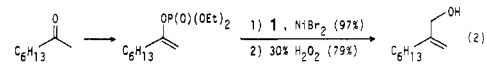
peracetic acid (entries 9–11). In the last case 30% H_2O_2 gave only the protonolysis product (entry 10).

One of the most characteristic features is that the OH group is introduced exclusively onto the carbon atom to which the silicon atom has been attached, even in allylic silanes. Thus, this reaction provides the first successful procedure for the direct conversion of allylsilanes to allyl alcohols without an allylic transposition.[12] Also noteworthy is the stereo- and regiocontrolled hydroxymethylation of allylic halides. For example, geranyl and neryl chlorides are converted to the corresponding homoallylic alcohols with the highest efficiency ever reported (entries 6 and 7).[13] Furthermore, under these oxidation conditions neither epoxidation of olefin nor oxidation of amine, nitrile, and thiophene was observed.

While the present method cannot be applied to carbonyl groups since the Peterson olefination[14] may result, the regioselective, reductive hydroxymethyltion of ketones has been accomplished via a nickel-catalyzed Grignard coupling with the enol phosphate,[15] as exemplified by eq 2.



In view of the ready availability of the starting material, compatibility of several functional groups, high regio- and stereoselectivity, mildness of oxidation step, and high overall yields, the present method may prove to be of great use for nucleophilic hydroxymethylation of various kinds of compounds.

Acknowledgment. We thank Shin-etsu Chemical Industrial Co., Ltd., for partial support and a gift of chlorosilanes, and Mitsubishi Gas-Chemical Industrial Co., Ltd., for a gift of 90% hydrogen peroxide.

Registry No. 1, 85719-58-0; 2, 2212-08-0; *n*-$C_8H_{17}Br$, 111-83-1; (*E*)-PhCH=CHBr, 588-72-7; (*E*)-$C_6H_{13}CH$=CHBr, 51751-87-2; (*Z*)-$C_6H_{13}CH$=CHBr, 42843-49-2; (*E*)-$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=$CHCH_2Cl$, 5389-87-7; (*Z*)-$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=$CHCH_2Cl$, 20536-36-1; 4-$MeOC_6H_4Br$, 104-92-7; 4-NCC_6H_4Br, 623-00-7; 4-$EtO_2CC_6H_4Br$, 5798-75-4; 2-$MeO_2CC_6H_4Br$, 610-94-6; (*i*-PrO)$_2$MeSiCH_2-*n*-C_8H_{17}, 85719-59-1; (*E*)-(*i*-PrO)$_2$MeSiCH_2CH=CHPh, 85719-60-4; (*E*)-(*i*-PrO)$_2$MeSiCH_2CH=CHC_6H_{13}, 85719-61-5; (*Z*)-(*i*-PrO)$_2$MeSiCH_2CH=CHC_6H_{13}, 85719-62-6; (*E*)-(*i*-PrO)$_2$MeSiCH_2CH_2CH=$C(CH_3)CH_2CH_2CH$=$C(CH_3)_2$, 85719-64-8; (*Z*)-(*i*-PrO)$_2$MeSiCH_2CH_2CH=$C(CH_3)CH_2CH_2CH$=$C(CH_3)_2$, 85719-65-9; (*i*-PrO)$_2$MeSi$CH_2C_6H_4$-*p*-OMe, 85719-66-0; (*i*-PrO)$_2$MeSi$CH_2C_6H_4$-*p*-CN, 85719-67-1; (*i*-PrO)$_2$MeSi$CH_2C_6H_4$-*p*-CO_2Et, 85719-68-2; (*i*-PrO)$_2$MeSi$CH_2C_6H_4$-*o*-CO_2Me, 85719-69-3; *n*-$C_8H_{17}CH_2OH$, 143-08-8; (*E*)-PhCH=$CHCH_2OH$, 4407-36-7; (*E*)-$C_6H_{13}CH$=$CHCH_2OH$, 31502-14-4; (*E*)-$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=$CHCH_2CH_2OH$, 459-88-1; (*Z*)-$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=$CHCH_2CH_2OH$, 74380-61-3; 4-$MeOC_6H_4CH_2OH$, 105-13-5; 4-$NCC_6H_4CH_2OH$, 874-89-5; 4-$EtO_2CC_6H_4CH_2OH$, 15852-63-8; (*Z*)-$C_6H_{13}CH$=$CHCH_2OH$, 41453-56-9; 1-bromocyclooctene, 4103-11-1; 3-bromothiophene, 872-31-1; 3-bromopyridine, 626-55-1; methylbis(1-methylethoxy)(1-cyclooctenylmethyl)silane, 85719-63-7; methylbis(1-methylethoxy)(3-thienylmethyl)silane, 85719-70-6; methylbis(1-methylethoxy)(3-pyridylmethyl)silane, 85719-71-7; 1-methanol-1-cyclooctene, 56900-55-1; 1(3*H*)-isobenzofuranone, 87-41-2; 3-thiophenemethanol, 71637-34-8; 3-[(trimethylsilyloxy)methyl]pyrideine, 85719-72-8.

