The First Tri- and Tetraalkoxysilanes with Four Different Substituents

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Unsymmetrically substituted tri- and tetraalkoxysilanes were surprisingly found to be configurationally stable and easy to prepare. It was found that compounds of type $MeSi(OR)_2(OR')$, $MeSi(OR)(OR')(OR'')$, $Si(OR)_2(OR')_2$, $Si(OR)_2(OR')(OR'')$, $Si(OR)_3(OR')$, and even $Si(OR)(OR')(OR'')(OR^*)$ could be obtained by sequential addition of a variety of chiral and achiral alcohols to methyltrichlorosilane or tetrachlorosilane in the presence of pyridine. In the case of $MeSi(OR)(OR')(OR'')$ and $Si(OR)(OR')(OR'')(OR^*)$, two types of compounds that have never been prepared before, were obtained in good yield.

Introduction

Silyl ethers have found great utility in organic synthesis not only as protecting groups[1a] but also as reagent in many different reactions.[1b] A particularly interesting use of silicon has been as a tethering agent to achieve various kinds of selectivity in organic synthesis.[2] However it has mainly been monoalkoxysilanes that have been employed in the various applications, while dialkoxysilanes have been much less used, and tri- and tetraalkoxysilanes not at all. This is intriguing because the synthetic potential of chiral tri- and tetraalkoxysilanes is tremendous. They might be employed as chiral tethers, chiral protection groups, or reagents. A chiral tether would allow not only regio- and diastereoselectivities but also enantioselectivity in the product after removal of the tether. Particularly compounds that could be made from tetrachlorosilane (**8**) or alkyltrichlorosilanes such as methyltrichlorosilane (**1**) and optically active alcohols from the chiral pool would be readily accesible and thus potentially be of great use.

Oligoalkoxysilanes have generally been known to be configurationally unstable and succeptible to hydrolysis and disproportionation. (Thus for example, $Si(OMe)_4$ reacts with water in an exothermic reaction.[3]) This view was supported by a search of the literature, which revealed that only symmetrical compounds of structure $MeSi(OR)_3$ and $Si(OR)_4$ were known with very few exceptions.[4,5] Most tri- and tetraalkoxysilanes known have been made with R being small aliphatic alkyl groups allowing products to be be isolated by distillation. Only one example with chiral alkoxygroups was known. Prey and Gump synthesized various symmetrically substituted alkoxysilanes of chiral alcohols. The most complex of these compounds were tri- and tetraalkoxysilanes with the alkoxy group of a carbohydrate derivative (Figure 1).[6] These compounds were obtained in quite low yields (shown in Figure 1).

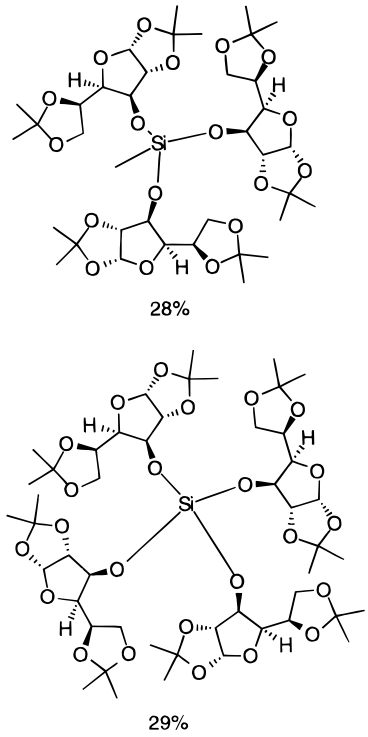

Figure 1.

In contrast, our experiences with dialkoxydimethylsilanes with bulky alkoxy groups had shown us that these compounds were rather stable compounds that could be subjected to chromatography.[7] We therefore have endeavored to investigate whether unsymmetrical alkoxysilanes could be made in good yields in a controlled manner and whether they would be configurationally or hydrolytically unstable or undergo spontaneous disproportionation. In this paper we report our findings, which surprisingly show that these compounds are completely stable and that it is even possible to prepare a tetraalkoxysilane with four different alkoxygroups. We

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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(2) Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253−1277.

(3) *Gmelins handbook of inorganic chemistry*, 8th ed; Verlag Chemie GMBH: Weinheim; Vol. 15c, pp 329−332.

(4) (a) Byk-Guldenwerke. German Patent DE 662732, 1933. (b) Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* **1980**, *186*, 13−17.

(5) (a) Onaka, M.; Higuchi, K.; Nanami, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2638−45. (b) Matsumoto, H.; Hoshino, Y.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1279−80. (c) Sakurai, H.; Ando, M.; Kawada, N. Sato, K.; Hosomi, A. *Tetrahedron Lett.* **1986**, *27*, 75−76. (d) Schraml, J.; Krapivin, A. M.; Luzin, A. P.; Kilesso, V. M.; Pestunovich, V. A. *Collect. Czech. Chem. Commun.* **1984**, *49*, 2897−2902. (e) Sekine, H. *Chem. Lett.* **1979**, 801. (f) Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1975**, *102*, 543−550.

(6) Prey, V.; Gump, K. -H. *Liebigs Ann. Chem.* **1965**, *682*, 228−241.

(7) Bols, M. *Tetrahedron* **1993**, *49*, 10049−10060 and references therein.

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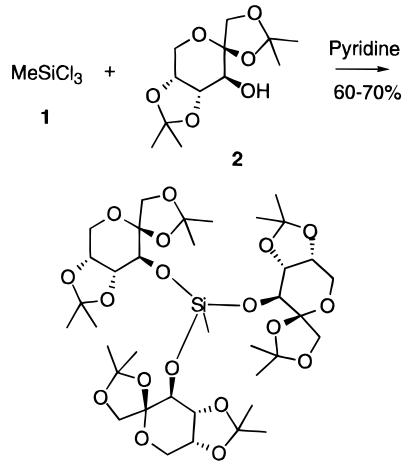
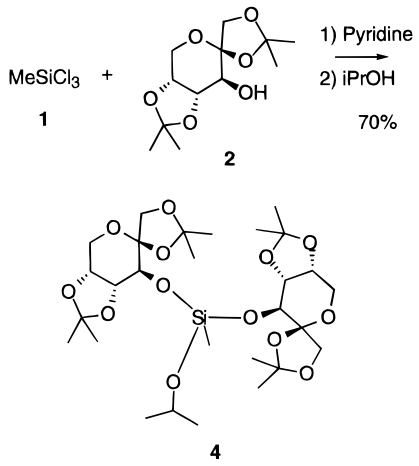
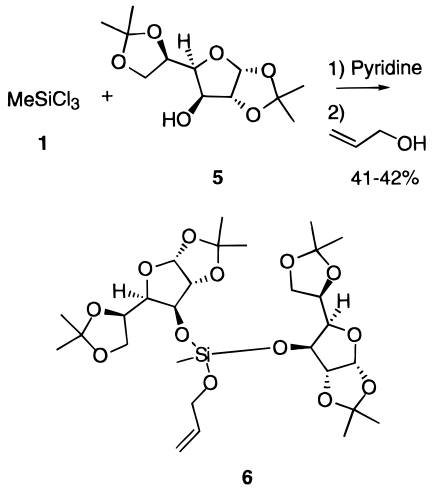
Scheme 1



Scheme 2



Scheme 3



demonstrate that simple chiral silyl protection groups can be created, which can be used to determine the ee of an alcohol.

