synthesis of α- and β-*C*-glycosyl aldehydes.[22,25] The reaction of these aldehydes with compound **4** is therefore a general method for the synthesis of *C*-glycosyl amino acid analogs of the other O-linked structures.

Subsequent reduction of the olefin with diimide[26] afforded the *C*-glycosyl oxazolidinone **6**, which was protected with a *tert*-butoxycarbonyl (BOC) group and cleaved with $CsCO_3$[27] to give the protected amino alcohol **7**. For compatibility with Fmoc-based automated peptide synthesis,[28] the BOC group was replaced with Fmoc by treatment of compound **7** with trifluoroacetic acid followed by *N*-(9-fluorenylmethoxycarbonyloxy)succinimide (Fmoc-OSu) to give compound **8**. Jones oxidation of compound **8** gave the Fmoc-protected amino acid **2** which was incorporated into an automated peptide synthesizer to provide the protected *C*-glycopeptide **9** (Figure 2). Deprotection of compound **9** by catalytic hydrogenolysis (H_2, 10% Pd/C) afforded the desired *C*-glycopeptide **10**, which was purified by reversed-phase HPLC.

The alanine-based sequence of peptide **10** was designed by Baldwin and co-workers to assess the helix-forming tendencies of amino acids at position X.[29] The α-helix content of *C*-glycopeptide **10** was measured by the mean residue ellipticity at 222 nm ($[\theta]_{222}$) and compared to the alanine-substituted peptide **11**. Under the conditions used (see supplementary material), peptide **11** contains 40% α-helix ($[\theta]_{222} = -12\,194 \pm 500$ deg cm^2 dmol^{-1}) whereas glycopeptide **9** is only 18% α-helical ($[\theta]_{222} = -5349 \pm 500$ deg cm^2 dmol^{-1}). Therefore, substitution of only one C-glycosyl unit has a strong destabilizing effect on the helix.

Similar results have been reported previously for both N-linked[30] and O-linked[31] glycopeptides. In these studies, glycosylation of small peptides led to a large reduction in helicity and an absence of ordered structure. This effect can result from unfavorable steric interactions, limitation of the conformational space of the glycosyl side chain,[32] and disruption of hydrogen bonding in the helix backbone.[33,34] The similar helix-breaking effects of both C- and O-glycosylation raises the possibility that C-linked and O-linked carbohydrates exert similar conformational restrictions on a peptide backbone.

The incorporation of these *C*-glycosyl amino acids into pharmacologically active peptides may have a dramatic effect on their activity and metabolism. We are currently investigating the biological and conformational properties of *C*-glycosyl analogs of other commonly found *O*-glycopeptides. A detailed analysis of the conformational effects of glycosylation with respect to carbohydrate structure and chemical linkage (O-linked vs C-linked) will be the subject of further reports.

Acknowledgment. We thank Professor Mukund P. Sibi (North Dakota State University) for a detailed procedure for the synthesis of compound **4** and William R. Kobertz (UC Berkeley) for his contribution to the synthesis of compound **3**. M.D.B. thanks the American Cancer Society for a Junior Faculty Award and Eli Lilly for a Junior Investigator Award. C.R.B. thanks Eli Lilly for an ACS Medicinal Chemistry Fellowship and AT&T Bell Laboratories for a GRPW grant. This research was supported by National Institutes of Health award No. R29 GM43037-02.

Supplementary Material Available: Experimental procedures and spectral and analytical data for compounds **2**, **4**, and **5–10** and circular dichroism procedures and spectra for *C*-glycopeptide **10** and peptide **11** (11 pages). This material is contained in many libraries on microfiche, immediately 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.