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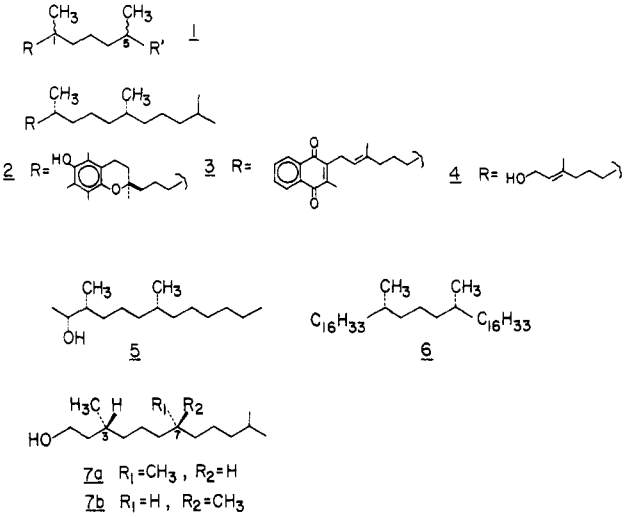
Chirality Transfer in Stereoselective Synthesis. A Highly Stereoselective Synthesis of Optically Active Vitamin E Side Chains

Summary: Employing the Carroll reaction as a means of chirality transfer, a highly efficient, stereochemically controlled, and generally applicable synthesis of optically active 1,5-dimethylated acyclic chains has been developed; as an example, the synthesis of the optically active C-15 vitamin E side chains **7a** and **7b** from (+)-pulegone in 12.6% and 11.7% overall yields, respectively, is described.

Sir: Stereocontrol originating from remote chiral centers during the construction of acyclic systems remains a central theme in the total synthesis of complex natural products.[1] One attractive solution to this end involves chirality transfer mediated by mechanistically well-defined, highly stereocontrolled rearrangement reactions.[2] Among the target molecules to which one could apply such methodology are the 1,5-dimethylated acyclic units **1**,



present in a number of biologically important natural products such as vitamin E (α-tocopherol, **2**), vitamin K (**3**), phytol (**4**), and insect pheromones of pine sawflies (**5**)[3]

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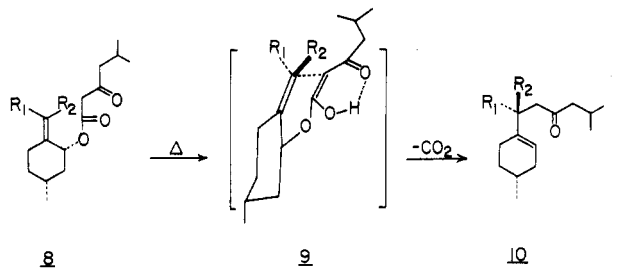
0022-3263/83/1948-2122$01.50/0

Scheme I



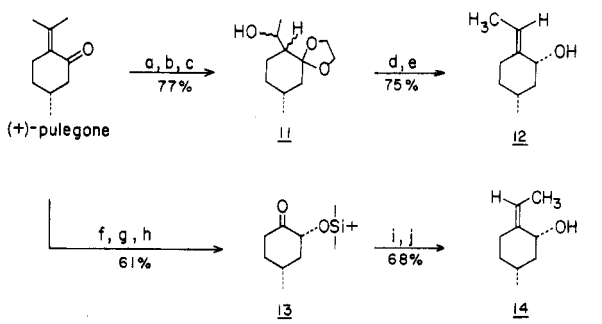
8 9 10

and tsetse flies (6).[4] In the following communication we delineate a highly efficient and versatile synthesis of optically active vitamin E side-chain alcohol **7a** (3*R*,7*R*)[5,6] and its heretofore unknown C-7 epimer **7b** (3*R*,7*S*), on the basis of the concept of chirality transfer.

The synthesis employs the Carroll reaction[7] of the conformationally rigid β-keto esters **8** in the key stereorelaying process (Scheme I). The chirality of the new asymmetric center reflects the stereochemistry of the hydroxyl in **8**, thus inducing high diastereoselectivity between the two methyls in **10**, a precursor to **7a** or **7b**.

The requisite optically active allylic alcohols **12**[8] (mp 58–59 °C; $[\alpha]^{23}_D$ +37.8° (*c* 0.955, $CHCl_3$)) and **14**[9] (mp 58–58.5 °C; $[\alpha]^{23}_D$ –63.5° (*c* 1.015, $CHCl_3$)) were efficiently prepared from (+)-pulegone[10] ($[\alpha]^{23}_D$ +24.2° (*c* 1.080, EtOH)) in five steps in 57.8% and 41.5% overall yields, respectively (Scheme II). Thus, (+)-pulegone was first ketalized with concomitant migration of the double bond,[11] followed by ozonolysis and reductive workup, to provide

Scheme II[a]