Results and Discussion

We have undertaken a systematic investigation and, from **1** or **8**, attempted to synthesize all the possible types of unsymmetrically substituted alkoxysilanes (type 1−6): $MeSi(OR)_2(OR)$, $MeSi(OR)(OR')(OR'')$, $Si(OR)_2(OR')_2$, $Si(OR)_2(OR')(OR'')$, $Si(OR)_3(OR')$, and $Si(OR)(OR')(OR'')(OR^*)$. Compounds of type 1, 2, 4, and 6 have to our knowledge not previously been prepared. A few examples of type 3[4] and type 5 are known.[5] In the study we have employed chiral alcohols that could function as chiral auxillaries.

Compounds of Type $MeSi(OR)_3$. Initially we investigated a symmetrically substituted compound similar to those of Prey and Gump,[6] by reacting 1 molar equiv of **1** with 3.3 molar equiv of 1,2:4,5-diisopropylidene-D-fructopyranose (**2**) in pyridine (Scheme 1). This gave the trialkoxysilane **3** as the only observed product in 70% yield. This experiment showed two things. A trialkoxysilane like **3** was completely stable on TLC or flash chromatography, which was essential if unsymmetrical alkoxysilanes were to be made. Second, as our investigations with **5** (see also below) suggested that **5** substituted more readily on silicon than **2**, the low yield of methyltris(1,2:5,6-diisopropylidene-D-glucopyranyloxy)silane obtained by Prey and Gump must have been a result of the particulars of those reaction conditions. (Only a catalytic amount of pyridine was used, which may not have been enough to allow the reaction to run to completion. Furthermore, purification was carried out by a complicated series of sublimation, extraction, and distillation.[6])

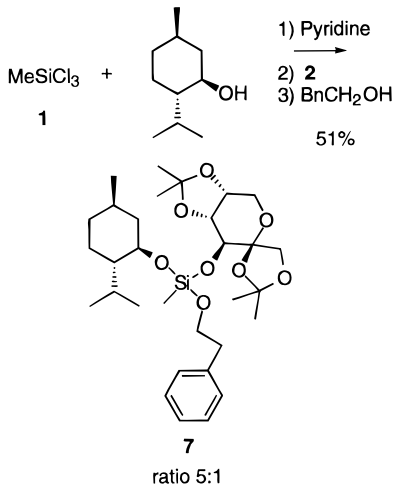
Compounds of Type $MeSi(OR)_2(OR')$. From TLC it became clear that **1** reacted with **2**, in the presence of pyridine, in a sequential manner, so that the silyl chloride $MeSi(OR)_2Cl$ (observed on TLC) could be formed with selectivity. When **1** and 2 molar equiv of **2** were reacted, and 1 molar equiv of 2-propanol was added later, mainly one product, **4**, was observed and isolated in 70% yield by flash chromatography (Scheme 2). Small amounts of the diisopropoxymonofructose derivative **4a** and **3** (7% each) were also isolated. This showed a high degree though not complete chemoselectivity in the substitution of the chlorides at silicon. The two fructose derivatives of **4** were nonidentical because of the prochiral nature of the silicon atom, and this could be observed by two different sets of signals of the fructose moities in the NMR spectrum. Similarly the spectrum of **4a** showed that the isopropoxy groups gave two sets of signals. This was interesting because it suggested that the fructose moiety had a considerable spacial influence on other substituents, which would be important in any application where stereoinduction was desired.

We also attempted sequential reaction of **1** with 2 molar equiv of 1,2:5,6-diisopropylidene-α-D-glucofuranose (**5**) and 1 molar equiv of prop-2-enol. In this case the reaction was less selective and the desired monopropenoxydiglucofuranose derivative **6** was obtained only in 41−42% yield after flash chromatography (Scheme 3). In addition a rather large amount (19%) of the triglucofuranose alkoxy-silane **6a** was obtained. Molecular models suggested that the steric hindrance around the silicon was reduced with **5** as a substituent compared to **2**. This lack of sterical hindrance probably made the sequential substitution less selective, by making the dialkoxychlorosilane more reactive than that in the above case. The fact that synthesis of this type of unsymmetrically substituted alkoxysilane was possible was particularly important because it opens wide opportunities for use in tethered reactions. When R* and R′ in trialkoxysilane $R^*Si(OR)_2(OR')$ could react and R was chiral, a potentially enantioselective reaction would occur.

Compounds of Type $MeSi(OR)(OR')(OR'')$. Given that the selectivity in the synthesis of **4** and **6** was limited, it could be anticipated that problems would arise

Figure 2. HPLC of **7** in 5% EtOAc in hexane on Nucleosil 50-5.

Scheme 4



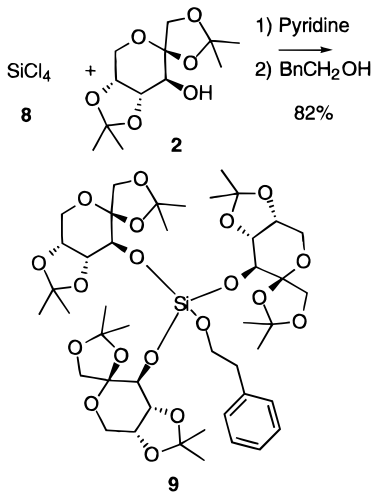
using the same method here. This was also the case. Sequential substitution to **1**, in the presence of pyridine, (−)-menthol, **2**, and phenethyl alcohol as well as many other alcohol combinations led to rather complex mixtures of trialkoxysilanes (Scheme 4). Probably the difference in reactivity between the two first chlorine atoms was too small to ensure clean formation of a monoalkoxysilane. We therefore turned to a method used previously by us for synthesis of unsymmetrical dimethyldialkoxysilanes.[7] The first alcohol, menthol, was reacted with excess **1**, and the excess **1** was removed by evaporation. Thus it was possible to get a solution of mono(menthyloxy)dichlorosilane in toluene and pyridine. Reaction of this compound with **2** followed by phenethyl alcohol now gave the mixed trisiloxane **7** relatively cleanly, and it could be isolated pure by flash chromatography in 51% yield.

Compound **7** was a mixture of two diastereoisomers at silicon. These could not be separated by flash chromatography or TLC, but the diastereomeric ratio could be measured by ^{13}C NMR. At 75 MHz small splittings of the signals (0.1 ppm) could be identified, consistant with a diasteomeric ratio of 5:1. This was confirmed by HPLC (Figure 2). It was interesting to note that **7** was not only a stable compound and its configuration at silicon remained unchanged on storage.

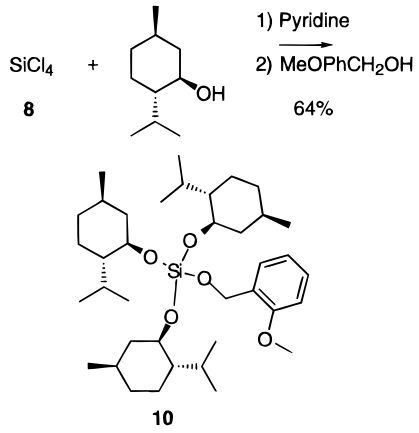
Nucleophilic substitution of silicon halides with oxygen nucleophiles generally gives inversion.[8] Thus the diastereomeric ratio in **7** should in principle depend on the order of addition of the alcohols. This was found to be true. When **1** was reacted with **2** first and then with (−)-menthol and finaly phenethyl alcohol, **7** was obtained

(8) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw-Hill Inc.: New York, 1965.