(25) Bertozzi, C. R.; Bednarski, M. D. *Tetrahedron Lett.* **1992**, *33*, 3109.
(26) Hart, D. J.; Hong, W.-P.; Hsu, L.-Y. *J. Org. Chem.* **1987**, *52*, 4665.
(27) Ishizuka, T.; Kunieda, T. *Tetrahedron Lett.* **1987**, *28*, 4185.
(28) Fields, G. B.; Noble, R. L. *Int. J. Peptide Protein Res.* **1990**, *35*, 161.
(29) Padmanabhan, S.; Marqusee, S.; Ridgeway, T.; Laue, T. M.; Baldwin, R. L. *Nature* **1990**, *344*, 268.
(30) Otvos, L., Jr.; Thurin, J.; Kollat, E.; Urge, L.; Mantsch, H. H.; Hollosi, M. *Int. J. Peptide Protein Res.* **1991**, *38*, 476.
(31) Filira, F.; Biondi, L.; Scolaro, B.; Foffani, M. T.; Mammi, S.; Peggion, E.; Rocchi, R. *Int. J. Biol. Macromol.* **1990**, *12*, 41.
(32) O'Neil, K. T.; DeGrado, W. F. *Science* **1990**, *250*, 646.
(33) Merutka, G.; Lipton, W.; Shalongo, W.; Park, S.-H.; Stellwagon, E. *Biochemistry* **1990**, *29*, 7511.
(34) Lyu, P. C.; Liff, M. I.; Marky, L. A.; Kallenbach, N. R. *Science* **1990**, *250*, 669.

Five-Membered Ring Annulation via Propargyl- and Allylsilanes

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Summary: Allyl- and propargylsilanes can serve as three-carbon components in a [3 + 2] annulation strategy for the synthesis of five-membered carbocycles and heterocycles.

The reaction of allenylsilanes with electron-deficient compounds constitutes a powerful method for the synthesis of five-membered carbocycles and heterocycles.[1,2] In this paper we now report the extension of this [3 + 2] annulation strategy to include two new classes of unsaturated organosilanes: *allyl-* and *propargylsilanes*.

Electrophilic substitution reactions of propargylsilanes have received considerable attention in recent years, and the application of this chemistry to the synthesis of substituted allenes is now well-documented.[3] Our prior experience with allenylsilane chemistry suggested to us that

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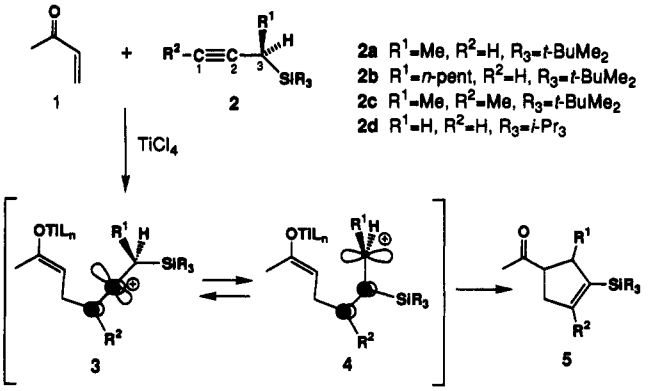
(1) (a) Cyclopentene synthesis: Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513. Danheiser, R. L.; Fink, D. M.; Tsai, Y.-M. *Org. Synth.* **1988**, *66*, 8. (b) Dihydrofurans and pyrrolines: Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) Isoxazoles: Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277. (d) Azulenes: Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 389. (e) Furans: Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407.
(2) For a review, see Panek, J. S. In *Comprehensive Organic Synthesis*; Schreiber, S. L., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, pp 596–607.
(3) For reviews, see: (a) Fleming, I. In *Comprehensive Organic Synthesis*; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, pp 563–593. (b) Schinzer, D. *Synthesis* **1988**, 263.

