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# SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS. 40.[1] METALATED (ALLYL)AMINOSILANES: A γ-REGIOSELECTIVE REACTION WITH ALDEHYDES AND AN APPROACH TO THE SYNTHESIS OF 2-DEOXY-C-NUCLEOSIDE SKELETONS

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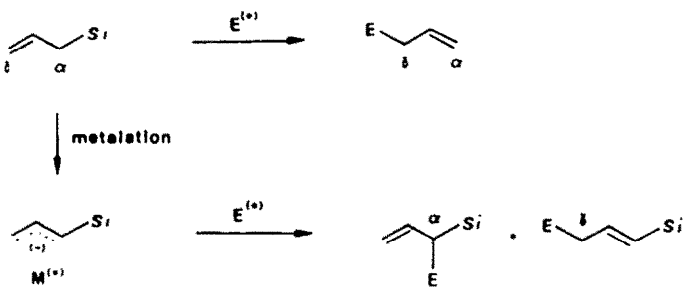
Abstract: An organocopper reagent, derived from allyl(diethylamino)dimethylsilane via metalation by n-BuLi/TMEDA followed by transmetalation, reacts with aldehydes regioselectively at the γ position to form 1-substituted (E)-3-buten-1-ol derivatives. Epoxidation of the double bond followed by hydrogen peroxide cleavage of the carbon-silicon bond affords 2,3-dihydroxy-tetrahydrofuran derivatives, which are further transformed into 2-deoxy-C-nucleoside skeletons via siloxymethylation at the anomeric position. One model system is presented, together with the stereochemical aspects.

Allylsilanes are now well recognized as useful synthetic reagents which react with electrophiles regioselectively at γ to silicon via cleavage of the silicon-carbon bond.[2] Metalation of allylsilanes and the subsequent reactions with electrophiles constitute another useful reaction, but an α vs. γ regiochemical problem arises, as shown in Scheme I.[3]

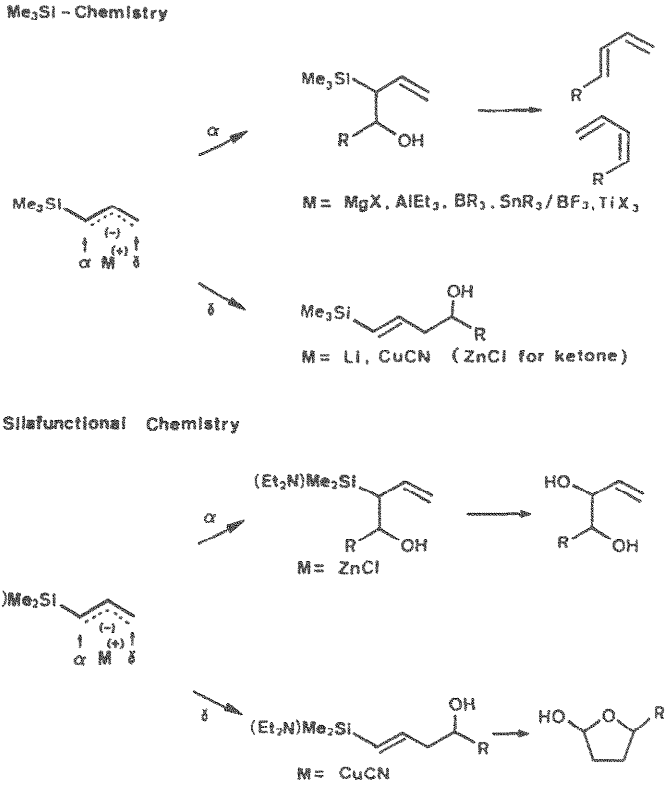
Scheme I




The regioselectivity is greatly dependent on the nature of electrophiles, counter cations, and the steric bulkiness of the silyl group.[3i,j] In the reaction with carbonyl compounds, the regioselectivity has been controlled mainly by changing the counter cation, as briefly summarized in Scheme II. The synthetic application of the α products has so far been limited only to the stereoselective synthesis of 1,3-dienes, while the γ products have been transformed into γ-lactones.[3b] The hitherto so limited synthetic applicability is apparently owing to the use of triorganosilyl, such as trimethylsilyl and triphenylsilyl,[3f] derivatives.

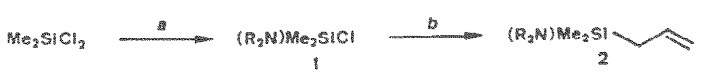
We have developed some unprecedented transformations in this field by using (allyl)aminosilanes, in which the aminosilyl groups are eventually converted to the hydroxy group by the hydrogen peroxide oxidation,[4] as shown in Scheme II. In our previous paper[5] we have reported that a zinc reagent derived from the allylsilane reacts with aldehydes regio- and stereo-selectively to form the α-erythro products which are oxidized to erythro-1,2-diol skeletons. This paper is concerned with the γ regioselective reaction of the corresponding copper reagent and the subsequent transformation into 2-deoxy-C-nucleoside skeletons.

Scheme II



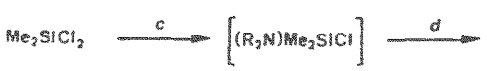

## RESULTS AND DISCUSSION

**Preparation of (Allyl)aminosilanes.** (Allyl)aminosilanes 2a-2c were prepared in two steps from $Me_2SiCl_2$ via partial amination and allylation of the remaining silicon-chlorine bond with the allyl Grignard reagent, as shown in eq (1). In the first step, the introduction of diethylamino and 1-pyrrolidinyl group proceeded smoothly, while diisopropylamine reacted sluggishly with $Me_2SiCl_2$, the monoamination being achieved in the presence of three molar excess of the amine under reflux of THF. Noteworthily, an attempted amination with lithium diisopropylamide (LDA) resulted in no reaction even at room temperature, whereas lithium diethylamide (1 equiv) reacted readily with $Me_2SiCl_2$ at 0 °C to form 1 selectively. Allylsilane 2a could thus be prepared in a one-pot procedure as shown in eq. (2). By this one-pot procedure 2d was also prepared (eq. 2). These (allyl)aminosilanes 2 were decomposed with water, but were all reasonably stable and could be handled in the air for a short period.




(1)

| | | | | | |
|---|---|---|---|---|---|
| 1a: | R = Et | 77% | 2a: | R = Et | 90% |
| 1b: | $R_2$ = -$(CH_2)_4$- | 62% | 2b: | $R_2$ = -$(CH_2)_4$- | 93% |
| 1c: | R = i-Pr | 82% | 2c: | R = i-Pr | 94% |

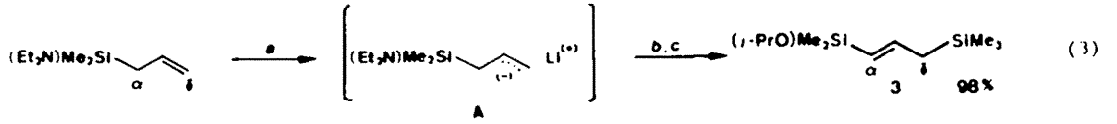



(2)

| | | |
|---|---|---|
| 2a: | $R_2N$ = $Et_2N$ | 55% |
| 2d: | $R_2N$ = $Me_2N(CH_2)_2NMe$ | 50% |

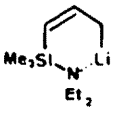
[a] $R_2NH$, $Et_3N$, THF. [b] $CH_2$=$CHCH_2MgCl$, $Et_2O$. [c] $R_2NLi$, THF, 0 °C. [d] $CH_2$=$CHCH_2MgBr$, $Et_2O$.

