the reaction fails in the case of trans-disubstituted olefins, (e.g., *trans*-5-decene, *trans*-stilbene). Other obvious types of unsaturated substrates have yet to be investigated. The observed product stereochemistries[14] (especially runs 1,4,5, and 6) may have important implications regarding the mechanism[15] of these reactions, a point which we are studying in further detail. In some cases (runs 1,2) small amounts of olefinic products (e.g., 3-ethylcyclooctene in run 1) are obtained in addition to the cyclopropanes, but we have not yet been able to establish which changes in reaction parameters are most clearly associated with the formation of these byproducts.

Having successfully developed a synthetically attractive method for ethylidenation of olefins, we are now more confident that related procedures for alkylidene transfer in general may be found.[16] Investigations are in progress in our laboratory to define the scope of these reactions with respect to the transfer of other groups, the use of several types of unsaturated substrates, and the development of reagents containing other metals in place of iron and other leaving groups in place of sulfonium salts. The complete details of this work will be described in a forthcoming full paper.

Acknowledgment. We are grateful to Professor Maurice Brookhart of the University of North Carolina for communicating his related results to us and the National Science Foundation (Grant CHE 7918019) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, (Grant No. 12032-ACl, 3) for providing the financial support for this research.

(14) Although our stereochemical assignments are based upon generally accepted ^{1}H NMR correlations,[4b,13] we consider all of these assignments to be tentative until we have completed a more thorough study based upon not only spectroscopic characterization but also chemical correlations.

(15) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097–6099. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282–7292.

(16) Recently Mr. M. Thaker has found in our laboratory that the reaction of $CpFe(CO)_2CH{=}CH_2$ with HBF_4 and cyclooctene affords the same cyclopropane (direct GLPC comparison) as in run 1 of Table I. This result serves to indicate the possibility of β protonation of the vinyl ligand and provides yet an additional, potentially general route for alkylidene transfer.

Chirality Transfer via Organopalladium Chemistry. A Synthesis of Optically Active Vitamin E Side Chain from D-Glucose

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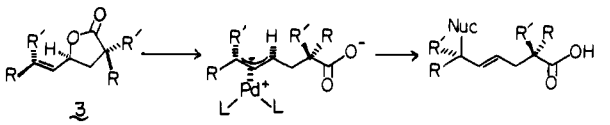
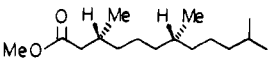
The control of stereochemistry in acyclic systems is an important methodological and synthetic challenge. We demonstrated such control of relative stereochemistry at remote chiral centers via organopalladium[1] and organocopper[2] intermediates. Success of these approaches (Scheme I) required (1) ionization of the substrate **3** from a single conformation, (2) formation of the new C–C bond faster than the rate at which the stereochemical integrity of the intermediate was lost, and (3) regioselective alkylation. In the case of palladium, such attack of the nucleophile took place from the face of the π-allyl opposite palladium. The process allowed net replacement of a C–O bond by a C–C bond with allyl inversion and retention of configuration. The advantage of this approach stemmed, in part, from the potential availability of the requisite substrates from carbohydrates[3,4] which would control

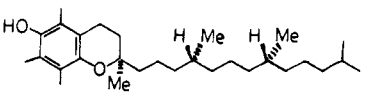
Scheme I



absolute as well as relative stereochemistry. In this paper, we realize that potential in the development of a synthesis of the side chain **1** of Vitamin E (**2**)[5,6] from D-glucose, which is also applicable to the synthesis of the side chain of Vitamin K.[1,12]

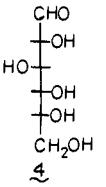


1

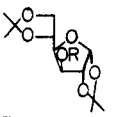


2

D-Glucose (**4**) was converted to its diacetonide **5**[7] ($ZnCl_2$, 85%,

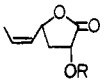


4

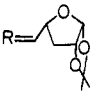


5 R=H
6 R=Ts

H_3PO_3, acetone, room temperature 3 days) and its free hydroxyl was tosylated[8] (1.5 equiv of TsCl, pyridine, 82%). Elimination of **6** to the olefin (KOH, 0.4 mm, 60 °C, 65%) followed by hydrogenation (3 atm of H_2, 10% Pd/C, EtOH, 92%) effected removal of the undesired hydroxyl group at C-3 and inversion of the C-4 center. Selective deprotection of the exo acetonide [HCl (catalytic), 1:1 MeOH:H_2O, 84%] followed by glycol cleavage [1.2 equiv of $NaIO_4$, H_2O (pH 6–7), 83%] afforded aldehyde **7**.[4d,e]