0022-3263/92/1957-6094$03.00/0

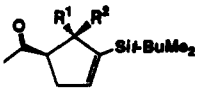
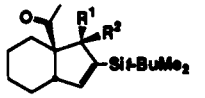
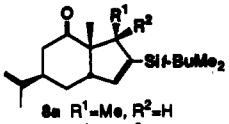
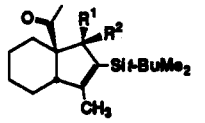
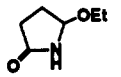
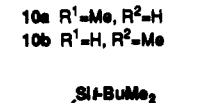
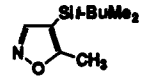
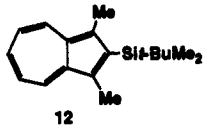
Scheme I



propargylsilanes could also serve as three-carbon annulation units, provided that derivatives bearing large trialkylsilyl groups were employed so as to suppress the normal desilylation pathway leading to allenes.[4,5] Scheme I outlines the course of the desired annulation process. Addition of an electrophile (e.g., MVK) to propargylsilane **2** is expected to take place at C-1 of the acetylene and anti to the carbon–silicon bond, thus generating a vinyl cation **3** which should undergo rapid and reversible rearrangement (1,2-silyl shift[1]) to **4**. Both carbocations are stabilized by hyperconjugative interaction with the adjacent carbon–silicon bond and may better be represented as bridged species. Finally, cyclization provides the desired cyclopentene **5**, in which the double bond is shifted relative to its position in our previous allenylsilane-derived annulation products.

The reaction of methyl vinyl ketone with propargylsilane **2a**[6a] established the feasibility of the new [3 + 2] annulation strategy. Optimal results were obtained by adding 1.2 equiv of $TiCl_4$ to a solution of MVK and 2 equiv of **2a** in CH_2Cl_2 at −78 °C. After 2 h, the desired cyclopentene was isolated in 78% yield as a 1:1 mixture of diastereomers.[9,10] As illustrated in Table I, the new [3 + 2] annulation strategy can be employed for the synthesis of a variety of five-membered carbocyclic and heterocyclic compounds, including diverse substituted cyclopentene derivatives, 3-pyrrolines, isoxazoles, and azulenes. We have found, however, that in contrast to allenylsilanes, propargylsilanes do not react in good yield with acylium ions to form furans.

Table I. [3+2] Annulation via Propargylsilanes

entry	electrophilic annulation unit	propargylsilane	product(s)	yield,[a] %
1	methyl vinyl ketone	2a	 **6a** R¹=Me, R²=H **6b** R¹=H, R²=Me	78 (1:1)
2	methyl vinyl ketone	2b	**6c** R¹=*n*-pent, R²=H **6d** R¹=H, R²=*n*-pent	51 (1:1)
3	1-acetylcyclohexene	2a	 **7a** R¹=Me, R²=H **7b** R¹=H, R²=Me	74 (2:1)
4	(R)-(-)-carvone	2a	 **8a** R¹=Me, R²=H **8b** R¹=H, R²=Me	75 (1:1)
5	1-acetylcyclohexene	2c	 **9a** R¹=Me, R²=H **9b** R¹=H, R²=Me	74 (2:1)
6		2a	 **10a** R¹=Me, R²=H **10b** R¹=H, R²=Me	53 (1:1)
7	$NOBF_4$	2a	 **11**	70
8	tropylium tetrafluoroborate	2c	 **12**	55

[a] Isolated yields of products purified by column chromatography on silica gel. IR, ^1H NMR, and ^{13}C NMR data were fully consistent with the assigned structures. Elemental analyses were obtained for all annulation products. Stereochemical assignments were based on NOE experiments.

As expected, the success of these annulations depends critically on the structure of the propargylsilane annulation component. Only derivatives with bulky trialkylsilyl groups such as *t*-$BuMe_2Si$ and *i*-Pr_3Si undergo the desired ring-forming process; Me_3Si derivatives afford cyclopentene products in less than 10% yield. In addition, propargylsilanes lacking alkyl substituents at the propargylic carbon (e.g., **2d**) fail to participate in the reaction, presumably because the requisite 1,2-silyl shift is unfavorable when a primary carbocation is produced.

The success of the propargylsilane-based annulation strategy suggested the possibility that allylsilanes might be similarly deployed for the synthesis of five-membered rings. Although the Lewis acid-promoted reaction of allylsilanes with α,β-enones normally results in conjugate allylation (the "Sakurai reaction"[11]), we hoped to be able

(4) The reaction of several propargyl*trimethyl*silanes with acetals has been reported to produce dihydrofuran byproducts along with the expected allenes: Pornet, J.; Miginiac, L.; Jaworski, K.; Randrianoelina, B. *Organometallics* **1985**, *4*, 333.