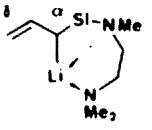
**Metalation and Regiocontrol.** Metalation of 2a was achieved readily by treatment with a hexane solution of n-BuLi (1.3 equiv) in ether in the presence of TMEDA (1 equiv) as an essential additive at 0 °C for 3 h. Quenching with $Me_3SiCl$ (3 equiv) followed by i-PrOH gave 3 in a quantitative yield (eq 3). The amino group on silicon was replaced by the i-PrO group by the final treatment with i-PrOH, in view of the compatibility of the $(i\text{-PrO})Me_2Si$ group to the usual, mild hydrolysis work-up. It should be noted here that in 3 the trimethylsilyl group was attached to the γ carbon regioselectively, no trace of α product being observed. Furthermore, the double bond in 3 was exclusively E ($J$ = 18.3 Hz). This implies that the metalated species may exist as the structure (A), without formation of a possible intramolecular chelation like (B). THF as a metalation solvent afforded somewhat lower yields (87% yield of 3), while no metalation occurred in hexane even in the presence of TMEDA.




(3)

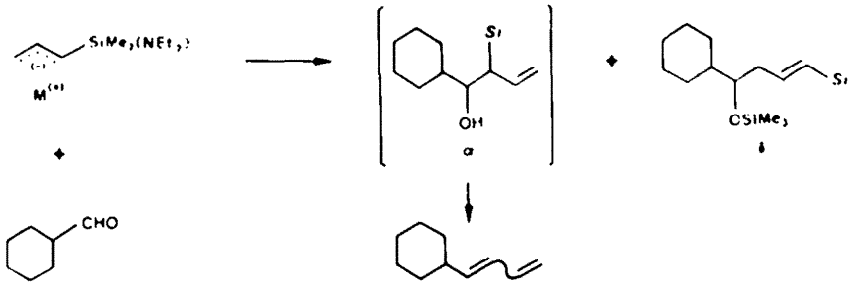
[a] n-BuLi, TMEDA, $Et_2O$, 0 °C, 3 h. [b] $Me_3SiCl$, 0 °C, 2 h. [c] i-PrOH, room temp, 12 h.




Regioselectivities of the reaction of metalated 2a with aldehydes were examined with variation of the counter cations which were changed by addition of an appropriate metal salt to the lithiated species. The α : γ ratios observed with cyclohexanecarboxaldehyde are summarized in Table I.

Table I. Regioselectivity in the reaction of metalated (allyl)(diethylamino)-dimethylsilane with cyclohexanecarboxaldehyde (Effect of counter cation)



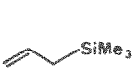

| entry | Reaction Conditions[a] | α : γ [b] |
|---|---|---|
| 1 | n-BuLi/TMEDA/0°C | 25 : 75 |
| 2 | n-BuLi/TMEDA/$MgBr_2$/0°C | 100 : 0 |
| 3 | n-BuLi/TMEDA/$ZnCl_2$/0°C | >95 : <5 |
| 4 | n-BuLi/TMEDA/$Ti(O\text{-}i\text{-}Pr)_4$/0°C | >95 : <5 |
| 5 | n-BuLi/TMEDA/CuI/-78°C | 24 : 76 |
| 6 | n-BuLi/TMEDA/CuSCN/-78°C | 13 : 87 |
| 7 | n-BuLi/TMEDA/CuCN/-78°C | <5 : >95 |

[a] $Et_2O$ was used as solvent. [b] The ratio of α/γ was determined by GLC. The γ product was obtained as a mixture of (E)- and (Z)-1,3-dienes.

The lithium reagent itself showed the ratio of 1:3, while the addition of $ZnCl_2$, $MgBr_2$ or $Ti(O\text{-}i\text{-}Pr)_4$ resulted in almost exclusive α selectivity; the product in these cases was 1,3-dienes arising from the Peterson olefination. In contrast, copper salts favored the formation of the γ product, with CuCN the highest ratio α : γ = 1 : 15 being obtained. The high γ selectivity with the copper reagents was consonant with the results reported by Corriu for allyltrimethylsilane.[3g]

The regioselectivity was greatly dependent on the nature of the amino group on silicon, as shown in Table II. Thus, both with the lithium and with the copper reagent the γ selectivity

Table II. Regioselectivity in the reaction of metalated (allyl)(amino)-dimethylsilanes with aldehydes (Effect of amino group)

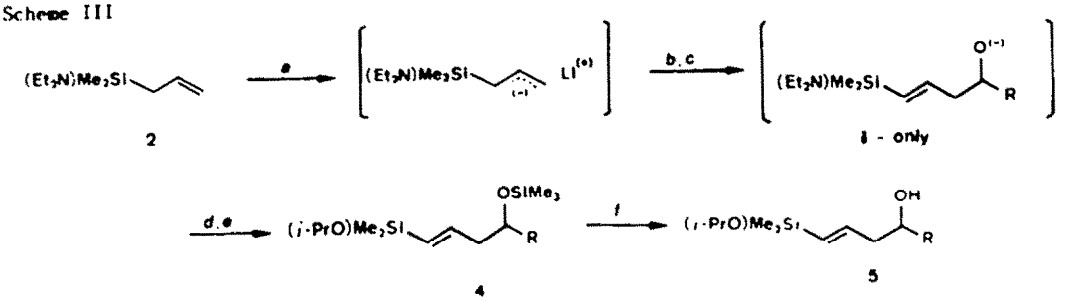
| Amino group | Reaction Condition[a] | $E^+$ | α : γ[b] |
|---|---|---|---|
|  | n-BuLi/TMEDA/0°C | PhCHO | 21 : 79 |
|  | n-BuLi/TMEDA/0°C | c-$C_6H_{11}CHO$[c] | 25 : 75 |
| | n-BuLi/TMEDA/-78°C | c-$C_6H_{11}CHO$[c] | 37 : 63 |
| | n-BuLi/TMEDA/CuCN/-78°C | PhCHO | <5 : >95 |
|  | n-BuLi/TMEDA/0°C | PhCHO | 40 : 60 |
| | n-BuLi/TMEDA/CuCN/-78°C | PhCHO | 78 : 22 |
|  | n-BuLi/0°C | c-$C_6H_{11}CHO$[c] | 0 : 100[d] |
| | n-BuLi/TMEDA/-70°C | c-$C_6H_{11}CHO$[c] | 0 : 100[d] |
|  | s-BuLi/TMEDA/-30°C | PhCHO | 17 : 83[e] |
| | s-BuLi/TMEDA/-76°C | p-TolCHO | 0 : 100[f] |

[a] $Et_2O$ was used as solvent. [b] The α/γ ratio was determined by GLC. The α product was obtained as a mixture of (E)- and (Z)-1,3-dienes in our study. [c] c-$C_6H_{11}CHO$ = cyclohexanecarboxaldehyde. [d] Yields were about 30%. [e] Ref. 3d. [f] Ref. 3b.

increased with a decrease of the steric bulkiness of the amino group, **2b** > **2a** > **2c**; highest with allyltrimethylsilane. With the lithium reagent from 2d only the γ product was obtained, but in rather low yield. The high γ selectivity in the last case may be due to the expected chelation by the dimethylamino group, as shown by (C). This may be supported by the fact that almost the same result was obtained by metalation of 2d in the absence of TMEDA which was essential for other non-chelating aminosilanes. Unfortunately, however, with 2b and 2d, displacement of the amino group by n-butyllithium in the metalation step occurred in substantial amounts. Consequently, the copper reagent derived from 2a was used in the present work.