9 R=H
10 R=CO Ph



7 R=O
8 R=CHCH$_3$ (Z)

Wittig olefination ($Ph_3P{\oplus}CH_2CH_3Br{\ominus}$, KO-*t*-Bu, THF, 69%) gave entirely (*Z*)-olefin **8**[9] ($[\alpha]^{25}_D$ −49.17°, *c* 1.08, $CHCl_3$) by 270-MHz ^{1}H NMR (δ 5.56, ddq, J = 12.0, 7.0, and 1.5 Hz) and 15.04-MHz ^{13}C NMR spectroscopy (δ 12.59 for the vinyl methyl carbon).[10] Deprotection of the remaining acetonide [PTSA (catalytic), 10:1 CH_3CN:H_2O] and selective oxidation of the resulting diol (1.5 equiv of Ag_2CO_3/celite,[11] benzene, 41% over

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(5) For totally synthetic approaches, see: Cohen, N.; Lopresti, R. J.; Neukom, C.; Jancz, G. *J. Org. Chem.* **1980**, *45*, 582 and earlier references in this series.

(6) For microbially aided synthesis, see: (a) Fuganti, C.; Guselli, P. *J. Chem. Soc., Chem. Commun.* **1979**, 995. (b) Schmid, M.; Barner, R. *Helv. Chim Acta* **1979**, *62*, 464. (c) Zell, R. *Ibid.* **1979**, *62*, 474. (d) Heitzer, H. *Synthesis* **1979**, 888.

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(9) This compound has been fully characterized by spectral means and elemental composition utilizing high resolution mass spectrometry, and/or combustion analysis.

(10) The ^{13}C NMR signals of the cis vinyl methyl carbons in lactones of this type appear at δ 12.9–13.3, substantially upfield of the corresponding trans vinyl methyl carbons at δ 17.2–17.7. See also: Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426–431.

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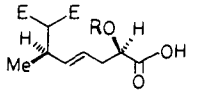
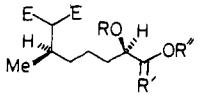
two steps) gave lactone **9**[9] ($[\alpha]^{25}_D$ −46.8°, c 1.0, $CHCl_3$) which was benzoylated (PhCOCl, pyridine, CH_2Cl_2, 95%) to produce **10** ($[\alpha]^{25}D$ −19.7°, *c* 1.0, $CHCl_3$, mp 88–90 °C), the purity of both compounds confirmed by chromatographic and ^1H and ^{13}C NMR criteria. The critical alkylation of **10** (1.3 equiv of sodiomalonate, 5% $Pd(PPh_3)_4$, THF, 95%) proceeded smoothly to yield **11**[9] ($[\alpha]^{25}_D$ −9.95°, *c* 1.11, $CHCl_3$) whose diastereomeric purity was established by 50.10-MHz ^{13}C NMR spectroscopy.

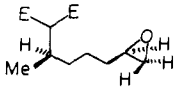


11 E = CO_2Me
R = COPh

Reduction of **11** (1 atm of H_2, PtO_2, EtOAc, 91%) produced **12**[9] ($[\alpha]^{25}_D$ +1.26°, *c* 2.2, $CHCl_3$), also diastereomerically pure by 50.10-MHz ^{13}C NMR spectroscopy. The epoxide **15**[9] was pro-

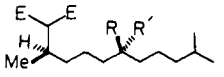


12 R = COPh; R′ = O; R″ = H
13 R = COPh; R′ = H,H; R″ = H
14 R = COPh; R′ = H,H; R″ = Ts



15

duced by the straightforward series of steps of reduction to alcohol **13** [5 equiv of $BH_3{\cdot}S(CH_3)_3$, Et_2O, 93%], tosylation to **14** (2.2 equiv of TsCl, pyridine, 90%), and base catalyzed cyclization to **15** (1.3 equiv of NaOMe, MeOH, 60%) which was purified by preparative high-performance LC (25% EtOAc in hexane).[12] Organocuprate epoxide opening[13] (isopentylcopper cyanide, Et_2O, −10 °C, 64%) gave the enantiomerically pure alcohol **16**[9] ($[\alpha]^{25}_D$ +4.42°, *c* 2.78, $CHCl_3$), whose stereochemical purity was established chromatographically and spectrally by 270-MHz ^1H and 50.10-MHz ^{13}C NMR spectroscopy.



