oxygen-containing compounds employed as the starting material. The step from **1** to **2** would begin with the interaction of the oxygen atom in the substrate with silicon atom in $R_3SiCo(CO)_4$ leading to a silyloxonium ion with $Co(CO)_4^-$

as the counter anion. Then, the reaction would follow two major pathways. In one case, the cleavage of the carbon-oxygen bond and formation of the carbon-cobalt bond takes place in a concerted fashion. In the other, the silyloxonium ion breaks into a carbocation and a silyl ether (or a silyl ester). Another possible course would involve free radicals[19] although we have no experimental evidence yet for this possibility. Thus, a closer look at the step from **1** to **2** may be postulated as in Scheme II.

While it seems reasonable that the transition state for the ring opening of oxiranes would be formulated as **21**, that for the cyclic orthoacetate **12** may either be **22** or **23**. The latter is attractive since corresponding cyclic orthoformate (i.e., no 2-methyl group) did not react in the $HSiR_3/CO/Co_2(CO)_8$ system.



The intermediate in the reaction of benzylic type acetates such as **15** must be very close to a carbocation like **24**. The predominant formation of the β-isomer **18β** from **17** would require the intermediate **25**. Whether **20α** is obtained by a concerted displacement of silylated form of **19** or by diastereoselection on **26** is not clear. It has been known that the mechanism of the anomeric displacement of glycosides is highly sensitive to the substitution patterns, reagents, and reaction conditions, and is often not established.[20]



Summary

The basic feature of the stereochemistry of the catalytic siloxymethylation have been shown. The stereodetermining step is that of carbon-cobalt bond

formation, where two types of mechanisms, i.e., concerted and carbocationic, are operating. For the catalytic reaction to proceed, the substrate (oxygen-containing compounds) must be sufficiently reactive enough at room temperature. While the driving force for the reaction is provided by high oxophilicity of silicon, the reactivity depends on the structure of the substrates. The use of activating factors such as strain release in the case of oxiranes and carbon-oxygen double bond formation in the case of cyclic orthoesters results in highly stereoselective siloxymethylation with inversion. Activation of the substrate through stabilization of a developed positive charge by aromatic (furyl) or heteroatom (oxygen) group results in loss of stereoselectivity.

Experimental Section

Typical Procedure for the $Co_2(CO)_8$-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide. In a 10-mL reaction flask with an efficient condenser (dry-ice-CH_3OH) was placed $Co_2(CO)_8$ (0.1 mmol, 34 mg), after the flask was flashed with CO (1 atm from a stock balloon), $HSiMe_3$ (25 mmol, 3 mL) was added using a pressure syringe[21] at 25 °C. After 5 min, benzene (5 mL) and (*R*)-α-pentyl-2-furfuryl acetate (**15**) (2.5 mmol, 530 mg) was added and the mixture was stirred at 25 °C (bath temperature, under reflux of $HSiMe_3$) for 15 h under CO (1 atm). GLC analysis showed that [2-pentyl-(2-furanyl)propyloxy]trimethylsilane (**16**) was formed in 93% yield. Purification by column chromatography (silica gel, hexane/EtOAc) gave essentially pure **16** (496 mg, 81% yield). For the reactions using $HSiEt_2Me$, usually 7.5 mmol of the hydrosilane was used.

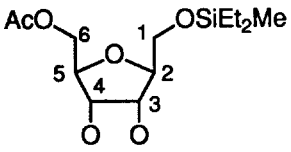
α-Chloroacetic acid 2-(2,2-dimethyl-1-oxa-2-silapropyl)-3,6,6-trimethyl-5-oxa-6-silaheptyl ester (7). Bp 170 °C/1 Torr; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H, CH_3Si), 0.12 (s, 9 H, CH_3Si), 0.84 (d, J = 6.3 Hz, 3 H, CH_3), 1.69 (m, 1 H, CH), 3.39 (dd, J = 8.5, 5.0 Hz, 1 H, CH_2OSi), 3.45 (dd, J = 10.0, 5.0 Hz, 1 H, CH_2OSi), 4.02 (m, 1 H, CHOSi), 4.05 (s, 2 H, CH_2Cl), 4.12 (dd, J = 7.8, 3.6 Hz, 1 H, CH_2O), 4.18 (dd, J = 11.4, 3.6 Hz, 1 H, CH_2O); IR (neat) 2975, 2910, 1750, 1400, 1280, 1245, 1170, 1080, 980, 830, 740, 675; mass spectrum, *m/e* (rel intensity) 340 (0, M^+ for ^{35}Cl), 325 (2, M^+ - Me), 211 (12), 209 (25), 189 (17), 103 (100); high resolution MS, M^+ 340.1277 (calcd for $C_{13}H_{29}ClO_4Si_2$ 340.1294).