Scheme 5



Scheme 6

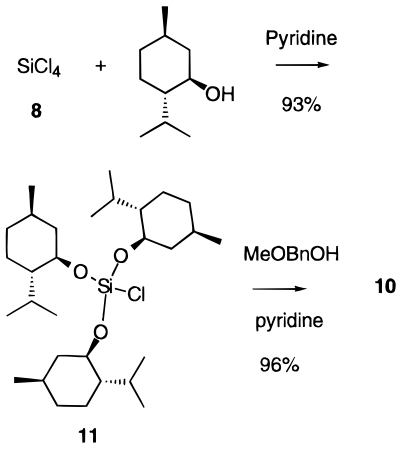


with a diastereomeric ratio of 1:2. Thus the diastereoisomer that previously had been minor isomer was now the major one. This suggested that the diastereomeric ratio was mainly determined by steric bias when ROSiMeCl$_2$ reacted with another alcohol. Interestingly this also suggests that there may be cases where alkoxysilanes with opposite stereochemistry at silicon can be made by a simple change in the order of addition of the reagents (in a one-pot reaction).

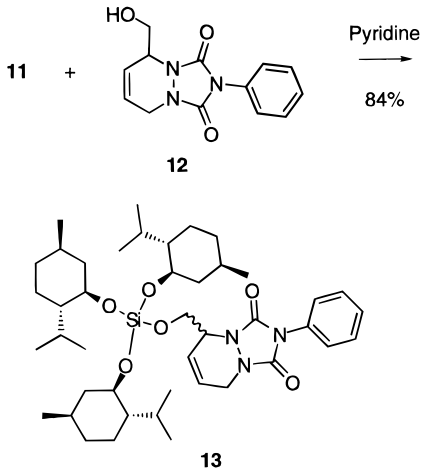
Compounds of Type Si(OR)$_3$(OR′). Stepwise reaction of 3 molar equiv of **2** and 1 molar equiv of phenethyl alcohol with tetrachlorosilane (**8**) in the presence of pyridine gave the expected tetraalkoxysilane **9** in 82% yield (Scheme 5). Similarly reaction of **8** with 3 molar equiv of menthol and 1 molar equiv of 2-methoxybenzyl alcohol gave the tetraalkoxysilane **10** in 64% yield (Scheme 6). This type of unsymmetrically substituted tetraalkoxysilane could potentially be useful as a chiral protection group. This was further explored.

We found that the tris(menthyloxy)silyl chloride **11** was quite stable and could be isolated. From **8** and 3 molar equiv of (−)-menthol, the trialkoxysilyl chloride **11** could be obtained in 93% yield (Scheme 7). This compound proved to be stable toward chromatography. (Interestingly this stability was very structure dependent as the corresponding trialkoxysilyl chlorides made from **2** or **5** decomposed during chromatography.) Compound **11** could be used as a reagent to silylate alcohols. Compound **11** reacted with 2-methoxybenzyl alcohol in pyridine and toluene to give **10** in 96% yield. Protection of the racemic alcohol **12**[9] with **11** gave the silylated

Scheme 7



Scheme 8



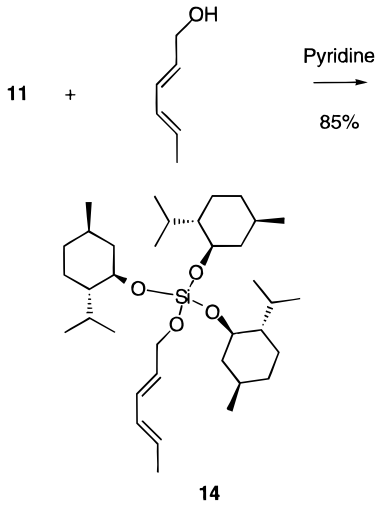
product **13** in 84% yield as a 1:1 mixture of diastereoisomers (Scheme 8). Note that the chiral silyl chloride had little selectivity for either enantiomer of **12**. The diastereomers could not be separated on TLC or coloumn, but were distinguishable in the ^{13}C NMR spectrum. Surprisingly there were no differences in the shifts from the pyridazine ring, but a 0.1 ppm splitting was observed at the C-1, C-2, and C-5 (the chiral centers) of the menthyloxy groups. Thus **11** could be used as a simple reagent for determining the ee of an alcohol.

The effect of using trialkoxysilyl groups as chiral auxillaries in a reaction was briefly explored. We carried out Diels−Alder reactions with two silylated sorbyl alcohols. Reaction of **11** with sorbyl alcohol gave chiral diene **14** in 85% yield (Scheme 9), while reaction of **8** with first 3 mol of **2** and then sorbyl alcohol gave **17** in 64% yield (Scheme 10). Diels−Alder reaction of **14** and **17** with 4-phenyl-1,2,4-triazoline-3,5-dione and maleic anhydride was then carried out (Scheme 11). The cycloadducts **15**, **16**, **18**, and **19** were obtained in good to excellent yield, but with no or in one case (**18**) low stereoselectivity (Scheme 11). The diastereomeric (pseudo-enantiomeric) ratio was readily determined by ^{13}C NMR. The cycloadducts of maleic anhydride (**16** and **19**) were obtained with total diastereomeric control with respect to giving the expected endo adducts.

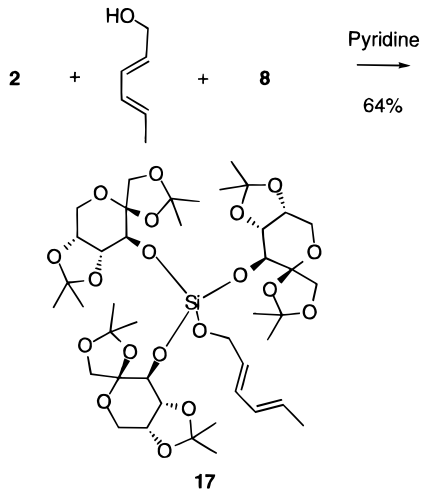
The ^{13}C NMR spectra of **17** and **18** showed differences in the signals of the two diastereoisomers of up to 0.4 ppm, while in **13**, **15**, and **16** only up to 0.1 ppm

(9) Bols, M.; Hazell, R.; Thomsen, I. *Chem. Eur. J.* **1997**, *3*, 940−7.