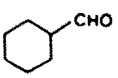
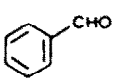
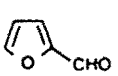
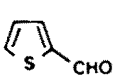
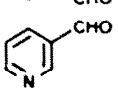
The standard reaction conditions are shown in Scheme III. With a variety of aldehydes products 4 were obtained in high yields, as summarized in Table III. It was essential to protect the hydroxy group by quenching with $Me_3SiCl$ followed by treatment with i-PrOH. 1,3-Dienes were formed in 5-15% yields in all cases and could be easily separated by Silica Gel chromatography. Attempts to isolate products without the trimethylsilylation failed; untractable mixtures resulted. The free alcohols 5 were however obtained from 4 by deprotection with i-PrOH in the presence of a catalytic amount of camphorsulfonic acid (CSA), except pyridyl derivative **4g** which required a stoichiometric amount of CSA.

Scheme III



a n-BuLi, TMEDA, $Et_2O$, 0 °C, 3 h. b CuCN, -78 °C, 1 h. c RCHO, -78~0 °C, 5 h.
d $Me_3SiCl$, 0 °C, 2 h. e i-PrOH, room temp, 12 h. f i-PrOH, CSA, room temp, 1 h.

Table III. Synthesis of Y-adducts 4 and 5 from allylsilane (2a) and aldehydes

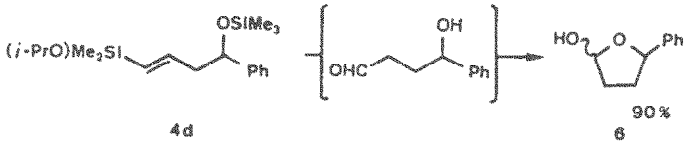
| Entry | RCHO | 4 | | | 5 | |
|---|---|---|---|---|---|---|
| | | No | R | Yield(%)[a] | No. | Yield(%) |
| 1 | $n$-$C_7H_{15}$CHO | 4a | $n$-$C_7H_{15}$ | 82[b] | 5a | 95 |
| 2 | ($n$-$C_4H_9$)(Et)CHCHO | 4b | ($n$-$C_4H_9$)(Et)CH | 60[b] | | — |
| 3 |  | 4c |  | 78[c,d] | | — |
| 4 |  | 4d |  | 94[c] | 5d | 91 |
| 5 |  | 4e |  | 75[c] | 5e | 89 |
| 6 |  | 4f |  | 57[c] | 5f | 95 |
| 7 |  | 4g |  | 76[c] | 5g | 58[c] |

a Isolated yield based on aldehyde, unless otherwise stated.
b α/γ = 1/5.6-5.7. The α products were obtained as the corresponding 1,3-dienes. c γ > 95%. Only trace amounts of 1,3-dienes were detected.
d GLC yield. e A stoichiometric amount of CSA was used.

**A Model System for 2-Deoxy-C-nucleoside Skeletons.** We have examined oxidative transformations of the γ-adduct with benzaldehyde and subsequent conversion into 2-deoxy-C-nucleoside skeletons as a model system.

**(1) Oxidative Transformations of 4 and 5.** Direct oxidation of 4d with 30% $H_2O_2$ in the presence of KF and $KHCO_3$[6] gave 6 in 90% yield (eq 4).

Epoxidation of 4d with MCPBA in dichloromethane and the subsequent oxidation of the carbon-silicon bond with hydrogen peroxide[7] gave 7 in only 30% overall yield. Since free homoallyl alcohols might undergo highly diastereoselective epoxidation,[8] the free alcohols 5 were subjected

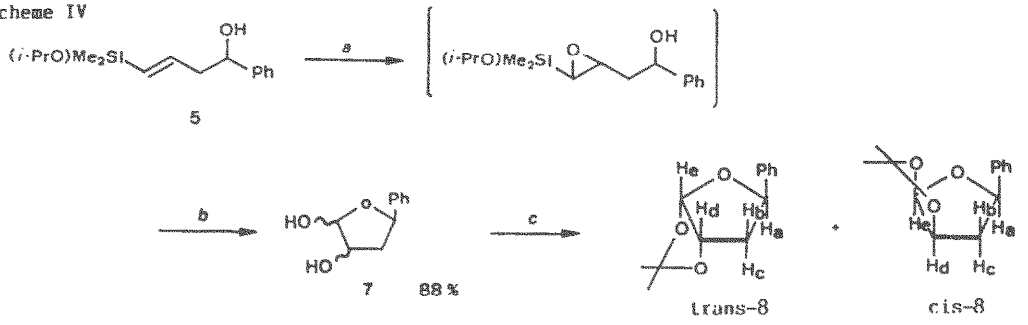



4d 6 (4)

30% $H_2O_2$ (3.3 eq), KF (2 eq), $KHCO_3$ (1 eq), MeOH, THF, room temp, 18 h.

to the same transformation. Thus, 5d was epoxidized with MCPBA and subjected to the hydrogen peroxide oxidation to give 7 in 88% overall yield, as shown in Scheme IV. The diastereoselectivity was examined after conversion to the acetonides 8 which consisted of a nearly 1 : 1 mixture of stereoisomers (Scheme IV). Epoxidation by t-BuOOH in the presence of $VO(acac)_2$ also afforded almost the same stereoselectivity as above in a lower overall yield (56%).