(1-Methyl-3-octyloxypentyloxy)trimethylsilane (9). ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H, CH_3Si), 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 1.12 (d, J = 5.4 Hz, 3 H, CH_3), 1.14 (d, J = 5.1 Hz, 3 H, CH_3), 1.25-1.33 (m, 6 H, CH_2), 1.48-1.58 (m, 8 H, CH_2), 3.20-3.30 (m, 1 H, CHOSi), 3.47-3.62 (m, 2 H, CH_2O), 3.97-4.12 (m, 1 H, CHO); IR (neat) 2968, 2936, 2864, 1462, 1418, 1378, 1340, 1296, 1250, 1174, 1056, 1126, 1092, 1060, 978, 950, 888, 842; mass spectrum, *m/e* (rel intensity) 288 (0, M^+), 273 (2, M^+ -Me), 232 (10), 188 (11), 158 (24), 143 (37), 117 (100), 86 (30), 85 (27), 75 (45), 73 (87), 71 (96).

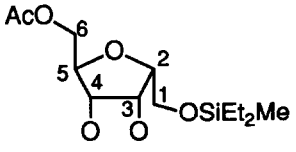
(2*R*, 4*S*, 6*R*)-2-Heptyl-6-methyl-4-trimethylsiloxy-1,3-dioxane (11). ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H, CH_3Si), 0.87 (t, *J* = 6.8 Hz, CH_3), 1.22 (d, *J* = 6.2 Hz, CH3), 1.24-1.72 (m, 14 H, CH_2), 3.61-3.77 (m, 1 H, CHO), 4.54 (t, *J* = 5.4 Hz, 1 H, OCHO), 4.90 (dd, *J* = 9.3, 2.4 Hz, 1 H, OCHOSi); IR (neat) 2962, 2932, 2860, 2734, 1462, 1394, 1343, 1250, 1176, 1154, 1115, 1099, 1025, 981, 876, 847. 757; mass spectrum, *m/e* (rel intensity) 288 (0, M^+), 201 (13), 143 (99), 129 (26), 119 (80), 103 (72), 101 (28), 75 (100), 73 (93).

(2*S*, 4*R*)-(4-Acetoxy-2methylpentyloxy)trimethylsilane (13). $[\alpha]_D^{19}$ = 11.7° (*c* = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H, CH_3Si), 0.88 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.21 (d, *J* = 6.1 Hz, 3 H, CH_3), 1.58-1.72 (m, 3 H, CH_2, CH), 2.01 (s, 3 H, CH_3O), 3.30-3.43 (m, 2 H, CH_2O), 4.99-5.06 (m, 1 H, CHO); IR (neat) 2964, 2908, 1742, 1464, 1418, 1368, 1140, 1040, 960, 842, 734; mass spectrum, *m/e* (rel intensity) 232 (0, M^+), 130 (43), 117 (89), 103 (47), 83 (66), 73 (100); Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 56.80; H, 10.45.

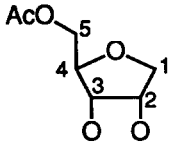
[2-Pentyl-(2-furanyl)propyloxy]trimethylsilane (16). $[\alpha]_D^{18.2}$ = 4.45° (*c* = 1.15, $CHCl_3$); Bp 120 °C/10 Torr (bath temp); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H, CH_3Si), 0.86-1.69 (m, 11 H, CH_2, CH_3), 2.83-2.85 (m, 1 H, CH), 3.65 (dd, *J* = 10.0, 6.9 Hz, 1 H, CH), 3.75 (dd, *J* = 10.0, 6.4 Hz, 1 H, CH_2O), 6.04 (m, 1 H, furan), 6.28 (m, 1 H, furan), 7.31 (m, 1 H, furan); ^{13}C NMR ($CDCl_3$) δ -0.62 (CH_3Si), 14.03 (CH_3), 22.52 (CH_2), 26.88 (CH_2), 30.10 (CH_2), 31.85 (CH_2), 42.09 (CH), 65.26 (CH_2O), 105.62 (furan), 109.90 (furan), 140.73 (furan), 156.85 (furan); IR: (neat) 2910, 2860, 1460, 1250, 1090, 1010, 875, 840, 800, 730; mass spectrum, *m/e* (rel intensity) 254 (7, M^+), 239 (10, M^+ -Me), 151 (60), 103 (76), 73 (100) Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 65.90; H, 10.50.