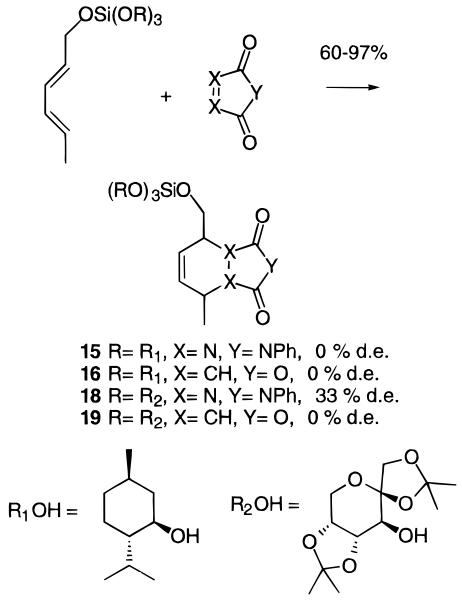
Scheme 9



Scheme 10

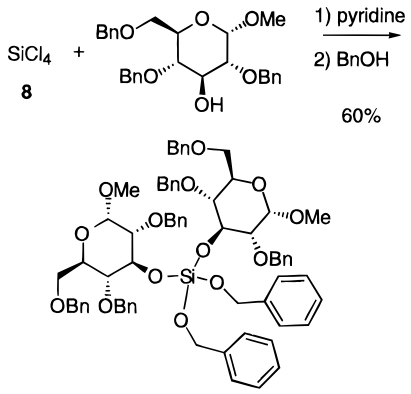


Scheme 11

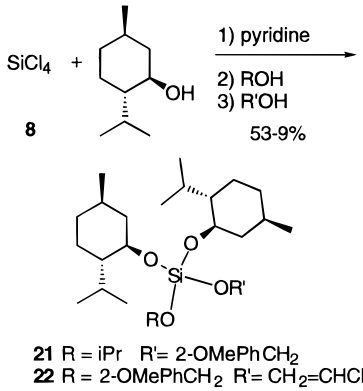


differences between diastereomeric signals was observed. This suggested that the fructose moity influenced its surroundings much more profoundly than a menthyloxy group. This could be the cause of the better stereoselectivity obtained with this group.

Scheme 12



Scheme 13



21 R = iPr R'= 2-OMePhCH$_2$
22 R = 2-OMePhCH$_2$ R'= CH$_2$=CHCH$_2$

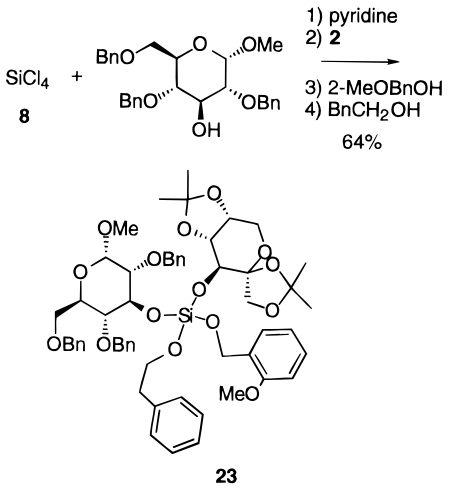
It may seem surprising that some stereoselectivity was observed in the reaction of **17** with 4-phenyl-1,2,4-triazoline-3,5-dione and not in the reaction of **17** with maleic anhydride, since the latter reaction was much slower which should favor selectivity. Inspection of molecular models of **18** and **19** suggested, however, that steric interaction between the Ph group and the fructose derivatives would occur in formation of **18**. The poor stereoselectivity (pseudo-enantioselectivity) in these reactions is probably a result of the freedom of rotation the silyl group and its substituents have, as different rotamers may induce different possibly opposite selectivity. More rigid silicon substituents (such as diols) might improve this.

Compounds of Type Si(OR)$_2$(OR′)$_2$. An example of this type of alkoxysilane was prepared by reacting **8** with 2 mol of readily available methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside followed by benzyl alcohol. Tetraalkoxysilane **20** was obtained in 60% yield (Scheme 12). Note that steric crowding around silicon is quite severe in **20**.

Compounds of Type Si(OR)$_2$(OR′)(OR″). Two compounds of this type were made. First **8** was reacted with 2 mol of menthol, then 2-propanol and finaly 2-methoxybenzyl alcohol to give tetraalkoxysilane **21** in 59% yield. When 2-propanol was substituted with 2-methoxybenzyl alcohol, and 2-methoxybenzyl alcohol was substituted with allyl alcohol, 53% of **22** was obtained (Scheme 13). The control of synthesis and stability of this type of derivative was particularly noteworthy as it allows precursors for tethered reactions to be made where R′OH and R″OH were reactants. This opens opportunities for a very easy way of carrying out enantioselective tethered reactions.

Compounds of Type Si(OR)(OR′)(OR″)(OR*). This was the most difficult tetraalkoxysilane to obtain pure

Scheme 14



in reasonable yield. The reaction with several alcohols gave complex mixtures suggesting that the difference in reactivity of the first, second, and third chlorine atom was quite small. We therefore employed the sterically demanding methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside as the first alcohol, anticipating that this group would slow further substitution.

This compound was reacted with excess **8** and pyridine, and the excess of **8** was removed by distillation. Then 1 equiv of **2**, 2-methoxybenzyl alcohol, and finaly phenethyl alcohol were added. This gave tetraalkoxysilane **23** in 62% yield after flash chromatography (Scheme 14). This compound had a chiral silicon atom, and ^{13}C NMR revealed that two diastereoisomers at silicon were present in a ratio of 5:1, which was confirmed by HPLC. The configuration remained constant on storage.

It is remarkable that an alkoxysilane of this complexity could be made in a one-pot reaction in so good a yield. This emphasizes the high degree of selectivity that can be obtained and the great possibilities of engineering chiral silyl groups from alkoxysilanes. Thus it may, in principle, be possible to synthesize chiral auxillaries from one set of chiral alcohols with opposite stereochemistry at silicon simply by a change in addition of reactants. Such pseudo-enantiomeric compounds might very well induce opposite enantioselectivity in a reaction, and this would be achieved without requiring the antipodes of the chiral alcohols.

All of the compounds prepared above were relatively insensitive to hydrolysis. They did however slowly hydrolyze in 10% aqueous THF. In the case of the comparable compounds **3** and **9**, hydrolysis of the tetraalkoxysilane **9** was faster. Hydrolysis of **9** was complete in 5 d at 25 °C, while conversion of **3** was 50% in the same timespan. This also suggests that oligoalkoxysilyl groups have a stability comparable to that of trimethylsilyl groups.

Conclusion. This work has surprisingly shown that unsymmetrical alkoxysilanes are stable compounds that can be isolated in pure form and do not undergo spontaneous decomposition or disproportionation. Even tri- and tetraalkoxysilanes with four different substituents could be made. They could readily be prepared from oligochlorosilanes by sequential addition of alcohols in the presence of pyridine. The fact that this type of compound is so readily available opens tremendous opportunities of using them as chiral protection groups or chiral tethers. In both cases it can be anticipated that

considerable investigation is required to identify those alkoxy groups necessary to obtain good stereoselectivity. We have demonstrated the use of chiral trialkoxysilyl groups as chiral protection groups, but in those cases no or small stereoinduction was obtained. The chiral auxilaries employed are perhaps too flexible, and the use of more rigid systems (such as, for example, C-2 symmetric diols as alkoxy substituents) might very well improve this. Research is in progress in our laboratory to try to solve this problem as well as investigations of the performance of these compounds in many other applications.

However one interesting observation was that the chiral trialkoxysilyl groups could be used for simple determination of the enantiomeric ratio of an alcohol by ^{13}C NMR. It was found that when the trialkoxysilyl group contained a carbohydrate derivative, particularly **2**, the largest differences between the ^{13}C signals of diastereoisomers were observed. With fructose groups differences of up to 0.5 ppm were observed on individual signals. As these compounds are extremely easy to prepare and have a stability close to a trimethylsilyl (TMS) group, they may find use as a chiral equivalent of a TMS group.

Experimental Section

General experimental procedures were as previously described.[9] The pyridine was dried over KOH.