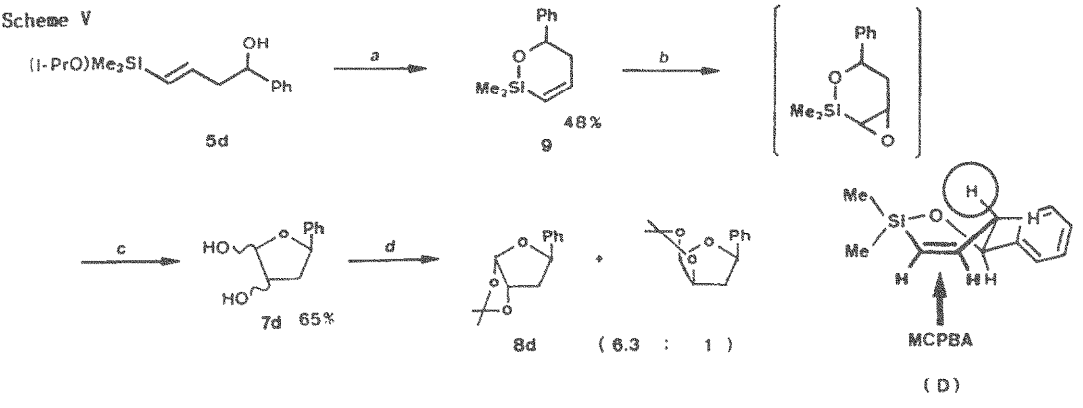
Scheme IV




[a] MCPBA, $CH_2Cl_2$, 0 °C room temp, 6 h or t-BuOOH, $VO(acac)_2$ (2 mol%), $C_6H_6$, 55 °C, 2 h. [b] 30% $H_2O_2$, KF, $KHCO_3$, MeOH, THF, room temp, 5 h. [c] $Me_2C(OMe)_2$, p-TsOH, room temp, 2 h.

We reasoned that the observed low diastereoselectivity might be due to the E geometry of the olefin part in 5 and hence we carried out photochemical isomerization to (Z) olefin. Thus, irradiation of 5d in dichloromethane by a high-pressure mercury lamp formed an isomerization-cyclization product 9 in 48% yield after 100% conversion of 5d, as shown in Scheme V. In acetonitrile the isomerization stopped at about 40% conversion and in hexane no change was observed. Epoxidation and hydrogen peroxide oxidation of the cyclic (Z) olefin 9 proceeded smoothly to form 7 in 65% yield. GLC and NMR analysis of the acetonides 8 revealed that the isomer ratio was 6.3 : 1, high diastereoselection being achieved as expected. The major isomer had a 1,3-trans configuration. Inspection of molecular models reveals that the most favorable conformation of 9 may be visualized as (D). The preferential equatorial orientation of the phenyl group makes one hydrogen atom of the adjacent methylene group (circled hydrogen) to reach the center of the ring. Since this hydrogen atom may block the upper side of the double bond, MCPBA may attack the double bond from the lower side preferentially to give the observed stereochemical consequence.

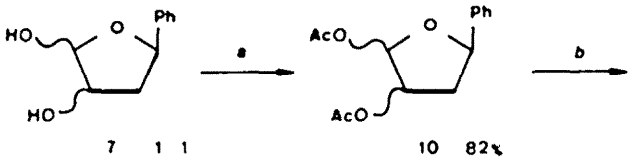
Scheme V



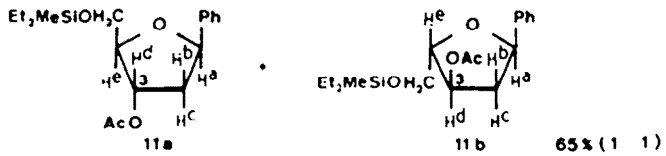

[a] $h\nu$, $CH_2Cl_2$, 26 h. [b] MCPBA, $CH_2Cl_2$, room temp, 3 h.
[c] 30% $H_2O_2$, KF, $KHCO_3$, MeOH, THF, 0 °C, 3 h. [d] $Me_2C(OMe)_2$, p-TsOH, room temp, 2 h.

**(2) Hydroxymethylation of 7 at the anomeric position.** Recently, Murai, Sonoda and their coworkers reported an elegant method for the introduction of a siloxymethyl group into the anomeric position of sugars.[9] This method was applied to our present system. Thus, **7** was converted to diacetate **10** which was treated with diethylmethylsilane in the presence of dicobalt octacarbonyl in dichloromethane under the carbon monoxide atmosphere (1 atm) to give siloxymethylated products **11a** and **11b** as a 1:1 isomeric mixture in 65% combined yield. Each isomer was isolated by preparative TLC on Silica Gel and characterized by 400 MHz NMR; the NOE data being shown in the experimental section. It should be noted that the siloxymethyl group has been introduced trans to the adjacent ($C^3$) acetate group, in consonant with Murai's results.

Scheme VI




7 1 1 10 82%




65% (1 1)

[a] $Ac_2O$; pyridine, room temp, 2 h. [b] $HSiMeEt_2$, $Co_2(CO)_8$, CO, $CH_2Cl_2$, 30 °C, 26 h.

**Conclusion.** We have presented herein that (allyl)aminosilanes may serve as a useful starting material for transformation of aldehydes to 2-deoxy-C-nucleoside skeletons. Lithiation and transmetalation of (allyl)aminosilanes, their regioselective reaction with aldehydes, and the subsequent oxidative transformation of the products have been established. Our efforts are currently devoted to refinement of the present methodology and further applications to sugar chemistry.

## EXPERIMENTAL

### General

$^1H$ NMR, MS, and GLC facilities have been described in a previous paper.[1d] NMR data reported are those observed at 100 MHz, unless othrewise stated. All solvents were dried and distilled just before use under nitrogen.

### Preparation of aminochlorosilanes (1).

**(Diethylamino)(chloro)dimethylsilane (1a).** To a white suspention of $Me_2SiCl_2$ (146 mL; 1.20 mol) and triethylamine (185 mL; 1.32 mol) in dry THF (150 mL) was slowly added a solution of diethylamine (125 mL; 1.20 mol) in THF (100 mL) at 0 °C over 2 h. The white mixture was warmed to room temperature, stirred for 6 h, diluted with pentane and filtered. The filtrate was evaporated at atmospheric pressure, and then the residue was distilled under reduced pressure to give 153 g (77% yield) of **1a**: bp 84-87/90 mmHg. $^1H$ NMR ($CCl_4$) δ 0.39 (s, 6H), 1.03 (t, J = 6.9 Hz, 6H), 2.88 (q, J = 6.9 Hz, 4H).

**(1-Pyrrolidino)(chloro)dimethylsilane (1b).** Prepared as above in 61% yield: bp 93-97 °C/80 mmHg. $^1H$ NMR ($CCl_4$) δ 0.39 (s, 6H), 1.63-1.97 (m, 4H), 2.87-3.16 (m, 4H).

**(Diisopropylamino)(chloro)dimethylsilane (1c).** A white mixture of $Me_2SiCl_2$ (122 mL; 1.0 mol) and diisopropylamine (420 mL; 3.0 mol) was refluxed for 8 h with stirring. Work-up as described for **1a** gave 135 g (82% yield) of **1c**: bp 95-98 °C/50 mmHg. $^1H$ NMR ($CCl_4$) δ 0.47 (s, 6H), 1.12 (d, J = 6.6 Hz, 12H), 3.30 (septet, J = 6.6 Hz, 2H).