18β, 20β



18α, 20α



2,5-Anhydro-1-O-diethylmethylsilyl-D-allitol triacetate (18β). $[\alpha]_D^{20.7}$ = 8.89° (*c* = 1.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3 H, CH_3Si), 0.60 (q, *J* = 8.1 Hz, 4 H, CH_2Si), 0.96 (t, *J* = 8.1 Hz, 6 H, CH_3CSi), 2.07 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 3.71 (dd, *J* = 11.0, 3.7 Hz, 1 H, H1), 4.07 (q, *J* = 3.7 Hz, 1 H, H1'), 4.11 (dd, *J* = 11.7, 5.9 Hz, 1 H, H6), 4.19 (dt, *J* = 5.9, 3.7 Hz, 1 H, H5), 4.30 (dd, *J* = 11.7, 3.7 Hz, 1 H, H6'), 5.13 (dd, *J* = 5.9, 3.7 Hz, 1 H, H4), 5.25 (dd, *J* = 5.9, 3.7 Hz, 1 H, H3); ^{13}C NMR ($CDCl_3$) δ -5.14 (CH_3Si), 6.07 (CH_2Si), 6.60 (CH_3CSi), 20.50, 20.60, 20.74 (CH_3CO), 62.58 (C1), 64.14 (C6), 71.82, 72.31, 78.38, 83.08 (C2, C3, C4, C5), 169.67, 169.87, 170.65 (C=O); IR ($CDCl_3$) 2960, 1740, 1460, 1380, 1240, 1090, 905, 790, 730; mass

spectrum, *m/e* (rel intensity) 390 (0, M^+), 361 (31, M^+ -Et), 259 (10), 199 (40), 131 (65), 43 (100). Anal. Calcd for $C_{17}H_{30}O_8Si$: C, 52.29; H, 7.74. Found: C, 52.49; H, 7.95.

2,5-Anhydro-1-O-diethylmethylsilyl-D-altritol triacetate (18α). Identified as a corresponding trimethylsilyl ether. ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H, CH_3Si), 2.41 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 2.12 (s, 3 H, CH_3CO), 3.77 (t, *J* = 6.6 Hz, 2 H, C1), 4.10 (dd, *J* = 12.5, 5.1 Hz, 1 H, H6), 4.21 (ddd, *J* = 8.8, 5.1, 2.9 Hz, 1 H, H5), 4.26 (dd, *J* = 6.6, 3.7 Hz, 1 H, H2), 4.31 (dd, *J* = 12.5, 2.9 Hz, 1 H, H6'), 5,26 (dd, *J* = 8.1, 4.4 Hz, 1 H, H4), 5.55 (dd, *J* = 4.4, 3.7 Hz, 1 H, H3).

2,5-Anhydro-1-O-diethylmethylsilyl-3,4-O-(1-methylethylidene)-D-allitol acetate (20β). ^1H NMR ($CDCl_3$) δ 0.07 (s, 3 H, CH_3Si), 0.57-0.62 (m, 4 H, CH_2Si), 0.95 (t, *J* = 7.9 Hz, 6 H, CH_3CSi), 1.35 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3CO), 3.68 (d, *J* = 3.9 Hz, 2 H, H6), 4.09-4.13 (m, 1 H, H5'), 4.15-4.18 (m, 1 H, H4), 4.24 (dd, *J* = 10.8, 4.2 Hz, 1 H, H5), 4.47 (dd, *J* = 6.4, 4.3 Hz, 1 H, H3), 4.64 (dd, *J* = 6.4, 3.1 Hz, 1 H, H2); ^{13}C NMR ($CDCl_3$) δ -5.09 (CH_3Si), 6.07 (CH_2Si), 6.65 (CH_3CSi), 20.79 (CH_3CO), 25.54 (CH_3), 27.40 (CH_3), 63.41 (C5 or C6), 64.82 (C1 or C6), 82.19, 82.34, 82.73, 85.23 (C2, C3, C4, C5), 113.80 (OCO), 170.69 (C=O); IR ($CDCl_3$) 2960, 2880, 1740, 1465, 1395, 1385, 1255, 1220, 1160, 1140, 1100, 1080, 1045, 1010, 870, 805; mass spectrum, *m/e* (rel intensity) 346 (0, M^+), 331 (10, M^+ -Me), 317 (30), 259 (10), 199 (68), 171 (15), 169 (16), 157 (10), 143 (16), 131 (90), 115 (14), 111 (10), 103 (30), 101 (24), 97 (17), 89 (38), 81 (21), 73 (27), 69 (11), 61 (20), 59 (11), 55 (14), 45 (14), 43 (100). Anal. Calcd for $C_{16}H_{30}O_6Si$: C, 55.46; H, 8.73. Found: C, 55.31; H, 8.81.