(5) $Cp(CO)_2FeCH_2C{\equiv}CH$ and related compounds participate in a [3 + 2] "transition-metal mediated cycloaddition" of limited scope. For a review, see: Chan, D. M. T. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 271–314.

(6) (a) Propargylsilane **2a** was prepared in 97% yield by isomerization of 1-(*tert*-butyldimethylsilyl)-1-methylallene[1e] with 1.5 equiv of *n*-BuLi in Et_2O (25 °C, 12 h). (b) Propargylsilane **2b** was prepared in 27% yield by silylation of octyne according to the general procedure of Brandsma.[7] (c) Propargylsilane **2c** was synthesized in 96% yield by methylation of the lithium derivative of **2a**. (d) Propargylsilane **2d** was prepared in 77% yield from 1-(*tert*-butyldimethylsilyl)propyne[8] by reaction with (i) *t*-BuLi, THF (−78 °C, 2 h) and then *i*-Pr_3SiCl (−78 °C, 2 h, 25 °C, 2 h), followed by (ii) $AgNO_3$ and KCN in H_2O–ethanol.

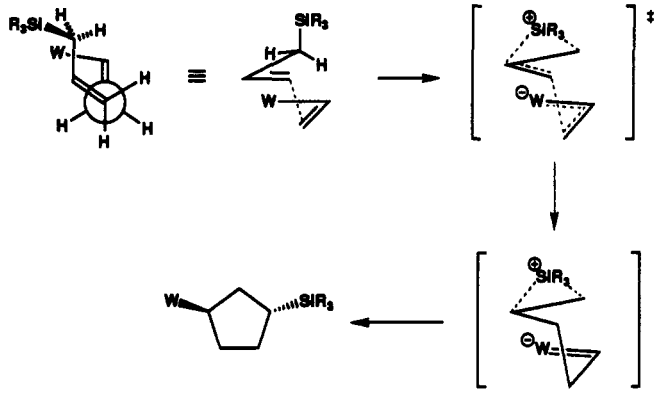
(7) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1980**, *99*, 113.

(8) Fitzmaurice, N. J.; Jackson, W. R.; Perlmutter, P. *J. Organomet. Chem.* **1985**, *285*, 375.

(9) Treatment of the annulation products with 1.1 equiv of LiOMe in methanol (25 °C, 12 h) gave **6a** and **6b** as an 8:1 mixture in 90% yield.

(10) Annulations involving less reactive enones (Table I, entries 3–5) were best achieved by portionwise addition of the propargylsilane to a solution of the enone and $TiCl_4$ in CH_2Cl_2 at room temperature; see supplementary material for details.

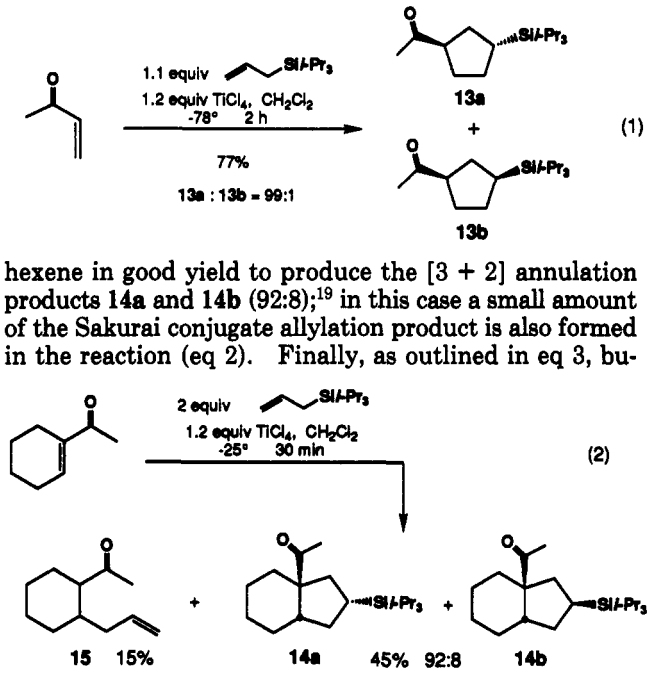
Scheme II



to direct the course of these reactions to yield cyclopentanes through our usual stratagem of employing compounds with sterically shielded silyl groups.