**Preparation of allyl(amino)silanes (2).**

**(Allyl)(diethylamino)dimethylsilane (2a).** To a suspension of allylmagnesium chloride (1.0 mol) in 1 L of dry ether was slowly added **1a** (120 g; 0.72 mol) at 0 °C over 30 min. After the addition was completed, the reaction mixture was warmed to room temperature, refluxed for 6 h with stirring, and then filtered. The filtrate was evaporated at atmospheric pressure and the residue was distilled to give 111 g (90% yield) of **2a**: bp 78–81 °C/46 mmHg. $^1$H NMR ($CCl_4$) δ 0.06 (s, 6H), 1.02 (t, J = 7 Hz, 6H), 1.54 (d, J = 8 Hz, 2H), 2.80 (q, J = 7 Hz, 4H), 4.74 (d, J = 10 Hz, 1H), 4.76 (d, J = 15 Hz, 1H), 5.80 (ddt, J = 8, 10, and 15 Hz, 1H). Anal. Calcd for $C_9H_{21}NSi$: C, 63.08; H, 12.35. Found: C, 62.76; H, 12.62.

**(Allyl)(1-pyrrolidino)dimethylsilane (2b).** Prepared similarly in 93% yield: bp 102–106 °C/72 mmHg. $^1$H NMR ($CCl_4$) δ 0.03 (s, 6H), 1.57 (d, J = 7.8 Hz, 2H), 1.58–1.91 (m, 4H), 2.81–3.09 (m, 4H), 4.77 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 5.73 (ddt, J = 7.8, 10.8, and 15.6 Hz, 1H).

**(Allyl)(diisopropylamino)dimethylsilane (2c).** 94% yield: bp 79–81 °C/13 mmHg. $^1$H NMR ($CCl_4$) δ 0.10 (s, 6H), 1.07 (d, J = 6.3 Hz, 12H), 1.55 (d, J = 8.3 Hz, 2H), 3.21 (m, J = 6.3 Hz, 2H), 4.65 (d, J = 11.1 Hz, 1H), 4.63 (d, J = 14.2 Hz, 1H), 5.71 (ddt, J = 8.3, 11.1, and 14.2 Hz, 1H).

A one-pot syntheais of 2a. A solution of n-BuLi (80 mmol) in hexane was added dropwise to a solution of diethylamine (8.3 mL; 80 mmol) in dry THF (80 mL) at 0 °C over 1 h. After being stirred for 3 h, this lithium diethyamide solution was added to a solution of $Me_2SiCl_2$ (9.7 mL; 80 mmol) in dry THF (30 mL) at 0 °C over 1 h, and the mixture was stirred for 1.5 h. To the reaction mixture was further added a solution of allylmagnesium bromide (80 mmol) in ether at 0 °C over 0.5 h. After the addition was completed, the reaction mixture was refluxed for 2 h. Filtration and distillation, as described above for the stepwise preparation of 2a, gave 8.1 g (55% yield) of 2a.

**(Allyl)[(2-dimethylaminoethyl)methylamino]dimethylsilane (2d).** In essentially the same manner as above, reaction of $Me_2SiCl_2$ (6.0 g; 49 mmol) with the lithio salt of N,N,N'-trimethylethylenediamine (5.0 g; 49 mmol) followed by treatment with the allyl Grignard ragent afforded 4.9 g (50% yield) of **2d**: bp 78–81 °C/8 mmHg. $^1$H NMR ($CCl_4$) δ 0.05 (s, 6H), 1.56 (d, J = 8.1 Hz, 2H), 2.14 (s, 6H), 2.23 (t, J = 7.4 Hz, 2H), 2.48 (s, 3H), 2.78 (t, J = 7.4 Hz, 2H), 4.77 (d, J = 10.8 Hz, 1H), 4.80 (d, J = 14.6 Hz, 1H), 5.71 (ddd, J = 8.1, 10.8, and 14.6 Hz, 1H).

**Metalation of 2d, followed by quenching with $Me_3SiCl$.**

To a solution of **2a** (345 mg; 2.01 mmol) and TMEDA (0.31 mL; 2.05 mmol) in dry ether (4 mL) was added dropwise n-BuLi (2.60 mmol) in hexane at 0 °C and the reaction mixture was stirred for 6 h. To this pale yellow solution of metalated allylaminosilane was added $Me_3SiCl$ (0.75 mL; 6.0 mmol) at 0 °C. resulting in the formation of white precipitates immediately. After 2 h-stirring at room temperature, the mixture was treated with i-PrOH (0.8 mL) and stirred overnight. The reaction mixture was quenched with water and extracted with hexane twice. The combined organic layer was washed with brine and dried over $MgSO_4$. Bulb-to-bulb distillation afforded 452 mg (98% yield) of (*E*)-3-trimethylsilyl-1-isopropoxydimethylsilyl-1-propene (**3**): bp 105–120 °C/90 mmHg. $^1$H NMR ($CCl_4$) δ −0.05 (s, 9H), 0.03 (s, 6H), 1.06 (d, J = 6.6 Hz, 1H), 1.65 (d, J = 7.8 Hz, 2H), 3.93 (m, 1H), 5.39 (d, J = 18.3 Hz, 1H), 6.07 (dt, J = 7.8 and 18.3 Hz, 1H).

**A typical procedure for a sequence of metaltion of 2a, transmetaltion, reaction with aldehydes and isolation of 4.**

**Prepration of (E)-1-phenyl-4-isopropoxydimethylsilyl-3-buten-1-ol O-trimethylsilyl ether (4d).** To a solution of **2a** (12.3 g; 72 mmol) and TMEDA (11 mL; 72 mmol) in dry ether (80 mL) was added dropwise n-BuLi (67 mmol) in hexane at 0 °C over 0.5 h and the mixture was stirred at 0 °C for 3 h. After being cooled to −78 °C, the mixture was treated with copper(I) cyanide (6.5 g; 73 mmol) and stirred at this temperature for 1 h. To the greenish suspension was slowly added a solution of benzaldehyde (6.0 g; 57 mmol) in 10 mL of dry ether at −78 °C over 1 h. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was treated with $Me_3SiCl$ (14 mL; 110 mmol) at room temperature and stirred for 2 h. This was followed by addition of i-PrOH (22.7 mL; 330 mmol) and stirred overnight. The resulting mixture was then diluted with ether and insoluble materials were filtered off. The filtrate was washed with water and brine, dried over $MgSO_4$, and distilled to give 17.9 g (94% yield based on benzaldehyde) of **4d**: bp 92–96 °C/0.5 mmHg. $^1$H NMR ($CCl_4$) δ 0.03 (s, 9H), 0.09 (s, 6H), 1.08 (d, J = 6.6 Hz, 6H), 2.28–2.66 (m, 2H), 3.84 (septet, J = 6.6 Hz, 1H), 4.59 (t, J = 6.0 Hz, 1H), 5.52 (d, J = 17.4 Hz, 1H), 6.01 (dt, J = 6.0 and 17.4 Hz, 1H), 7.01–7.34 (m, 5H). Mass spectrum: m/e (relative intensity); 336 ($M^+$, 0.3), 215 (68), 179 (100). Anal. Calcd for $C_{18}H_{32}O_2Si_2$: C, 64.23; H, 9.58. Found: C, 64.48; H, 9.82.

Other compounds **4a–4c** and **4e–4g** were prepared similarly, yields being listed in Table III.