2,5-Anhydro-1-O-diethylmethylsilyl-3,4-O-(1-methylethylidene)-D-altritol acetate (20α). ^1H NMR ($CDCl_3$) δ 0.09 (s, 3 H, $SiCH_3$), 0.57-0.64 (m, 4 H, CH_2Si), 0.96 (t, *J* = 7.9 Hz, 6 H, CH_3CSi), 1.33 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3CO), 3.78 (dd, *J* = 10.6, 6.5 Hz, 1 H, H6), 3.90 (dd, *J* = 10.6, 5.5 Hz, 1 H, H6'), 4.00-4.05 (m, 1 H, H1), 4.05 (dd, *J* = 11.6, 5.3 Hz, 1 H, H5'), 4.15 (dd, *J* = 11.6, 5.8 Hz, 1 H, H5), 4.26 (br t, *J* = 5.0 Hz, 1 H, H4), 4.66 (dd, *J* = 6.0, 1.3 Hz, 1 H, H3), 4.75 (dd, *J* = 6.0, 3.8 Hz, 1 H, H2); ^{13}C NMR ($CDCl_3$) δ -4.99 (CH_3Si), 6.21 (CH_2Si), 6.65 (CH_3CSi), 20.84 (CH_3CO), 25.10 (CH_3), 26.32 (CH_3), 61.25 (C1 or C6), 63.70 (C1 or C6), 81.02, 81.80, 82.29, 82.83 (C2, C3, C4, C5), 112.77 (OCO), 170.55 (C=O); IR ($CDCl_3$) 2950, 2870, 1740, 1460, 1375, 1250, 1170, 1095, 1045, 1010, 810; mass spectrum, *m/e* (rel intensity) 346 (0, M^+), 331 (21, M^+ - Me), 317 (70), 259 (55), 211 (23), 199 (100), 131 (65), 89 (53), 43 (81). Anal. Calcd for $C_{16}H_{30}O_6Si$: C, 55.46; H, 8.73. Found: C, 55.57; H, 9.02.

1-Deoxy-2,3-O-(1-methylethylidene)-D-ribofuranose acetate. (A reduction product found in eq 8, structure not shown in the text). ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3CO), 3.94 (dd, *J* = 10.6, 4.2 Hz, 1 H, H1), 4.00 (dd, *J* = 10.6, 1.6 Hz, 1 H, H1'), 4.06 (dd, *J* = 11.6, 4.9 Hz, 1 H, H5'), 4.14 (dd, *J* = 11.8, 6.1 Hz, 1 H, H5), 4.25 (ddd, *J* = 6.4, 4.6, 1.8 Hz, 1 H, H4), 4.59 (dd, *J* = 6.3,

1.8 Hz, 1 H, H3), 4.82 (ddd, J = 6.0, 4.4, 1.7 Hz, 1 H, H2); ^{13}C NMR ($CDCl_3$) δ 20.84 (CH_3CO), 25.10 (CH_3), 26.60 (CH_3), 63.31, 73.24 (C1 or C5), 81.17, 82.39, 82.40 (C2, C3, C4), 113.06 (OCO), 170.60 (C=O); IR ($CDCl_3$) 3150, 2990, 2945, 2880, 1745, 1470, 1395, 1385, 1240, 1220, 1165, 1115, 1100, 1080, 1050, 995, 865; mass spectrum, *m/e* (rel intensity) 216 (0, M^+), 201 (68, M^+ -Me), 81 (63), 69 (13), 59 (19), 57 (15), 43 (100). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.16; H, 7.58.

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21. We have designed a special apparatus for the handling of $HSiMe_3$, which has a low boiling point of 7.6 °C.[2b]