In considering the feasibility of the proposed annulation strategy, we were encouraged to note that on several occasions in the past *cyclic compounds* had even been observed (albeit as *minor byproducts*) in Sakurai reactions involving simple unhindered allyltrimethylsilanes.[12] Initially disturbing to us, however, was the fact that in most cases these byproducts had been assigned structures as cyclobutylmethylsilane derivatives (i.e., [2 + 2] addition products). More encouraging were the findings of Butler, who in 1981 had identified the minor byproduct (11% yield) of the reaction of allyltrimethylsilane with PTAD (4-phenyl-1,2,4-triazoline-3,5-dione) as a [3 + 2]-type cycloadduct.[13] In addition, Knölker and co-workers[12h] have recently used X-ray analysis to reexamine the structure of Santelli's byproduct[12b] (14% yield) from the Sakurai reaction of allyltrimethylsilane with acetylcyclohexene; Knölker's study has unequivocally established the identity of this compound as a [3 + 2]-type cycloadduct. These and other observations,[12i-k,14] taken together with our results (vide infra), suggest that all cyclic Sakurai byproducts noted previously may in fact be silylcyclopentane derivatives.

As illustrated with the following examples, we have found that the desired [3 + 2] annulation becomes an efficient process when allylsilanes bearing large trialkylsilyl groups are employed in place of Me_3Si derivatives. One significant finding to emerge from our initial studies is that five-membered rings are formed in good yield even when the allylsilane lacks the C-3 substituent that is crucial for success in the propargylsilane-based strategy. Thus, addition of allyltriisopropylsilane[15] to MVK in the presence of $TiCl_4$ proceeds smoothly at −78 °C to afford a mixture of products (99:1) whose structures were unambiguously established as the desired cyclopentanes **13a** and **13b**[16,17] (eq 1). The same allylsilane combines with acetylcyclohexene in good yield to produce the [3 + 2] annulation products **14a** and **14b** (92:8);[19] in this case a small amount of the Sakurai conjugate allylation product is also formed in the reaction (eq 2). Finally, as outlined in eq 3, butenylsilanes **16a**[20] and **16b**[20,21] also can function as three-carbon units in the [3 + 2] annulation;[22] noteworthy in this case is the participation of the Me_3Si derivative **16b**, although a small amount (15%) of Sakurai product is also produced in this reaction.



16a R_3=*t*-BuMe$_2$ 92% **17a : 17b : 17c : 17d** = 67 : 18 : 11 : 4
16b R_3=Me$_3$ 55% **18a : 18b : 18c : 18d** = 71 : 13 : 10 : 6

A remarkable and unanticipated feature of these [3 + 2] annulations is that they proceed with a *high degree of*

(11) Reviewed in: Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(12) (a) Hartman, G. D.; Traylor, T. G. *Tetrahedron Lett.* **1975**, 939. (b) Pardo, R.; Zahra, J.-P.; Santelli, M. *Tetrahedron Lett.* **1979**, 4557. (c) Hosomi, A.; Kobayashi, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 955. (d) Danishefsky, S.; Kahn, M. *Tetrahedron Lett.* **1981**, *22*, 485. (e) House, H. O.; Gaa, P. C.; Van Derveer, D. *J. Org. Chem.* **1983**, *48*, 1661. (f) Nickisch, K.; Laurent, H. *Tetrahedron Lett.* **1988**, *29*, 1533. (g) Majetich, G.; Defauw, J.; Ringold, C. *J. Org. Chem.* **1988**, *53*, 50. (h) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, 429. (i) Imazu, S.; Shimizu, N.; Tsuno, Y. *Chem. Lett.* **1990**, 1845. (j) Majetich, G. In *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic Press: San Diego, 1991; Vol. 3, pp 295–346. (k) Snider, B. B.; Zhang, O. *J. Org. Chem.* **1991**, *56*, 4908.