**(E)-1-Isopropoxydimethylsilyl-1-undecen-4-ol O-trimethylsilyl ether (4a).** Bp 90–93 °C/0.5 mmHg. $^1$H NMR ($CCl_4$) δ 0.05 (s, 9H), 0.91 (br t, 3H), 1.10 (d, J = 6.0 Hz, 6H), 1.05–1.62 (m, 12H), 2.24 (t, J = 6.0 Hz, 2H), 3.53–3.82 (m, 1H), 3.95 (septet, J = 6.0 Hz, 1H), 5.60 (d, J = 18.0 Hz,

1H), 6.10 (dt, J = 6.0 and 18.0 Hz, 1H). MS: 358 ($M^+$, 0.03), 201 (100). Anal. Calcd for $C_{19}H_{42}O_2Si_2$: C, 63.62; H, 11.80. Found: C, 63.34; H, 11.97.

**(E)-1-Isopropoxydimethylsilyl-5-ethyl-1-nonen-4-ol O-trimethylsilyl ether (4b).** Bp 90-97 °C/0.5 mmHg. $^1H$ NMR ($CCl_4$) δ 0.08 (s, 9H), 0.12 (s, 6H), 0.96-1.07 (m, 6H), 1.09-1.54, m, including d at 1.11, J = 6.0 Hz, total 15H), 2.22 (t, J = 6.0 Hz, 2H), 3.64-3.83 (m, 1H), 3.93 (septet, J = 6.0 Hz, 1H), 5.56 (d, J = 18.0 Hz, 1H), 6.05 (dt, J = 6.0 and 18.0 Hz, 1H). Anal. Calcd for $C_{19}H_{42}O_2Si_2$: C, 63.62; H, 11.80. Found: C, 63.44; H, 12.06.

**(E)-1-Cyclohexyl-4-isopropoxydimethylsilyl-3-buten-1-ol O-trimethylsilyl ether (4c).** $^1H$ NMR ($CCl_4$) δ 0.00 (s, 9H), 0.02 (s, 6H), 0.52-1.18 (m, including d at 1.01, J = 6.5 Hz, total 12H), 1.18-1.80 (m, 5H), 2.19 (t, J = 7.0 Hz, 2H), 3.17-3.31 (m, 1H), 3.91 (septet, J = 6.5 Hz, 1H), 5.68 (d, J = 18.5 Hz, 1H9, 6.00 (dt, J = 7.0 and 18.5 Hz, 1H).

**(E)-1-(2-Furyl)-4-isopropoxydimethylsilyl-3-buten-1-ol O-trimethjylsilyl ether (4e).** Bp 82-84 °C/0.5 mmHg. $^1H$ NMR ($CCl_4$) δ 0.04 (s, 9H), 0.12 (s, 6H), 1.11 (d, J = 6.0 Hz, 6H), 2,64 (t, J = 6.3 Hz, 2H), 3.97 (septet, J = 6.0 Hz, 1H), 4.74 (t, J = 6.3 Hz, 1H), 5.75 (d, J = 18.3 Hz, 1H), 6.17 (dt, J = 6.3 and 18.3 Hz, 1H), 6.15-6.41 (m, 2H), 7.34-7.49 (m, 1H). MS: 326 ($M^+$, 0.1), 169 (100). Anal. Calcd for $C_{16}H_{30}O_3Si_2$: C, 58.84; H, 9.26. Found: C, 59.23; H, 9.65.

**(E)-1-(2-Thienyl)-4-isopropoxydimethylsilyl-3-buten-1-ol O-trimethylsilyl ether (4f).** Bp 84-92 °C/0.5 mmHg. $^1H$ NMR ($CCl_4$) δ 0.07 (s, 9H), 0.14 (s, 6H), 1.12 (d, J = 6.0 Hz, 6H), 2.35-2.60 (m, 2H), 3.83 (septet, J = 6.0 Hz, 1H), 4.86 (t, J = 6.3 Hz, 1H), 5.58 (d, J = 18.3 Hz, 1H), 6.04 (dt, J = 6.3 and 18.3 Hz, 1H), 6.65-6.93 (m, 2H), 6.98-7.17 (m, 1H). MS: 259 ($M^+$-thiophene, 0.2), 185 (80), 73 (100). Anal. Calcd for $C_{16}H_{30}O_2OSi_2$: C, 56.09; H, 8.83. Found: C, 56.37; H, 8.86.

**(E)-1-(3-Pyridyl)-4-isopropoxydimethylsilyl-3-buten-1-ol O-trimethylsilyl ether (4g).** Bp 99-102 °C/0.2 mmHg. $^1H$ NMR ($CCl_4$) δ 0.03 (s, 9H), 0.11 (s, 6H), 1.10 (d, J = 6.0 Hz, 6H), 2.38-2.62 (m, 2H), 3.94 (septet, J = 6.0 Hz, 1H), 4.76 (t, J = 6.3 Hz, 1H), 5.56 (d, J = 18.3 Hz, 1H), 6.13 (dt, J = 6.3 and 18.3 Hz, 1H), 7.12-7.36 (m, 1H), 7.49-7.64 (m, 1H), 8.30-8.66 (m, 1H). MS: 337 ($M^+$, 0.2), 180 (100). Anal. Calcd for $C_{17}H_{31}NO_2Si_2$: C, 60.48; H, 9.26. Found; C, 60.57; H, 9.53.

**Deprotection of 4.**

**(E)-1-phenyl-4-isopropoxydimethylsilyl-3-buten-1-ol (5d).** A mixture of 4d (12.2 g; 36 mmol), 500 mL of i-PrOH and camphorsulfonic acid (10 mg) was stirred at room temperature until the starting material was consumed completely, as monitored by GLC. In this case, it took 1 h. The mixture was treated with $K_2CO_3$ powder (5 g) and stirred for 0.5 h. The salt was removed by filtration and the filtrate was stripped of the solvent. The residue was diluted with ether, washed with water twice, and dried over $MgSO_4$. Bulb-to-bulb distillation gave 9.2 g (95% yield) of 5d: bp 110-120 °C/1 mmHg (bath temperature). $^1H$ NMR ($CCl_4$) δ 0.10 (s, 6H), 1.10 (d, J = 6.3 Hz, 2H), 2.20 (br s, 1H), 2.58 (t, J = 6.3 Hz, 2H), 3.76 (m, 1H), 4.59 (t, J = 6.3 Hz, 1H), 5.61 (d, J = 18.6 Hz, 1H), 6.02 (dt, J = 6.3 and 18.6 Hs, 1H), 7.00-7.32 (m, 5H). Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 67.88; H, 9.30.

**(E)-1-Isopropoxydimethylsilyl-1-undecen-4-ol (5a).** Bp 115-125 °C/0.5 mmHg. $^1H$ NMR ($CCl_4$) δ 0.04 (s, 6H), 0.85 (br t, 3H), 1.06 (d, J = 6.3 Hz, 6H), 1.08-1.60 (m, 13H), 2.09-2.46 (m, 2H), 3.39-3.73 (m, 1H), 3.94 (septet, J = 6.3 Hz, 1H), 5.68 (d, J = 18.3 Hz, 1H), 6.13 (dt, J = 6.0 and 18.3 Hz, 1H).

