Registry No. **2**, 111-82-0; (*Z*)-**3**, 109585-97-9; (*E*)-**3**, 109585-96-8; **4**, 629-23-2; $PhCO_2Me$, 93-58-3; $PhCO_2Pr$-*i*, 939-48-0; $PhCO_2Bu$-*t*, 774-65-2; $PhCO_2Ph$, 93-99-2; $MeCO_2C_8H_{17}$, 112-14-1; $BuCO_2Me$, 624-24-8; *i*-$BuCO_2Me$, 556-24-1; *i*-$PrCO_2Me$, 547-63-7; $H_2C{=}CH(CH_2)_8CO_2Me$, 111-81-9; $C_8H_{17}CH{=}CH(CH_2)_7CO_2Me$, 112-62-9; $MeCH{=}CHCO_2Et$, 623-70-1; $BuCO_2CH_2CH{=}CH_2$, 6321-45-5; $PrCO_2CH_2CH{=}CHPr$, 53398-83-7; $MeCHBr_2$, 557-91-5; $C_5H_{11}CHBr_2$, 58133-26-9; *i*-$BuCHBr_2$, 62127-59-7; *c*-$C_6H_{11}CHBr_2$, 52470-92-5; CH_2Br_2, 74-95-3; CH_3CHI_2, 594-02-5; (*Z*)-MeCH=C(Ph)OMe, 4518-65-4; (*E*)-MeCH=C(Ph)OMe, 4541-69-9; (*Z*)-Ph(OMe)C=CHC_5H_{11}, 109612-96-6; (*E*)-Ph(OMe)C=CHC_5H_{11}, 109612-97-7; (*Z*)-*i*-BuCH=C(OMe)Ph, 109585-87-7; (*E*)-*i*-BuCH=C(OMe)Ph, 109585-88-8; (*Z*)-*c*-C_6H_{11}CH=C(OMe)Ph, 109585-89-9; (*E*)-*c*-C_6H_{11}CH=C(OMe)Ph, 109585-90-2; (*Z*)-MeCH=C(OPr-*i*)Ph, 70812-87-2; (*E*)-MeCH=C(OPr-*i*)Ph, 70812-88-3; (*Z*)-MeCH=C(OBu-*t*)Ph, 109585-91-3; (*E*)-MeCH=C(OBu-*t*)Ph, 109585-92-4; (*Z*)-MeCH=C(OPh)Ph, 109585-93-5; (*E*)-MeCH=C(OPh)Ph, 109585-94-6; $H_2C{=}C$(OPh)Ph, 19928-57-5; (*Z*)-MeCH=C(Me)OC_8H_{17}, 109585-95-7; $MeCO(CH_2)_2Ph$, 2550-26-7; (*E*)-MeCH=C(OMe)$C_{11}H_{23}$, 109585-98-0; (*Z*)-C_5H_{11}CH=C(OMe)Bu, 109585-99-1; (*E*)-C_5H_{11}CH=C(OMe)Bu, 109586-00-7; (*Z*)-*i*-BuCH=C(OMe)Bu, 109586-01-8; (*E*)-*i*-BuCH=C(OMe)Bu, 109586-02-9; (*Z*)-*c*-C_6H_{11}CH=C(OMe)Bu, 109586-03-0; (*E*)-*c*-C_6H_{11}CH=C(OMe)Bu, 109586-04-1; (*Z*)-C_5H_{11}CH=C(OMe)Bu-*i*, 109586-05-2; (*E*)-C_5H_{11}CH=C(OMe)Bu-*i*, 109586-06-3; (*Z*)-C_5H_{11}CH=C(OMe)Pr-*i*, 109586-07-4; (*Z*)-MeCH=C(OMe)$(CH_2)_8CH{=}CH_2$, 109586-08-5; (*E*)-MeCH=C(OMe)$(CH_2)_8CH{=}CH_2$, 109586-09-6; (*Z,Z*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-11-0; (*E,E*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-10-9; (*Z,E*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-20-1; (*E,Z*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-21-2; (*Z,E*)-C_5H_{11}CH=C(OEt)CH=CHMe, 109586-12-1; (*E,E*)-C_5H_{11}CH=C(OEt)CH=CHMe, 109586-13-2; (*Z*)-C_5H_{11}CH=C(Bu)-$OCH_2CH{=}CH_2$, 109586-14-3; (*E*)-C_5H_{11}CH=C(Bu)$OCH_2CH{=}CH_2$, 109586-15-4; (*Z,E*)-C_5H_{11}CH=C(Pr)CH_2CHCHPr, 109586-16-5; (*E,E*)-C_5H_{11}CH=C(Pr)CH_2CHCHPr, 109586-17-6; (*Z*)-Ph-$(CH_2)_2$(Me)C=CHC_5H_{11}, 109586-18-7; (*E*)-$Ph(CH_2)_2$(Me)C=CHC_5H_{11}, 109586-19-8; $C_7H_{15}CH(OH)(CH_2)_2COEt$, 109586-24-5; $C_7H_{15}CH(OH)(CH_2)_2COC_6H_{13}$, 109586-27-8; (*Z*)-2-ethylidene-4-heptyl-2,3,4,5-tetrahydrofuran, 109586-22-3; (*E*)-2-ethylidene-4-heptyl-2,3,4,5-tetrahydrofuran, 109586-23-4; (*Z*)-4-heptyl-2-hexylidene-2,3,4,5-tetrahydrofuran, 109586-25-6; (*E*)-4-heptyl-2-hexylidene-2,3,4,5-tetrahydrofuran, 109586-26-7; (*Z*)-1,3-dihydro-1-hexylideneisobenzofuran, 109586-28-9; (*E*)-1,3-dihydro-1-hexylideneisobenzofuran, 109586-29-0; 5-heptyl-2(3*H*)-furanone, 104-67-6; 1(3*H*)-isobenzofuranone, 87-41-2.