(13) Ohashi, S.; Ruch, W. E.; Butler, G. B. *J. Org. Chem.* **1981**, *46*, 614.

(14) Panek and Yang have recently found that tetrahydrofurans are the principal products of the reactions of α- and β-alkoxy aldehydes with (*E*)-3-(dimethylphenylsilyl)-4-hexenoate esters: Panek, J. S.; Yang, M. *J. Org. Chem.* **1991**, *113*, 9868.

(15) Muchowski, J. M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, *26*, 5375.

(16) The identity of the annulation products as cyclopentane derivatives was established by subjecting **13a** to the sequence (a) *m*-CPBA (Baeyer–Villiger oxidation), (b) K_2CO_3–MeOH (acetate cleavage), and (c) PCC oxidation. IR and ^{13}C NMR analysis identified the resulting product as 3-(triisopropylsilyl)cyclopentanone rather than 2-((triisopropylsilyl)-methyl)cyclobutanone.

(17) The assignment of the major annulation product **13a** as the trans isomer is based on the stereochemistry assigned to the degradation product 3-(triisopropylsilyl)cyclopentanol prepared as described above.[18] This alcohol proved identical to the minor isomer obtained by Li-*s*-Bu_3BH reduction of 3-(triisopropylsilyl)cyclopentanone. Hydride reduction of 3-silylcyclopentanones is known to predominantly afford cis-substituted cyclopentanols.[18]

(18) De Jesus, M.; Rosario, O.; Larson, G. *J. Organomet. Chem.* **1977**, *132*, 301.

(19) Stereochemistry was assigned to **14a** by analogy with the results of Knölker.[12h]

(20) Prepared by hydrogenation of the corresponding 3-silyl-1-butyne (vide supra).

(21) Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223.

(22) The stereochemical identity of cyclopentanes **17** and **18** was determined by extensive NMR analysis and comparison with reference compounds obtained by hydrogenation of allenylsilane- and propargylsilane-derived annulation products. Details will be presented in the full paper.

stereoselectivity; the major product formed in each reaction has the electron-withdrawing carbonyl group and trialkylsilyl group substituted trans about the new five-membered ring.[23,24] As outlined in Scheme II, we believe that this stereoselectivity arises from a preference for a synclinal transition state, in accord with the general topological rule for Michael additions proposed in 1981 by Seebach and Golinski.[25,26] Furthermore, as in the case of the Diels–Alder reaction, the electron-withdrawing group shows a strong preference here for an endo rather than exo orientation; this arrangement minimizes charge separation in the dipolar transition state, and may also benefit from stabilizing secondary orbital interactions.

One consequence of this stereochemical model is the implication that the reaction of crotylsilanes with β-substituted enones should produce tri- and tetrasubstituted cyclopentanes with very high stereoselectivity. The results of our studies confirming this prediction will be detailed in the next paper in this series.

Acknowledgment. We thank the National Science Foundation for generous financial support of this research. B.R.D. was supported in part (Jan–May 1990) as a Fellow of the Squibb Institute for Medical Research.

Supplementary Material Available: Detailed experimental procedures for all annulation reactions and spectroscopic data for all products (15 pages). This material is contained in many libraries on microfiche, immediately 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.

(23) Similar stereochemical preferences have been observed in the Sakurai byproducts studied by Knölker[12h] and Snider.[12k]

(24) The cycloaddition of allylstannanes with α,β-unsaturated acyliron complexes shows an analogous stereochemical bias: Herndon, J. W.; Wu, C.; Harp, J. J.; Kreutzer, K. A. *Synlett* **1991**, 1.

(25) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413.

(26) For discussions of the stereochemical course of the Sakurai reaction, see (a) Yamamoto, Y.; Sasaki, N. In *Chemical Bonds—Better Ways to Make Them and Break Them*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; pp 363–441. (b) Pan, L.-R.; Tokoroyama, T. *Tetrahedron Lett.* **1992**, *33*, 1469 and references cited therein.