Methyltris(1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)silane (3). To 0.100 mL of H_3CSiCl_3 (**1**, 0.85 mmol) and 0.663 g of 1,2:4,5-diisopropylidenefructopyranose (**2**, 2.55 mmol) in 25 mL of dry toluene was added 0.25 mL of dry pyridine, and the solution was stirred overnight. The solution was washed with water (5 mL), dried ($MgSO_4$), and evaporated. Chromatography in Et_2O/petroleum ether (1:4) gave 0.483 g of **3** (70%). The material could be recrystallized in MeOH. Mp 173 °C. ^1H NMR ($CDCl_3$): δ 4.33 (d, 3H, $J = 8.8$ Hz), 4.08−4.17 (m, 9H), 3.98 (d, 3H, $J = 13.2$ Hz), 3.90 (d, 3H, $J = 7.2$ Hz), 3.88 (d, 3H), 1.53 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H), 0.49 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 111.8 (3C), 108.9 (3C), 104.8 (3C), 77.6 (3C), 73.8 (3C), 71.5 (3C), 71.2 (3C), 60.2 (3C), 28.2 (3C), 26.6 (3C), 26.2 (3C), 26.1 (3C), −4.8. MS (EI) *m/z* 820 (M^+).

Bis(1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)-isopropoxymethylsilane (**4**). To 0.59 mL of H_3CSiCl_3 (**1**, 5.0 mmol) and 2.6 g of 1,2:4,5-diisopropylidenefructopyranose (10.0 mmol) in 25 mL of dry toluene was added 2 mL of dry pyridine, and the solution was stirred overnight. Then 0.38 mL (0.3 g, 5.0 mmol) of dry 2-propanol was added, and the mixture was left overnight. The precipitated pyridine hydrochloride was removed by filtration and the solution evaporated. Purification by flash column chromatography in Et_2O/petroleum ether (1:4) gave in the second fraction 2.19 g of **4** (70%) as a viscous liquid. The first fraction was 141 mg of diisopropoxy((1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)methylsilane (**4a**, 7%). A third fraction of 303 mg of **3** (7%) was also isolated. **4**. ^1H NMR ($CDCl_3$): δ 4.22−4.15 (m, 3H), 4.1−4.0 (m, 6H), 3.95−3.78 (m, 6H), 1.49, 1.43, 1.40, 1.39 1.33, 1.29, 1.25, 1.23 (8s, 24H), 1.1 (d, 6H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 111.7, 111.5, 108.7, 108.6, 104.8, 104.7, 77.5, 77.4, 73.7, 73.6, 71.6, 71.3, 71.1, 70.6, 65.2, 60.2, 60.0, 28.1, 28.0, 26.6, 26.3, 26.2, 26.1, 26.0, 25.9, 25.4, −5.0. MS (EI) *m/z* 620 (M^+). **4a**. ^1H NMR ($CDCl_3$): δ 4.25−4.08 (m, 6H), 3.97 (d, 1H, $J_{1a,1b} = 13$ Hz), 3.89 (d, 1H, $J_{5,6} = 6$ Hz), 3.87 (d, 1H, $J_{3,4} = 8$ Hz), 1.49, 1.46, 1.38, 1.32 (4s, 12H), 1.15 (2d, 12H), 0.18 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 111.8, 108.7, 105.0, 77.6, 73.8, 71.7, 70.8, 64.9, 60.2, 28.2, 26.6, 26.3, 26.1, 25.5, 25.4 (2s, 4C), −5.1.

(Allyloxy)bis((1,2:5,6-diisopropylideneglucofuranos-3-yl)oxy)methylsilane (6). To 0.30 mL of H_3CSiCl_3 (**1**, 2.54 mmol) and 1.33 g of 1,2:5,6-diisopropylideneglucofuranose (**5**, 5.11 mmol) in 50 mL of dry toluene was added 0.5 mL of dry pyridine. The solution was left stirring for 2 h whereupon 0.15 g (2.59 mmol) of dry allyl alcohol was added, and the reaction was left stirring overnight. The mixture was filtered and concentrated. Flash column chromatography of the residue in Et_2O/petroleum ether (1:4) gave in the first fraction 0.65 g of **6** (41%) as viscous liquid. A second fraction of 0.39 g of tris-(1,2:5,6-diisopropylideneglucofuranos-3-oxy)methylsilane (**6a**, 19%) was also obtained. **6**. ^1H NMR ($CDCl_3$): δ 5.9 (m, 1H), 5.84 (2d, 2H), 5.23 (dd, 1H, $J = 17$ Hz), 5.07 (dd, 1H, $J = 11$ Hz), 4.57 (bs, 2H), 4.46 (d, 1H, $J = 3.3$ Hz), 4.42 (d, 1H, $J = 3.8$ Hz), 4.30 (m, 2H), 4.23 (m, 2H), 4.1−3.9 (m, 6H), 1.44 (s, 6H), 1.36 (s, 6H), 1.29 (s, 6H), 1.26 (d, 6H), 0.22 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 136.0, 114.8, 111.7, 111.6, 109.0, 108.9, 105.1, 85.2, 81.8, 81.6, 75.2, 75.1, 72.2, 67.4, 67.3, 63.6, 26.7, 26.2, 25.1, 25.0, −6.7. MS (EI) *m/z* 618 (M^+). **6a**. ^1H NMR ($CDCl_3$): δ 5.87 (d, 3H, $J = 3.9$ Hz), 4.61 (d, 3H, $J = 2.2$ Hz), 4.47 (d, 3H, $J = 3.9$ Hz), 4.24 (m, 3H), 4.1−3.96 (m, 9H), 1.46 (s, 9H), 1.38 (s, 9H), 1.31 (s, 9H), 1.27 (s, 9H), 0.29 (s, 3H).

Methyl(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-oxy)((1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)(2-phenylethoxy)silane (**7**). To 1 mL of H_3CSiCl_3 (**1**, 8.5 mmol) and 0.20 g of (−)-menthol (1.28 mmol) in 25 mL of dry toluene was added 0.2 mL of dry pyridine, and the mixture was stirred for 1 h. Half the volume of the solution was removed by distillation and then refilled with toluene. Then 0.35 g of 1,2:4,5-diisopropylidenefructopyranose (**2**, 1.35 mmol) and 0.2 mL of dry pyridine were added at 0 °C, and the mixture was left overnight at rt. Next 0.20 mL of phenethyl alcohol (1.67 mmol) and 0.2 mL of pyridine was added, and the mixture was again stirred for 2 d. Filtration and evaporation followed by column chromatography (Et_2O/petroleum ether (1:4)) gave 0.39 g of **7** (51%). HPLC (Nucleosil 50-5, EtOAc−hexane 1:19) and ^{13}C NMR showed a 1:5 mixture of diastereomers. Major stereoisomer. ^1H NMR ($CDCl_3$): δ 7.31−7.20 (m, 5H), 4.23−3.86 (m, 9H), 3.71 (dt, 1H, $J = 4.4$ Hz), 2.87 (t, 2H, $J = 7.5$ Hz), 2.2 (m, 1H), 1.96 (bd, 1H), 1.62 (dt, 2H), 1.51, 1.49, 1.42, 1.35 (4s, 12H), 1.1−0.8 (m, 14H), 0.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.8, 129.0, 128.2, 126.1, 111.8, 108.8, 105.0, 77.7, 73.8, 72.5, 71.6, 70.9, 63.5, 60.2, 49.7, 44.9, 39.0, 34.4, 31.6, 28.1, 26.6, 26.3, 26.2, 25.4, 22.8, 22.2, 21.1, 15.7, −5.8. Minor stereoisomer. ^{13}C NMR ($CDCl_3$): identical to major except for δ 77.6, 73.7, 72.4, 71.0, 45.0, 25.2, 22.7, 15.6. MS (PDMS) *m/z* 578 (M^+), 563 ($M - CH_3$).