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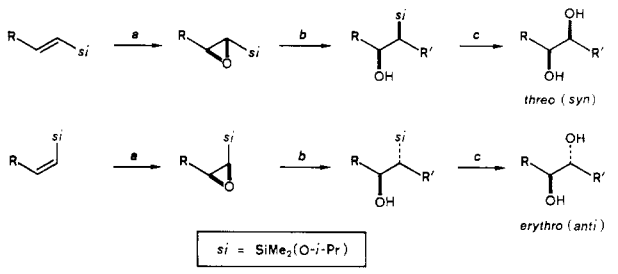
Silafunctional α,β-Epoxy Silanes: Transformation into Erythro and Threo 1,2-Diol Skeletons and Its Application to the Synthesis of (±)-*exo*-Brevicomin[1]

Summary: Stereodefined *E* and *Z* α,β-epoxy silanes containing an isopropoxy group on silicon can be transformed into threo and erythro 1,2-diol skeletons, respectively, by regioselective ring opening with carbon nucleophiles followed by hydrogen peroxide oxidation of the carbon–silicon bonds; application to the synthesis of (±)-*exo*-brevicomin is also reported.

Sir: Epoxidation of stereodefined olefins and the subsequent ring opening with nucleophiles have provided one of the most efficient methods for stereoselective synthesis of polyfunctional compounds.[2] However, it is not an easy task to control the regioselectivity of the ring opening in unsymmetrical epoxides.[2] It is noteworthy in this respect that α,β-epoxy silanes react with carbon or heteroatom nucleophiles regioselectively at carbon α to silicon exclusively to form β-hydroxy silanes.[3] This unique chemistry, however, has so far been applied only to the stereoselective synthesis of olefins,[3a,4c,f] haloolefins,[4a] enol ethers,[4a] enol esters,[4a,b,d] enamides,[4a] and enamines,[4e] as well as conversion to carbonyl functionalities.[5] Reported herein is a new transformation of α,β-epoxy silanes to 1,2-diol derivatives. Thus, as shown in Scheme I, stereodefined *E* and *Z* epoxy silanes undergo regioselective ring opening with carbon nucleophiles and the subsequent stereospecific oxidative cleavage of the carbon–silicon bond with retention of configuration[6] to form unambiguously threo and erythro 1,2-diol skeletons, respectively.[7] The presence of an alkoxy group on silicon is essential for the present process.[8]

Scheme I[a]



[a] (a) MCPBA (1 equiv)/CH_2Cl_2/room temperature/12 h; (b) R′MgX (3 equiv)/CuCN (0.3 equiv)/Et_2O/−20∼−30 °C/2–3 h; (c) 30% H_2O_2 (5–20 equiv)/KF (3 equiv)/$KHCO_3$ (3 equiv)/MeOH/THF/room temperature/12 h.

(1) Silafunctional Compounds in Organic Synthesis. 35. (a) Part 34: Tamao, K.; Yamauchi, T.; Ito, Y. *Chem. Lett.* **1987**, 171. (b) Part 33: Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 957. (c) Part 32: Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100. (d) Part 31: Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090.