Osmium-Mediated Asymmetric Synthesis of Glycosyl-*myo*-inositols from Oxanorbornanes[1]

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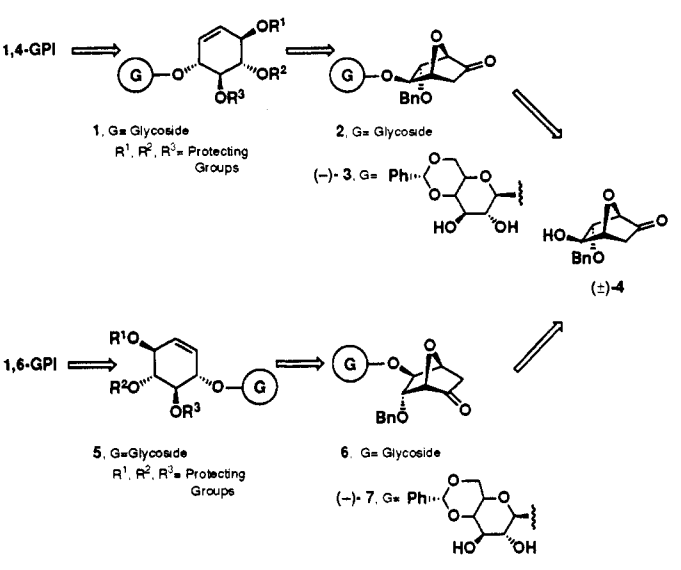
Summary: The osmium-catalyzed cis-dihydroxylation of "symmetrical" 4-*O*-glycosyl-1-*O*-acetyl-conduritol B derivatives occurs syn to the allyic acetate with high π-facial selectivity and affords glycosyl-*myo*-inositols in excellent yield.

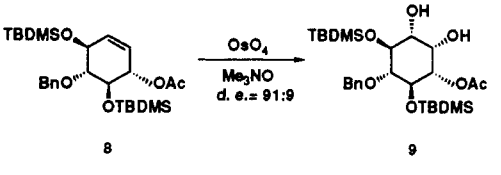
7-Oxanorbornene derivatives are useful intermediates in organic synthesis[2] and their chemistry has received a great deal of attention in recent years. On the other hand, differentially protected *myo*-inositols and, particularly, glycosylinositols, remain challenging and current synthetic targets[3–5] due to the well-documented biological activity of inositol derivatives.[6] In connection with our interest in the chemistry of 7-oxanobornenes,[7] we envisioned that suitably protected precursors of 1,4- and 1,6-glycosyl-phosphatidylinositol derivatives (GPI) could be prepared from glycosylconduritol B precursors **1** and **5** (Scheme I) if conditions to achieve the π-facial selective cis-dihydroxylation anti to the glycoside oxygen were developed. Conduritols **1** and **5** could be prepared from glycosyloxanorbornanes **2** and **6** by cleavage of the oxygen bridge;[8] these compounds would be derived from racemic ketone (±)-**4**[9] by glycosidation and separation of diastereomers. Thus, we intended to take maximum advantage of the symmetry of *myo*-inositols and of the inherent chirality of the carbohydrate in our approach.

Recently, we reported the preparation of model glycosyloxanorbornanes (−)-**3** ($[\alpha]_D$ = −28.0, *c* = 0.1, MeOH) and (−)-**7** ($[\alpha]_D$ = −9.32, *c* = 1.04, $CHCl_3$) (Scheme I), separable in multigram scale by a straightforward trituration of the mixture with $CHCl_3$. Also, we described a new, highly diastereoselective synthesis of a differentially protected *myo*-inositol **9**, via catalytic osmylation of conduritol B acetate **8**.[10] Encouraged by this remarkable selectivity, we have examined the osmium-catalyzed bis-hydroxylation

Scheme I



of glycosylconduritol B substrates **1** and **5** (R_1 = Ac) and we now disclose these results.



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