16 R = OH; R′ = H
17 R = OTs; R′ = H
18 R = H; R′ = Me

Creation of the last chiral center required tosylation to **17** (2.2 equiv of TsCl, pyridine, 75%) and organocuprate coupling [5 equiv of $Li(CH_3)_2Cu$, ether, −15 °C]—a sequence that produced the desired **18** contaminated by elimination products. Separation of the olefin was facilitated by selective epoxidation (0.5 equiv of *m*-chloroperbenzoic acid, CH_2Cl_2). Decarbomethoxylation (KOAc, Me_2SO, 140 °C) of the mixture of **18** and epoxidized olefins produced a readily resolved (high-performance LC, 2% EtOAc in hexane) mixture from which pure **1**[9] was isolated in 26% overall yield from the starting tosylate. Optically active **1** ($[\alpha]^{25}_D$ +4.44°, *c* 1.12, $CHCl_3$) was diastereomerically pure as established by 67.9-MHz ^{13}C NMR spectroscopy.[1] Its enantiomeric purity was established by saponification (2.5 equiv of KOH, 4:1 CH_3OH:H_2O, 69%) to give the corresponding acid ($[\alpha]^{25}_D$ +5.39°, *c* 1.82, $CHCl_3$) which agrees with the reported rotation for this acid ($[\alpha]^{25}D$ +5.43°, *c* 5.0, $CHCl_3$) derived from phytol.[14]

We have previously shown that both γ-butyrolactones and δ-valerolactones serve as substrates in this stereorelay process.[1,2] The availability of both structural types from carbohydrates provides an approach for the chiral synthesis of natural products with a great ability to vary the separation between the chiral centers. The demonstrated facile synthesis of **1**, where the chiral centers are in a 1,5 relationship, from such a common sugar as D-glucose, attests to this fact. Acyclic units bearing a large number of chiral centers, such as the macrocyclic rings of the ansa ring antibiotics,[15,16] represent another challenge for this methodology.

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Supplementary Material Available: A detailed description of spectral data for compounds in this synthesis (6 pages). Ordering information is available on any current masthead.

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(12) This epoxide is a chiral synthon for other 1,5-methyl substituted compounds. (a) Pine sawfly pheromone: Ade, E.; Helmchen, S.; Heligenmann, G. *Tetrahedron Lett.* **1980**, *21*, 1175. (b) Tsetse fly pheromone: Baker, R.; Winton, P. M. *Ibid.* **1980**, *21*, 1137.
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New Tungstophosphates: $Cs_6W_5P_2O_{23}$, $Cs_7W_{10}PO_{36}$, and $Cs_7Na_2W_{10}PO_{37}$

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Contribution No. 2867
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We wish to report the facile preparations of three new tungstophosphates and crystal-structure determinations on two of them. These preparations depend on the use of cesium as a counterion and emphasize the important role that counterions can play in determining solid-state heteropolyanion structure.

The three new tungstophosphates are $Cs_6W_5P_2O_{23}{\cdot}7.5H_2O$, $Cs_7W_{10}PO_{36}{\cdot}7H_2O$, and $Cs_7Na_2W_{10}PO_{37}{\cdot}8H_2O$. The first is prepared by adding cesium hydroxide to tungstic acid (15 g) in water (100 mL) until pH 13 is reached. Phosphoric acid is then added to lower the pH to 7, and the solution is chilled. Crystalline $Cs_6W_5P_2O_{23}{\cdot}7.5H_2O$ separates in 60% yield. The infrared spectrum is quite similar to that of $Na_6Mo_5P_2O_{23}$,[1] and structure determination reveals that $W_5P_2O_{23}^{6-}$ is indeed isostructural with $Mo_5P_2O_{23}^{6-}$ (Figure 1).

$Cs_6W_5P_2O_{23}{\cdot}7.5H_2O$ can be recrystallized from water if the solution is not heated beyond 60 °C. Above this temperature, and most rapidly at 100 °C, aqueous solutions of $Cs_6W_5P_2O_{23}$ separate the relatively insoluble salt $Cs_7W_{10}PO_{36}{\cdot}7H_2O$. The crystallographically determined structure of $Cs_7W_{10}PO_{36}{\cdot}7H_2O$ (Figure 2) can be derived from the Keggin structure[2] by a 60° rotation of each of two W_3O_{13} sets and removal of the two octahedra that become edge shared as a result of these rotations. This structure is particularly interesting, because 60° rotations of two W_3O_{13} sets in the Keggin structure give one of the proposed, but as yet unreported, Baker–Figgis isomers;[3] furthermore, Pope[4]

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