(2) Gorzynski Smith, J. *Synthesis* **1984**, 629. Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67. Rossiter, B. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York: 1985; Vol. 5, pp 193–246. Pfenninger, A. *Synthesis* **1986**, 89.

(3) (a) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. (b) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2615. (c) Davis, A. P.; Hughes, G. J.; Lowndes, P. R.; Robbins, C. M.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1934. (d) Ager, D. J. *Synthesis* **1984**, 384.

(4) (a) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993. (b) Magnus, P.; Roy, G. *J. Chem. Soc., Chem. Commun.* **1978**, 297. (c) Hudrlik, P. F.; Hudrlik, A. M.; Misra, R. N.; Peterson, D.; Withers, G. P.; Kulkarni, A. K. *J. Org. Chem.* **1980**, *45*, 4444. (d) Croudace, M. C.; Schore, N. *J. Org. Chem.* **1981**, *46*, 5357. (e) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Tetrahedron* Lett. **1985**, *26*, 139. (f) Kitano, Y.; Matsumoto, T.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1323.

(5) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080. Tamao, K.; Maeda, K. *Tetrahedron Lett.* **1986**, *27*, 65.

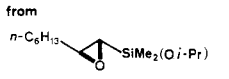
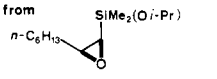
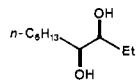
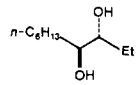
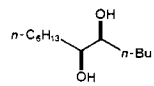
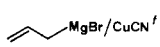
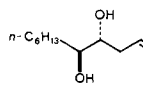
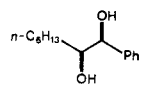
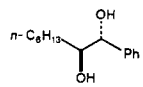
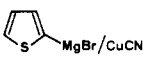
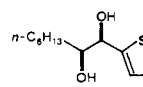
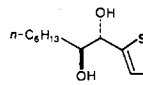
(6) (a) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (b) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.

(7) Although we use Noyori's erythro/threo nomenclature (Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem.* Soc. **1983**, *105*, 1598), the syn/anti nomenclature proposed by Masamune is also given in Scheme I (Masamune, S.; Kaiho, T.; Garvey, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5521).

(8) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; pp 231–242. An isopropoxy group was chosen in the present transformation, since the isopropoxydimethylsilyl moiety is usually tolerated by the organometallic reagents and to the usual hydrolytic workup, but exhibits a reasonable reactivity toward the final oxidative cleavage of the carbon–silicon bonds.[6b]

0022-3263/87/1952-4412$01.50/0

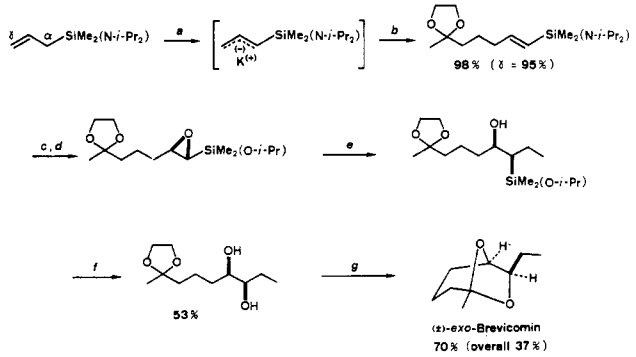
Table I. Preparation of Threo and Erythro 1,2-Diols from Epoxy Silanes[a]

organometallics[b]	product[c] and overall yield, %[d] from 	from 
EtMgBr/CuCN	 56	 45
$(n\text{-Bu})_2Cu(CN)Li_2$/$BF_3$[e]	 62	
	g	 65
PhMgBr/CuCN	 39[i,j]	 76[k]
	 34[j]	 62

[a] Carried out on a 2–3-mmol scale in the standard manner described for a typical procedure (see text), unless otherwise stated. [b] Unless otherwise mentioned, a mixture of a Grignard reagent (3 equiv) and 10 mol % of CuCN in ether was allowed to react with epoxides at −30∼−20 °C for 2–4 h. [c] No other stereoisomer was detected by GLC analysis and 400-MHz NMR of the corresponding acetonides. [d] Isolated overall yields based on vinylsilanes as precursors of epoxides. Epoxides and products are all racemic. [e] Carried out at −78 °C for 2 h by use of $n\text{-Bu}_2Cu(CN)Li_2$ (1.3 equiv) and $BF_3{\cdot}OEt_2$ (1.4 equiv) in a mixture of hexane and THF, according to the Normant's procedure (ref 13). The use of 3 equiv of the cuprate resulted partially in butylation on the silicon atom. [f] Allyl-MgBr (1.5 equiv)/CuCN (0.5 equiv). Allylation of isopropoxysilyl group was accompanied when 3 molar equiv of the allyl-Grignard reagent was used. [g] Allylation on the silicon atom predominated. [h] Intermediate β-hydroxy silane derivatives could be isolated in 67–68% yield. [i] Reaction in THF resulted in mostly the Peterson olefination. [j] The Peterson elimination product, (*E*)-1-aryl-1-octene, was formed in ca. 40% yield. [k] The Peterson elimination product, (*Z*)-1-phenyl-1-octene, was formed in 7% yield.