Alternatively, to 1 mL of H_3CSiCl_3 (**1**, 8.5 mmol) and 0.331 g of **2** (1.27 mmol) in 20 mL of dry toluene was added 0.2 mL of dry pyridine, and the mixture was stirred for 2 h. Half the volume of the solution was removed by distillation and then refilled with toluene. Then 0.2 g of (−)-menthol (1.28 mmol) and 0.2 mL of dry pyridine was added at 0 °C, and the mixture was left overnight at rt. Next 0.20 mL of phenethyl alcohol (1.67 mmol) and 0.2 mL of pyridine were added, and the mixture was stirred for 18 h. Filtration and evaporation followed by column chromatography (Et_2O/petroleum ether (1:4)) gave 0.33 g of **7** (43%), but in this case HPLC (Nucleosil 50-5, EtOAc−hexane 1:19) and ^{13}C NMR showed a 2:1 mixture of diastereomers.

(2-Phenylethoxy)tris((1,2:4,5-diisopropylidenefructo-pyranos-3-yl-oxy)silane (9). To 0.68 g of 1,2:4,5-diisopropylidenefructopyranose (**2**, 2.62 mmol) and 0.10 mL of $SiCl_4$ (0.87 mmol) in 25 mL of toluene was added 0.4 mL of pyridine, and the solution was stirred 1 h at 50 °C. Then 0.106 g of phenethyl alcohol (0.87 mmol)) was added at rt, and the mixture was stirred overnight. Filtration and column chromatography (Et_2O/petroleum ether (1:4)) gave crystalline **9** in 82% yield (0.76 g). The material could be recrystallized from MeCN. Mp 150 °C. ^1H NMR ($CDCl_3$): δ 7.3−7.1 (m, 5H), 4.3−4.1 (m, 17H), 3.96 (d, 3H, $J_{1a,1b} = 13$ Hz), 3.90 (d, 3H, $J_{5,6} = 7$ Hz), 2.93 (t, 2H), 1.52 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H). MS (EI) *m/z* 926 (M^+).

Chlorotris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-oxy)silane (**11**). To 2 mL of $SiCl_4$ (**8**, 17.4 mmol) and 8.17 g of (−)-menthol (52 mmol) in 80 mL of toluene was added 4.5 mL of pyridine, and the mixture was stirred 4 h at 50 °C. Then 100 mL of petroleum ether was added, and the mixture was filtered through a short column of silica and eluted with petroleum ether. Evaporation of the eluate gave 6.5 g of trimer

11 (70%) as an oil, which was sufficiently pure for further use. ^{1}H NMR ($CDCl_3$): δ 3.75 (dt, 3H), 2.2 (dp, 3H), 2.1 (bd, 3H), 1.6 (m, 6H), 1.4 (m, 3H), 1.1−0.8 (m, 12H), 0.9 (2d, 18H), 0.8 (d, 9H). ^{13}C NMR ($CDCl_3$): δ 74.5, 49.5, 44.3, 34.4, 31.6, 25.3, 22.7, 22.1, 21.2, 15.7. MS (EI) *m*/*z* 528 (M^+), 530 (M + 2).

((2-Methoxybenzyl)oxy)tris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)silane (10). To 0.10 mL of $SiCl_4$ (0.87 mmol) and 0.41 g of (−)-menthol (2.62 mmol) in 25 mL of toluene was added 0.25 mL of pyridine, and the mixture was stirred for 1 h at 50 °C. Then 0.120 g of 2-methoxybenzyl alcohol (0.87 mmol) was added, and the reaction was left overnight, while cooling to rt. Filtration and evaporation followed by column chromatography in CH_2Cl_2/petroleum ether (1:4) gave 354 mg (64%) of **10**. 25 mg of bis((2-methoxybenzyl)-oxy)bis(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-silane was obtained as the second fraction. **10**. ^{1}H NMR ($CDCl_3$): δ 7.5 (d, 1H), 7.2 (t, 1H), 7.0 (t, 1H), 6.8 (d, 1H), 4.9 (s, 2H), 3.8 (s, 3H), 3.7 (dt, 3H), 2.3 (dp, 3H), 2.1 (bd, 3H), 1.6 (m, 6H), 1.4 (m, 3H), 1.2−0.8 (m, 12H), 0.9 (2d, 18H), 0.8 (d, 9H). MS (EI) *m*/*z* 630 (M^+).

Alternatively 0.276 g of (2 mmol) 2-methoxybenzyl alcohol and 2.2 g of **11** (4.15 mmol) in 40 mL of toluene was added to 0.4 mL of pyridine, and the mixture was stirred for 3 h. Filtration and evaporation followed by column chromatography in CH_2Cl_2/petroleum ether (1:4) gave 1.21 g (96%) of **10**.

(((8-Phenyl-7,9-dioxo-1,6,8-triaza[4.3.0]bicyclonon-3-en-2-yl)methyl)oxy)tris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)silane (13). To a solution of 0.260 g of **12**[7] (1.0 mmol) and 1.0 g of **11** (1.89 mmol) in 20 mL of toluene was added 0.2 mL of pyridine, and the solution was stirred overnight. The solution was filtered through silica with toluene, evaporated, and column chromatographed in Et_2O/petroleum ether (1:2) giving 0.630 g of **13** (84%). ^{1}H NMR ($CDCl_3$): δ 7.5−7.2 (m, 5H), 5.95 (d, 2H), 4.55 (bs, 1H), 4.2 (d, 1H), 4.0 (m, 3H), 3.8 (m, 3H), 2.1 (m, 3H), 1.9 (bd, 3H), 1.5 (dt, 6H), 1.2−0.8 (m, 15H), 0.8 (2d, 18H), 0.7 (d, 9H). ^{13}C NMR ($CDCl_3$): δ 152, 150, 131, 128.8, 127.7, 125.1, 123.8, 120, 73.4, 73.3 (3C), 62.1, 54.7, 49.6, 49.5 (3C), 44.7 (3C), 43.3, 34.4 (3C), 31.6, 31.5 (3C), 25.2 (3C), 22.6 (3C), 22.2 (3C), 21.1 (3C), 15.5 (3C). MS (PDMS) *m*/*z* 751 (M^+).

((*E*,*E*)-Hexa-2,4-dienyloxy)tris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)silane (14). To 1.5 g of **11** (2.83 mmol) and 0.20 mL of sorbyl alcohol (1.77 mmol) in 20 mL of toluene was added 3 mL of pyridine, and the mixture was left stirring overnight. The solution was filtered through silica with toluene, and the filtrate was evaporated. The residue was purified using column chromatography in petroleum ether. First eluted was the starting material when eluting with petroleum ether, whereafter **14** was eluted with 1% Et_2O in petroleum ether. Yield of **14**: 0.890 g (85%). ^{1}H NMR ($CDCl_3$): δ 6.3−6.0 (m, 2H), 5.75−5.55 (m, 2H), 4.35 (d, 2H), 3.7 (dt, 3H), 2.3 (dp, 3H), 2.1 (bd, 3H), 1.8 (d, 3H), 1.6 (m, 6H), 1.4−1.0 (m, 15H), 0.9 (2d, 18H), 0.8 (d, 9H). ^{13}C NMR ($CDCl_3$): δ 131.2, 130.3, 129.3, 128.6, 73.3 (3C), 63.5, 49.8 (3C), 44.8 (3C), 34.5 (3C), 31.7 (3C), 25.2 (3C), 22.7 (3C), 22.2 (3C), 21.2 (3C), 18.1, 15.6 (3C).