**(E)-1-(2-Furyl)-4-isopropoxydimethylsilyl-3-buten-1-ol (5e).** Bp 102-108 °C/0.5 mmHg. $^1H$ NMR ($CDCl_3$) δ 0.10 (s, 6H), 1.10 (d, J = 6.0 Hz, 6H), 2.09 (br s, 1H), 2.70 (t, J = 6.0 Hz, 2H), 3.97 (septet, J = 6.0 Hz, 1H), 4.79 (t, J = 6.0 Hz, 1H), 5.82 (d, J = 18.3 Hz, 1H), 6.71 (dt, J = 6.0 and 18.3 Hz, 1H), 6.22-6.52 (m, 2H), 7.27-7.54 (m, 1H).

**(E)-1-(2-Thienyl)-4-isopropoxydimethylsilyl-3-buten-4-ol (5f).** Bp 115-125 °C/0.5 mmHg. $^1H$ NMR ($CCl_4$) δ 0.14 (s, 6H), 1.12 (d, J = 6.3 Hz, 6H), 2.18 (br s, 1H), 2.69 (t, J = 6.0 Hz, 2H), 3.96 (septet, J = 6.3 Hz, 1H), 5.05 (t, J = 6.0 Hz, 1H), 5.82 (d, J = 18.3 Hz, 1H), 6.21 (dt, J = 6.0 and 18.3 Hz, 1H), 6.91-7.09 (m, 2H), 7.28-7.37 (m, 1H). Anal. Calcd for $C_{13}H_{22}O_2SSi$: C, 57.73; H, 8.20. Found: C, 57.87; H, 8.10.

**(E)-1-(3-Pyridyl)-4-isopropoxydimethylsilyl-3-buten-1-ol (5g).** A mixture of 4g (906 mg; 2.68 mmol), camphorsulfonic acid (630 mg; 2.71 mmol), and i-PrOH (100 mL) was stirred at room temperature for 3 h. Work-up as above and preparative TLC on silica gel (EtOAc, $R_f$ 0.41) gave 390 mg (56% yield) of 5g. $^1H$ NMR ($CCl_4$) δ 0.05 (s, 6H), 1.07 (d, J = 6.0 Hz, 6H), 2.53 (t, J = 6.3 Hz, 2H), 2.90 (br s, 1H), 3.89 (J = 6.0 Hz, 1H), 4.76 (t, J = 6.3 Hz, 1H), 5.70 (d, J = 18.3 Hz, 1H), 6.10 (dt, J = 6.3 and 18.3 Hz, 1H), 7.11-7.35 (m, 1H), 7.55-7.75 (m, 1H), 8.23-8.59 (m, 2H). Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73. Found: C, 63.28; H, 8.80.

**Hydrogen peroxide oxidation of 4d. Preparation of 2-hydroxy-5-phenyltetrahydrofuran (6).**

To a mixture of 4d (670 mg; 2.0 mmol), KF (240 mg; 4.1 mmol), $KHCO_3$ (200 mg; 2.0 mmol), methanol (2 mL), and THF (2 mL) was added dropwise 30% $H_2O_2$ (0.75 mL; 6.6 mmol) at room temperature. After being stirred overnight, the reaction mixture was cooled to 0 °C and excess

$Na_2S_2O_3$ was added carefully in several portions for the purpose of decomposition of excess $H_2O_2$, which was confirmed by the starch-iodine test. The mixture was then diluted with ether, dried over $MgSO_4$, and filtered. The filtrate was stripped of the solvent and subjected to preparative TLC on silica gel (hexane/EtOAc 1/3, $R_f$ 0.23) gave 292 mg (90% yield) of **6**. $^1H$ NMR ($CCl_4$) δ 1.58-2.84 (m, 4H), 4.32-4.77 (br 1H, OH), 4.89-5.39 (m, 1H), 5.49-5.91 (m, 1H), 7.05-7.62 (m, 5H). Elemental analysis was performed after acetylation ($Ac_2O$, $Et_3N$, DMAP). 2-Acetoxy-5-phenyltetrahydrofuran. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 70.16; H, 7.00.

**Epoxidation of 5d, followed by hydrogen peroxide oxidation. Preparation of 2,3-dihydroxy-5-phenyltetrahydrofuran (7).**

To a solution of 5d (838 mg; 3.17 mmol) in dichloromethane (8 mL) was added MCPBA (980 mg; 70% pure; 5.7 mmol) at 0 °C. The solution was stirred at room temperature for 4 h. The mixture was cooled to 0 °C, diluted with hexane and filtered to remove the white solid. Evaporation of the solvents gave a crude epoxysilane. To a mixture of the crude epoxysilane, KF (560 mg; 9.6 mmol) and $KHCO_3$ (1.27 g; 12.7 mmol) in methanol (3 mL) and THF (6 mL) was added 30% $H_2O_2$ (1.5 mL; 13.3 mmol) at room temperature and the resulting mixture was stirred overnight. After usual work-up as mentioned above, the crude product was purified by preparativ TLC on silica gel (benzene/EtOAc 1/1; $R_f$ 0.22) to afford 509 mg (88% yield) of 7 as a stereoisomeric mixture. The stereochemistry was assigned after acetonide formation (vide infra). $^1H$ NMR ($CDCl_3$) δ 1.49-2.75 (m, 2H), 3.97-4.50 (m, 1H), 4.66-5.60 (m, 2H), 3.66-5.04 (br, 2H, OH), 6.95-7.70 (m, 5H).

5-Phenyl-2,3-diacetoxytetrahydrofuran (10). A mixture of 7 (460 mg; 2.65 mmol), acetic anhydride (3 mL), and pyridine (4.5 mL) was stirred for 2 h, and quenched with a cold $NaHCO_3$ solution. Extraction with ether, washing twice with a cold solution of 0.5 N HCl, with $NaHCO_3$ solution, and with brine, and purification by preparative TLC on silica gel (hexane/EtOAc 1/1, $R_f$ 0.65) afforded 550 mg (83% yield) of 10. The product consisted of four inseparable stereoisomers and showed a complicated NMR spectrum. $^1H$ NMR ($CCl_4$) δ 1.95-3.08 (m, 8H), 4.80-5.53 (m, 2H), 6.18-6.71 (m, 1H), 7.11-7.56 (m, 5H). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.62; H, 6.18.

**Photochemical isomerization of 4d. 3,3-Dimethyl-5-phenyl-3-sila-4-oxa-cyclohexene (9).**

A solution of 4d (1.520 g; 5.73 mmol) in dichloromethane (180 mL) was deaerated by bubbling nitrogen and then irradiated at 20 °C with a 100 W high pressure mercury lamp until the starting material disappeared completely, as monitored by GLC. The mixture was then evaporated and the residue was distilled to give 560 mg (48% yield) of 9 boiling over the range of 85-100 °C/15 mmHg (bath temperature), together with a viscous nonvolatile residue. $^1H$ NMR ($CCl_4$) δ 0.22 (s, 6H), 2.16-2.60 (m, 2H), 4.95 (dd, J = 6.6 and 7.5 Hz, 1H), 5.89 (d, J = 13.9 Hz, 1H), 6.81 (ddd, J = 4.0, 4.1, and 13.9 Hz, 1H), 7.04-7.55 (m, 5H). MS: 204 ($M^+$, 56), 130 (100). Exact mass: Calcd for $C_{12}H_{16}OSi$: 204.09704. Found: 204.09477.