Typically, (*E*)-1-(isopropoxydimethylsilyl)-1-octene[9] (2.4 mmol) was treated with *m*-chloroperbenzoic acid (2.4 mmol) in CH_2Cl_2 at room temperature for 12 h.[5b] The mixture was diluted with pentane and filtered to remove the precipitates. Evaporation of the solvents gave a crude epoxy silane almost quantitatively. To a cooled mixture of ethylmagnesium bromide in ether (7.2 mmol) and CuCN (0.72 mmol, 10 mol %) was added a solution of the crude epoxy silane in ether at −50 °C with stirring and the mixture was allowed to warm to −20 °C over 4 h. After hydrolysis with 10% NH_4Cl solution, extraction with ether, drying over $MgSO_4$, and evaporation, the resulting oil was stirred with 30% H_2O_2 (20 equiv), KF (3 equiv), and $KHCO_3$ (3 equiv) in methanol/THF (1:1) at room temperature overnight. Usual workup[11] and preparative TLC gave *threo*-3,4-decanediol[12] as a sole stereoisomer in 56% overall yield based on the vinylsilane.

Scheme II[a]



[a] (a) *t*-BuOK/*n*-BuLi/*n*-hexane/Et_2O/−78∼0 °C/6 h; (b) $CH_3\text{-}\overbrace{COCH_2CH_2O}CH_2CH_2I$/−78 °C∼room temperature/12 h; (c) HCl/*i*-PrOH/5 min; (d) MCPBA (1 equiv)/CH_2Cl_2/room temperature/12 h; (e) EtMgBr (3 equiv)/CuCN (0.3 equiv)/Et_2O/THF/−50 °C/5 h; (f) 30% H_2O_2 (5 equiv)/KF (3 equiv)/$KHCO_3$ (3 equiv)/MeOH/THF/room temperature/10 h; (g) acetone/H_2O/$HClO_4$/room temperature/12 h.

Several representative results are listed in Table I. Alkyl-, aryl-, allyl-, and heteroaryl-Grignard reagents were equally applicable with a few exceptions. The overall yields based on vinylsilanes are generally acceptable for a three-step procedure. Two points deserve comment. (1) For the smooth ring opening, it was essential to use the Grignard reagent together with a catalytic amount (about 10 mol %) of CuCN or to use diorganocuprates $R_2Cu(CN)Li_2$ in the presence of BF_3[13] to minimize an unusual deoxygenation of epoxy silanes back to the parent vinylsilanes.[14] (2) Conversion of *E* epoxides to threo diols was accompanied substantially by the Peterson olefination, while in the case of *Z* epoxides such a side reaction was almost negligible (see footnotes j and k of Table I); this difference may be ascribed to stereoelectronic effects.[15]

Since a variety of existing methods for the stereoselective synthesis of vinylsilanes[16] may be mostly applicable also to the synthesis of silafunctional vinylsilanes, the present developments should find wide application. As an example of the applications, we present a stereoselective synthesis of (±)-*exo*-brevicomin,[17] an aggregation pheromone of the female western pine beetle (*Dendroctonus brevicomis*), starting from allylaminosilane.[1b] Thus, as shown in Scheme II, the allylsilane was first metalated with *n*-BuLi/*t*-BuOK (Schlosser's base)[18] and then coupled with an appropriately protected alkyl iodide to give, after treatment with acidic *i*-PrOH, (*E*)-alkenylisopropoxysilane in an almost quantitative yield, the γ regioselectivity being

(9) Prepared by the usual hydrosilation of 1-octyne with $HSiMe_2Cl$ followed by treatment with *i*-PrOH in the presence of Et_3N and purified by fractional distillation. The *Z* isomer was prepared in 83% overall yield from $n\text{-}C_6H_{13}C{\equiv}CSiMe_2H$ by hydroalumination,[10] hydrolysis, and dehydrogenative alkoxylation (*i*-PrOH/$H_2PtCl_6{\cdot}6H_2O$ catalyst).