((((2,5-*cis*)-5-Methyl-8-phenyl-7,9-dioxo-1,6,8-triaza[4.3.0]-bicyclonon-3-en-2-yl)methyl)oxy)tris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)silane (15). A solution of 30 mg of *N*-phenylurazole (0.17 mmol) and 18 mg of *t*-BuOCl (0.17 mmol) in 2 mL of EtOAc was degassed by being purged with N_2 for 15 min. Then 100 mg of **14** (0.17 mmol) dissolved in 5 mL of EtOAc was added to the red solution, and the red color disappeared. The solution was evaporated, and the residue was column chromatographed in Et_2O/petroleum ether (1:4) giving 121 mg (93%) of **15**. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 5H), 6.0 (d, 1H), 5.9 (dd, 1H), 4.5 (bs, 2H), 4.35 (2dd, 1H), 4.05 (2dd, 1H), 3.7 (dt, 3H), 2.2 (dp, 3H), 2.0 (bd, 3H), 1.6 (d, 6H), 1.5 (d, 3H), 1.4−1.0 (m, 15H), 0.9 (2d, 18H), 0.8 (d, 9H). ^{13}C NMR ($CDCl_3$): δ 151.6, 128.9, 127.8, 127.6, 127.5, 125.3, 123.0, 73.4, 73.3 (3C), 63.2, 55.5, 55.4, 50.2, 50.1, 49.6 (3C), 44.7, 44.6 (3C), 34.4 (3C), 31.6 (3C), 25.2 (3C), 22.6 (3C), 22.2 (3C), 21.2 (3C), 19.1, 15.6 (3C). MS (PDMS) *m*/*z* 765 (M^+).

(((5-Methyl-7,9-dioxo-8-oxa[4.3.0]bicyclonon-3-en-2-yl)-methyl)oxy)tris(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)silane (16). To 100 mg of **14** (0.17 mmol) in 2 mL of CH_2Cl_2 was added 17 mg of maleic anhydride (0.17 mmol), and the solution was left stirring in the dark for 7 d. The solvent was evaporated, and the residue was column chromatographed in Et_2O/petroleum ether (1:4) giving 98 mg (84%) of **16**. ^{1}H NMR ($CDCl_3$): δ 5.95 (m, 1H), 5.8 (dt, 1H), 4.25 (dd, 1H, $J_{6'a6'b}$ = 10.4, $J_{66'a}$ = 7.1 Hz), 4.15 (2dd, 1H), 3.7 (dt, 3H), 3.5 (dd, 1H, $J_{1,5}$ = 9.3, $J_{5,6}$ = 6 Hz), 3.3 (dd, 1H, $J_{1,9}$ = 7.4 Hz) 2.5 (m, 2H), 2.3 (p, 3H), 2.0 (bd, 3H), 1.6 (d, 6H), 1.4 (d, 3H), 1.4−1.0 (m, 15H), 0.9 (2d, 18H), 0.8 (d, 9H). ^{13}C NMR ($CDCl_3$): δ 134.4, 134.3, 130.9, 73.4 (3C), 62.5, 49.6 (3C), 45.9, 44.7 (3C), 43.0, 42.9, 38.5, 38.4, 34.4 (3C), 31.6 (3C), 30.7, 30.6, 25.2 (3C), 22.6 (3C), 22.2 (3C), 21.2 (3C), 16.4, 15.6 (3C). MS (EI) *m*/*z* 688 (M^+).

((*E*,*E*)-Hexa-2,4-dienyloxy)tris((1,2:4,5-diisopropylidene-fructopyranos-3-yl)oxy)silane (17). To 1.36 g of 1,2:4,5-diisopropylidenefructopyranose (**2**, 5.23 mmol) and 0.2 mL of $SiCl_4$ (**8**, 1.74 mmol) was added 0.8 mL of pyridine, and the mixture was stirred for 3 h at 50 °C. Then 0.27 mL of sorbyl alcohol (2.38 mmol) was added. The solution was filtered and evaporated. Column chromatography in Et_2O/petroleum ether (1:3) gave first bis((*E*,*E*)-hexa-2,4-dienyloxy)bis(1,2:4,5-diisopropylidenefructopyranos-3-oxy)silane (230 mg, 18%) and second 1.00 g (64%) of **17**. ^{1}H NMR ($CDCl_3$): δ 6.1 (m, 2H), 5.6 (m, 2H), 4.4 (d, 2H), 4.2−3.9 (m, 21H), 1.7 (d, 3H), 1.5 (s, 9H), 1.45 (s, 9H), 1.35 (s, 9H), 1.3 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 131.0, 130.9, 129.2, 128.9, 111.4 (3C), 108.9 (3C), 104.5 (3C), 76.6 (3C), 73.6 (3C), 72.0 (3C), 71.9 (3C), 64.4, 60.8 (3C), 27.9 (3C), 26.3 (6C), 26.0 (3C), 18.0. MS (EI) *m*/*z* 902 (M^+).

((((2,5-*cis*)-5-Methyl-8-phenyl-7,9-dioxo-1,6,8-triaza[4.3.0]-bicyclonon-3-en-2-yl)methyl)oxy)tris((1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)silane (18). *N*-phenylurazol (30 mg) and 25 mg of *tert*-butyl hypochlorite in 10 mL of EtOAc was degassed by being purged with N_2 for 15 min. Then 150 mg of **17** dissolved in EtOAc was added to the red solution causing the red color to disappear. The solution was evaporated, and the residue was column chromatographed in Et_2O/petroleum ether (3:1) giving 175 mg (97%) of **18**. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 5H), 6.1 (m, 1H), 5.8 (m, 1H), 4.6 (m, 2H), 4.5 (m, 2H), 4.3−3.9 (m, 7H), 1.55 (d, 9H), 1.5 (d, 3H), 1.4 (s, 3H), 1.35 (s, 9H), 1.25 (s, 9H). ^{13}C NMR ($CDCl_3$): major isomer, δ 152.0, 151.5, 131.2, 128.9, 127.8, 127.6, 125.3, 123.0, 111.3 (3C), 108.9 (3C), 104.4 (3C), 76.4 (3C), 73.6 (3C), 72.3 (3C), 72.1 (3C), 63.9, 60.8 (3C), 55.2, 50.6, 27.9 (3C), 26.4 (3C), 26.1 (3C), 26.0 (3C), 19.1; minor isomer, δ 152.4, 151.1, 131.2, 128.9, 127.8, 127.6, 125.5, 122.8, 111.4 (3C), 108.8 (3C), 104.5 (3C), 76.4 (3C), 73.7(3C), 72.4(3C), 72.0 (3C), 64.0, 60.7 (3C), 54.8, 51.0, 28.0 (3C), 26.4 (3C), 26.1 (3C), 26.0 (3C), 19.4. MS (EI) *m*/*z* 1077 (M^+).