**Epoxidation and hydrogen peroxide oxidation of 9.**

In essentially the same manner as described for oxidation of 5d, 9 (500 mg; 2.45 mmol) was subjected to the MCPBA epoxidation and subsequent $H_2O_2$ oxidation. Preparative TLC on silica gel (hexane/EtOAc 1/3, $R_f$ 0.42) gave 285 mg (65% yield) of 7. The product 7 (240 mg; 1.33 mmol) was stirred with 2,2-dimethoxypropane (5 mL) and a catalytic amount of p-toluenesulfonic acid for 2 h. Quenching with $K_2CO_3$ followed by filtration and preparative TLC on silica gel (hexane/EtOAc 3/1) gave 158 mg (54% yield) of trans-8 ($R_f$ 0.57) and 25 mg (9% yield) of cis-8 ($R_f$ 0.48). The stereochemsitry of these two isomers was determined by NOE.

Trans-8: $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.371 (s, 3H), 1.592 (s, 3H), 1.788 (ddd, J = 4.40, 11.04, and 13.46 Hz, 1H), 2.419 (dd, J = 4.40 and 13.46 Hz, 1H), 4.841 (dd, J = 4.08 and 4.40 Hz, 1H), 5.204 (dd, J = 4.40 and 11.04 Hz, 1H), 6.002 (d, J = 4.08 Hz, 1H), 7.23-7.41 (m, 1H). NOE: Iraadiation at $H_a$ ( δ = 5.204) resulted in enhancement of the resonance peak due to $H_c$ ( δ = 2.419) and no significant enhancement in $H_d$ ( δ = 4.841) and $H_e$ ( δ = 6.002), while irradiation at $H_c$ resulted in a large enhancement in $H_a$ and no enhancement in $H_d$ and $H_e$. Irradiation at $H_d$ induced in an apparent enhancement in $H_b$ ( δ = 1.788) and $H_e$ and no enhancement in $H_a$ and $H_c$, while irradiation at $H_e$ caused an enlargement in $H_b$, $H_d$, and phenyl protons but no obvious enhancement in $H_a$ and $H_c$.

Cis-8: $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.242 (s, 3H), 1.300 (s, 3H), 2.382 (ddd, J = 1.95, 5.00, and 13.91 Hz, 1H), 2.535 (ddd, J = 6.35, 8.01, and 13.91 Hz, 1H), 4.833 (ddd, J = 1.95, 4.05, and 6.35 Hz, 1H), 5.190 (dd, J = 5.00 and 8.01 Hz, 1H), 5.897 (d, J = 4.05 Hz, 1H), 7.22-7.46 (m, 5H). NOE: Irradiation at $H_a$ ( δ = 5.190) induced significant NOE of $H_d$ ( δ = 4.833).

**Siloxymethylation of 5-phenyl-2,3-diacetoxytetrahydrofuran (10). Preparation of 11.**

In a flask fitted with a CO balloon was placed $Co_2(CO)_8$ (28 mg; 0.08 mmol). After flashing the apparatus with CO several times, $Et_2MeSiH$ (0.92 mL; 6.3 mmol) was added at room temperature and the mixture was stirred for 5 min. A solution of **10** (520 mg; 1.97 mmol) in dichloromethane (5 mL)

was added and the mixture was stirred at 30 °C for 26 h. After addition of one drop of pyridine followed by bubbling air through the mixture, the resulting black mixture was diluted with ether and insoluble materials were filtered off. The filtrate was stripped of the solvents and subjected to preparative TLC on silica gel (hexane/EtOAc 8/1) to afford 204 mg (32% yield; $R_f$ 0.44) of (3-O-acetyl-5-O-diethylmethylsilyl-2-deoxy-α-ribofuranosyl)benzene (**11b**) and 206 mg (32% yield; $R_f$ 0.40) of (3-O-acetyl-5-O-diethylmethylsilyl-2-deoxy-β-ribofuranosyl)benzene (**11a**). These two stereoisomers were characterized by NOE analysis.

**11a**: $^1$H NMR (400 MHz, $CDCl_3$) δ 0.000 (s, 3H), 0.523 (q, J = 7.69 Hz, 4H), 0.877 (t, J = 7.69 Hz, 6H), 1.975 (ddd, J = 5.83, 11.05, and 13.61 Hz, 1H), 2.020 (s, 3H), 2.176 (ddd, J = 0.65, 5.00, 13.61 Hz, 1H), 3.690 (dd, J = 4.03 and 10.74 Hz, 1H), 3.775 (dd, J = 3.54 and 10.74 Hz, 1H), 4.006 (ddd, J = 1.58, 3.54, and 4.03 Hz, 1H), 4.980 (dd, J = 5.00 and 11.05 Hz, 1H), 5.209 (ddd, J = 0.65, 1.58, and 5.86 Hz, 1H), 7.16-7.34 (m, 5H). Anal. Calcd for $C_{18}H_{28}O_4Si$: C, 64.25; H, 8.39. Found: C, 64.15; H, 8.65.

**11b**: $^1$H NMR (400 MHz, $CDCl_3$) δ 0.000 (s, 3H), 0.520 (q, J = 7.81 Hz, 4H), 0.867 (t, J = 7.81 Hz, 6H), 1.879 (s, 3H), 1.925 (ddd, J = 4.33, 7.08, and 13.43 Hz, 1H), 2.705 (ddd, J = 7.14, 7.20, and 13.43 Hz, 1H), 3.685 (dd, J = 3.85 and 10.98 Hz, 1H), 3.726 (dd, J = 3.85 and 10.98 Hz, 1H), 4.159 (dd, J = 3.06 and 3.85 Hz, 1H), 5.105 (dd, J = 7.08 and 7.20 Hz, 1H), 5.233 (ddd, J = 3.06, 4.33, and 7.14 Hz, 1H), 7.14-7.29 (m, 5H). Anal. Calcd for $C_{18}H_{28}O_4Si$: C, 64.25; H, 8.39. Found: C, 64.40; H, 8.68.

NOE data are as follows. **11a**: NOE of $H_e$ (δ = 4.006) was observed upon irradiation at $H_a$ (δ = 4.980). Irradiation at $H_d$ (δ = 5.209) induced significant NOE of the siloxymethyl protons and $H_b$ but no enhancement of $H_a$ and $H_e$. Irradiation at $H_e$ resulted in apparent NOE of $H_a$. **11b**: NOE of $H_d$ (δ = 5.233) was observed upon irradiation at $H_a$ (δ = 5.105). NOE was also obtained for $H_e$ (δ = 4.159) and phenyl protons upon irradiation at $H_b$ (δ = 1.925). Irradiation at $H_c$ (δ = 2.705) resulted in NOE of $H_a$ and $H_d$ and no enhancement of $H_e$. Irradiation at $H_d$ induced significant NOE of $H_a$, $H_c$, and siloxymethyl protons but no enhancement of $H_b$.

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