(10) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215.

(11) Tamao, K.; Ishida, N. *Tetrahedron Lett.* **1984**, *25*, 4245.

(12) Stereochemical assignments were made by 400-MHz NMR of the acetonides. Cf.: Nakanishi, K.; Schooley, D. A.; Koreeda, M.; Miura, I. *J. Am. Chem. Soc.* **1972**, *94*, 2865.

(13) Alexakis, A.; Jachiet, D.; Normant, J. F. *Tetrahedron* **1986**, *42*, 5607. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A.; Parker, D. *J. Org. Chem.* **1984**, *49*, 3928. Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947.

(14) Tamao, K.; Nakajo, E.; Ito, Y., submitted for publication.

(15) It has been reported that threo β-hydroxy silanes undergo the Peterson elimination four times faster than the erythro isomers: Yamamoto, K.; Kimura, T.; Tomo, Y. *Tetrahedron Lett.* **1984**, *25*, 2155.

(16) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

(17) Recent publications: Sato, F.; Takahashi, O.; Kato, T.; Kobayashi, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1638 and references cited therein.

(18) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741.

higher than 95%.[19] Epoxidation, ethylation, oxidation, and acidic deprotection gave *exo*-brevicomin in 37% overall yield.

Acknowledgment. We thank the Ministry of Education, Japan, for a Grant-in-Aid for Scientific Research (No. 61470093) and Shin-etsu Chemical Industrial Co., Ltd. for a gift of organosilicon compounds.

(19) It has recently been reported that metalation of allyltrimethylsilane with the Schlosser's base and coupling with alkyl halides gave a high γ regioselectivity: Kumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, *25*, 717. Chan, T. H.; Kumaglo, K. *J. Organomet. Chem.* **1985**, *285*, 109. This was the case also for our allylaminosilane which was used as the starting material in view of the compatibility with the highly reactive metalating agents. Details will be reported in due course.

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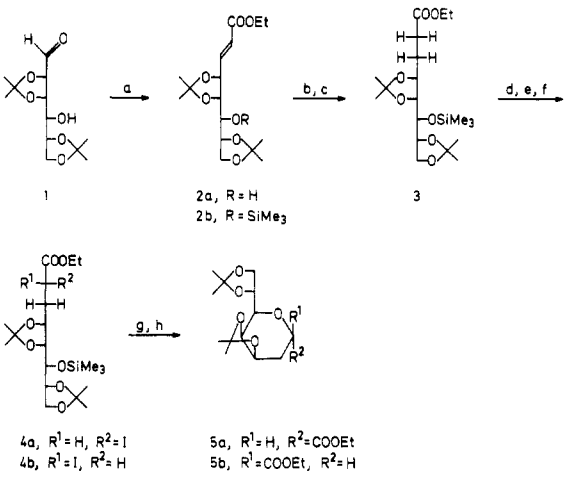
New Synthesis of a CMP-KDO Synthetase Inhibitor and of 2-Deoxy-KDO Derivatives Used in the Synthesis of Such Inhibitors

Summary: The deoxy-KDO derivatives **5a** and **5b**, which are useful in the synthesis of β-C-glycosides of KDO, were prepared in a stereospecific manner starting with a diacetonide of D-mannose (**1**). Deprotection of **5a** gives an acid that is a potent inhibitor of CMP-KDO synthetase.

Sir: During the course of work on design and synthesis of efficient inhibitors of the enzyme CMP-KDO synthetase[1,2] as potential, new antibacterial agents, we have found the diacetonides of ethyl (or methyl) 2,6-anhydro-3-deoxy-D-*glycero*-D-*talo*-(or *galacto*)octonates (**5a** and **5b**, respectively) to be particularly useful.[3,4] The first route chosen for the synthesis of **5** was via hydrogenolysis of the glycosyl chloride of KDO tetraacetate methyl ester which required KDO as a starting material.[4a] Although KDO can be prepared in practically useful yields (25–30%) by the Cornforth procedure,[2] the preparation is tedious and one of the starting materials is the rather expensive oxaloacetic acid.