(((5-Methyl-7,9-dioxo-8-oxa[4.3.0]bicyclonon-3-ene-2-yl)methyl)oxy)tris(1,2:4,5-diisopropylidenefructopyranos-3-yl)oxy)silane (**19**). To 150 mg of **17** (0.17 mmol) in 2 mL of EtOAc was added 16 mg of maleic anhydride (0.16 mmol), and the mixture was left to stir in the dark for 7 d. The solvent was evaporated, and the residue was subjected to column chromatography (Et_2O/petroleum ether (1:1)) to give 100 mg (60%) of **19**. ^{13}C NMR ($CDCl_3$): δ 171.4, 134.3, 134.2, 131.3, 131.0, 111.53, 111.48 (3C), 108.90, 108.87 (3C), 104.60, 104.56 (3C), 76.7 (3C), 73.6 (3C), 72.4 (3C), 72.1, 72.0 (3C), 63.6, 63.4, 60.84, 60.78 (3C), 46.0, 45.9, 43.0, 42.8, 38.2, 38.1, 30.6, 30.5, 28.0 (3C), 26.4 (3C), 26.1 (3C), 26.0 (3C), 16.4. MS (EI) *m*/*z* 1024 (M + Na).

Bis(benzyloxy)bis((1-*O*-methyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranos-3-yl)oxy)silane (20). To a solution of 125 mg of methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside in 10 mL of toluene was added first 0.17 mL of a 9.1% $SiCl_4$ (v/v) in toluene solution and then 0.2 mL of pyridine. After the solution was stirred for 1 h, 0.03 mL of BnOH was added to the reaction mixture, and the mixture was left to stir overnight. The mixture was filtered and concentrated. Column chromatography in Et_2O/petroleum ether (1:1) gave 95 mg (60%) of **20**. ^{1}H NMR ($CDCl_3$): δ 7.2−7.4 (m, 40H), 5.1 (d, 2H), 4.9 (d, 4H), 4.4−4.8 (m, 14H), 3.4−3.8 (m, 10H), 3.3 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 140.4, 138.7, 137.8, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 127.1, 126.5, 126.3, 98.0, 80.0, 78.4, 75.4, 74.2, 73.4, 73.1, 69.6, 68.6, 65.1, 54.9.

Bis(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-((2-methoxybenzyl)oxy)isopropoxysilane (21). To a solution of 0.10 mL of $SiCl_4$ (**8**, 0.87 mmol) and 272 mg of (−)-menthol (1.74 mmol) in 15 mL of toluene was added 0.2 mL of pyridine at −78 °C, and the solution was left stirring for 15 min, whereafter it was allowed to warm to rt. Then 52 mg of 2-propanol (0.87 mmol) and 0.1 mL of pyridine in 4 mL toluene were added. The mixture was stirred for 20 min, and then 120 mg of 2-methoxybenzyl alcohol (0.86 mmol) and 0.1 mL of pyridine were added. The mixture was stirred 18 h and then filtered and concentrated. Column chromatography in ether−pentane (1:1) gave 275 mg (59%) of **21**. ^{13}C NMR ($CDCl_3$): δ 156.1, 129.3, 127.5, 127.1, 120.2, 109.5, 73.28, 73.25 (2C), 65.9, 60.1, 55.0, 49.7 (2C), 44.7 (2C), 34.5 (2C), 31.6 (2C), 25.3 (2C), 25.2 (2C), 22.8 (2C), 22.2 (2C), 21.2 (2C), 15.7 (2C). MS (EI) *m*/*z* 534 (M^+).

(Allyloxy)bis(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)((2-methoxybenzyl)oxy)silane (22). A solution of 0.10 mL of $SiCl_4$ (**8**, 0.87 mmol) in 15 mL of toluene was slowly added to a solution of 272 mg of (−)-menthol (1.74 mmol) and 0.15 mL of pyridine in 5 mL of toluene. The solution was left stirring for 1 h, and then 120 mg of 2-methoxybenzyl alcohol (0.86 mmol) and 0.1 mL of pyridine in 5 mL of toluene were added. The mixture was stirred overnight, and then a solution of 51 mg of allyl alcohol (0.88 mmol), and 0.1 mL of pyridine in 2 mL of toluene was added. The mixture was stirred overnight and then filtered and concentrated. Column chromatography in ether−pentane (1:1) gave 248 mg (53%) of **22**. ^1H NMR ($CDCl_3$): δ 7.4 (d, 1H), 7.1 (t, 1H), 6.9 (d, 1H), 6.7 (d, 1H), 5.9 (m, 1H), 5.2 (dd, 1H), 5.0 (dd, 1H), 4.8 (s, 2H), 4.2 (m, 2H), 3.7 (s, 3H), 3.6 (h, 2H), 2.2 (m, 2H), 2.0 (m, 2H), 1.5 (m, 4H), 1.3 (m, 2H), 1.1 (m, 2H), 0.8−1.0 (m, 6H), 0.8 (d, 12H), 0.7 (d, 6H). MS (EI) *m*/*z* 532 (M^+).

((1,2:4,5-Diisopropylidenefructopyranos-3-yl)oxy)((2-methoxybenzyl)oxy)((1-*O*-methyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranos-3-yl)oxy)(2-phenylethoxy)silane (23). A solution of 1.0 mL of $SiCl_4$ (**8**) in 35 mL of toluene was mixed with 465 mg of methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (1 mmol) and 0.2 mL of pyridine and stirred for 2 d. The solution was concentrated to half volume by distillation at reduced pressure, and 260 mg of **2** (1 mmol) and 0.2 mL of pyridine were added. The mixture was stirred for 4 d. Next 138 mg of 2-methoxybenzyl alcohol (1 mmol) was added, and stirring was continued for 18 h. Finally 122 mg of phenethyl alcohol (1 mmol) was added, and the mixture was stirred for 4 h. The mixture was then filtered and concentrated. Column chromatography in ether−pentane (1:2) gave 630 mg (62%) of **23**. HPLC (Nucleosil 50-5 in EtOAc−hexane 1:3) revealed a 5:1 mixture of diastereoisomers at silicon. ^1H NMR ($CDCl_3$): δ 7.6 (d, 1H), 7.2−7.4 (m, 21H), 7.0 (t, 1H), 6.8 (d, 1H), 5.15 (s, 2H), 5.1 (d, 1H), 4.9 (d, 1H), 4.6 (m, 6H), 4.5 (d, 1H) 4.2−4.4 (m, 7H), 3.9 (d, 1H), 3.8 (s, 3H), 3.75 (m, 4H), 3.6 (dd, 1H), 3.3 (s, 3H), 2.9 (t, 2H), 1.6 (s, 3H), 1.55 (s, 3H), 1.5 (s, 3H), 1.4 (m, 3H). ^{13}C NMR ($CDCl_3$): major stereoisomer, δ 155.8, 138.6, 138.5, 138.4, 137.7, 126.9−128.8, 125.8, 120.0, 111.5, 109.1, 108.6, 104.6, 97.7, 79.8, 78.1, 76.9, 75.2, 74.0, 73.6, 73.2, 72.8, 71.4, 71.3, 69.3, 68.5, 64.5, 60.7, 60.1, 54.7 (2C), 38.5, 27.9, 26.7, 26.2, 25.9; minor stereoisomer, same as major except for δ 155.8, 109.2, 26.8. MS (PDMS) *m*/*z* 1032 (M + Na).

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Supporting Information Available: NMR peak assignments and ^{13}C NMR spectra of compounds **3**−**4**, **6**−**7**, **9**−**11**, and **13**−**23** (25 pages). This material is contained in libraries on microfiche, immidiatly follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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