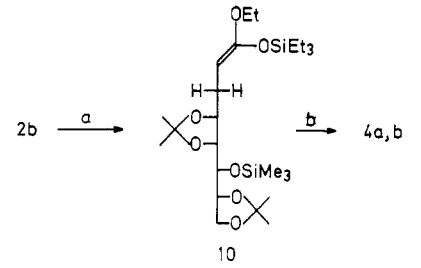
The presently reported method (Scheme I) for synthesis of **5**, which should be applicable to the syntheses of many other C-glycosides,[5] starts with 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (here depicted in the open-chain form **1**) which is available in ≥95% yield from D-mannose and acetone.[6] The reported conversion of this compound into the ester **2a** proceeds in practically quantitative yield.[7] Addition of a trace of benzoic acid,[8] which was not used in the earlier preparations of **2a**,[7] completely prevented it from cyclizing to the tetrahydrofurans **6**

Scheme I[a]



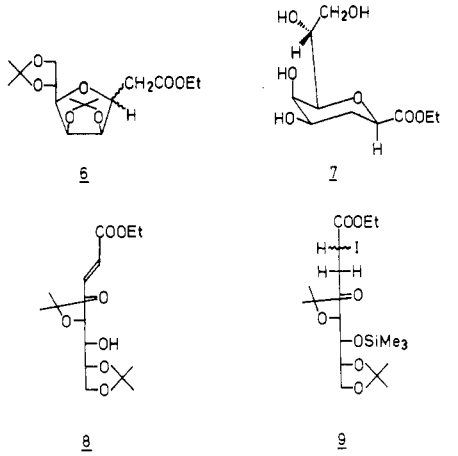
[a] (a) $Ph_3P{=}CHCOOEt$, toluene, 90 °C for ~5 h; (b) H_2 (Pd/C), EtOAc; (c) Me_3SiCl, pyridine–ether; (d) $LiN(i\text{-}C_3H_7)_2$, THF, −70 °C for 0.5 h; (e) $ZnCl_2$ (1 equiv) at −70 °C, then stirring for 1 h; (f) I_2 (1.2 equiv) in THF; (g) Bu_4NF (0.9 equiv), EtOAc–EtOH (9:1), room temperature for 5 min; (h) K_2CO_3 (3 equiv), stirring for 30 h.

Scheme II[a]



[a] (a) Et_3SiH, $(Ph_3P)_3RhCl$, toluene, 50 °C, 2 h; (b) ICl, pyridine, 0 °C.

Chart I



(1) KDO is an abbreviation for 3-deoxy-D-*manno*-2-octulosonic acid which links the *O*-antigen to lipid A in the lipopolysaccharide of gram-negative bacteria.[2]

(2) Review on the chemistry and biochemistry of KDO: Unger, F. M. *Adv. Carbohydr. Chem. Bichem.* **1981**, *38*, 323–388.

(3) The 2,6-anhydrooctonic acid obtained by complete removal of the protective groups from **5a** is the best inhibitor of CMP-KDO synthetase known so far; the corresponding acid from **5b** is inactive. Claesson, A; Luthman, K.; Gustafsson, K.; Bondesson, G. *Biochem. Biophys. Res. Commun.* **1987**, *143*, 1063–1068. Luthman, K. Doctoral Thesis, Dec. 1986. *Acta Universitatis Upsaliensis. Comprehensive Summaries of Uppsala Dissertations from the Faculty of Pharmacy. No 23*, Almquist & Wiksell International, Stockholm, 1986.

(4) (a) Luthman, K.; Orbe, M.; Wåglund, T.; Claesson, A. *J. Org. Chem.* **1987**, *52*, 3777–3784. (b) Luthman, K.; Claesson, A.; Jansson, A.; Pring, B. G. *Carbohydr. Res.*, in press. (c) After submission of the present manuscript the methyl ester of **5b** was reported by still another route: Norbeck, D. W.; Kramer, J. B.; Lartey, P. A. *J. Org. Chem.* **1987**, *52*, 2174–2179.

(5) The synthesis of C-glycosides is of great interest due to their occurrence in antibiotics and as potential chiral building blocks. For leading references, see: Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622–623.

(6) Bell, D. J. *J. Chem. Soc.* **1947**, 1461. The diacetonide of D-mannose is now commercially available from several companies.

(7) Zhadanov, Y. A.; Uzlova, L. A. *Zh. Obshch. Khim.* **1971**, *41*, 1396–1399. Collins, P. M.; Overend, W. G.; Shing, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1139.

(8) Buchanan, J. G.; Edgar, A. R.; Power, M. J.; Theaker, P. D. *Carbohydr. Res.* **1974**, *38*, C22.

0022-3263/87/1952-4414$01.50/0