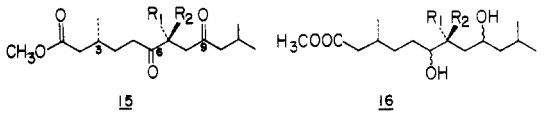
(+)-pulegone 11 12 13 14

[a] Conditions: (a) $(CH_2OH)_2$ (7 equiv), $HC(OEt)_3$ (3 equiv), *p*-TsOH (catalytic), 55 °C, 4 h (83%); (b) O_3, MeOH, –78 °C; (c) $NaBH_4$ (5 equiv), –78 °C to room temperature, 3 h (92%); (d) PPTS (0.33 equiv), wet acetone, reflux, 36 h (80%); (e) $NaBH_4$ (1 equiv), $CeCl_3$ (1 equiv), MeOH, room temperature, 5 min (94%); (f) same as e (76%); (g) *t*-$BuMe_2SiCl$ (2 equiv), imidazole (4 equiv), DMF, 45 °C, 12 h (90%); (h) O_3, $MeOH/CH_2Cl_2$, –78 °C to room temperature, 4 h (89%); (i) $Ph_3P^+CH_2CH_3Br^-$, lithium diisopropylamide, 0 °C, 1 h; (j) $(n\text{-}Bu)_4N^+F^-$ (2.5 equiv), 0 °C to room temperature, 20 h.

the hydroxy ketal **11** in 77% overall yield. Deketalization of **11** with pyridinium *p*-toluenesulfonate (PPTS),[12] followed by spontaneous dehydration afforded predominantly the *E* enone, with an *E*/*Z* ratio of over 30:1, which was subsequently reduced to **12** with $NaBH_4/CeCl_3$.[13] Isomer **14** was likewise synthetized from (+)-pulegone by a sequence of reduction, protection, and oxidative cleavage of the olefin to afford the ketone **13** in 61% overall yield. Interestingly, the Wittig reaction of **13** with ethylidenetriphenylphosphorane gave cleanly the *Z* isomer, which was deprotected to provide **14**.

The crucial chirality transfer was effected by using the β-keto esters **8a** and **8b**, which were obtained by treatment of **12** (92%) and **14** (90%) with 5-isovaleryl-Meldrum's acid[14] in benzene at 55 °C. Thus, heating **8a** and **8b** neat at 220 °C for 2 h smoothly produced the rearranged products **10a**[15] and **10b**[16] in 65% and 70% yields, respectively. Stereoselectivity of the Carroll reaction was determined to be greater than 98% in both cases, judging from the high-field (90.56 MHz) ^{13}C NMR spectra of the products. Both **10a** and **10b** were treated successively with (1) O_3, acetone, –78 °C and (2) CH_2N_2, ether, 0 °C to afford the diketo esters **15a** (71%) and **15b** (73%).

The removal of the 6,9-diketones to complete the synthesis proved to be troublesome. Namely, thioketalization of both **15a** and **15b** with 1,2-ethanedithiol (10 molar



15 16

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(6) Throughout the text, the letters a and b associated with the compound numbers represent compounds having $R_1 = CH_3$, $R_2 = H$ and $R_1 = H$, $R_2 = CH_3$, respectively.

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(8) For **12**: 360-MHz ^1H NMR ($CDCl_3$) δ 0.934 (d, 3 H, *J* = 6.3 Hz), 1.639 (dd, 3 H, *J* = 1.5, 6.8 Hz), 4.008 (br ddd, 1 H, *J* = 1.9, 2.0, 11.2 Hz) 5.467 (dq, 1 H, *J* = 1.9 for d, 6.8 Hz for q); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 12.1 (q), 21.7 (q), 26.3 (t), 31.5 (d), 35.3 (t), 45.9 (t), 72.2 (d), 111.5 (d), 141.4 (s).

(9) For **14**: 360-MHz ^1H NMR ($CDCl_3$) δ 1.038 (d, 3 H, *J* = 6.8 Hz), 1.801 (dd, 3 H, *J* = 0.9, 7.2 Hz), 4.472 (m, 1 H, $\Delta W_{1/2}$ = 31 Hz), 5.274 (dq, 1 H, *J* = 3.0 for d, 7.2 Hz for q); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 13.1 (q), 21.4 (q), 29.8 (d), 32.8 (t), 35.0 (t), 43.3 (t), 71.2 (d), 118.2 (d), 140.3 (s).

(10) Purchased from Fluka Chemical Co., Hauppauge, NY. For the enantiomeric purity of the natural pulegone, see ref 5a and 5b.

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(15) For **10a**: 360-MHz ^1H NMR ($CDCl_3$) δ 0.895 (d, 6 H, *J* = 6.6 Hz), 0.924 (d, 3 H, *J* = 6.0 Hz), 0.984 (d, 3 H, *J* = 6.8 Hz), 5.377 (br s, 1 H, $\Delta W_{1/2}$ = 10.5 Hz); 90.56-MHz ^{13}C NMR ($CDCl_3$) δ 19.56 (q), 21.72 (q), 22.69 (q), 24.53 (d), 25.99 (t), 28.67 (d), 31.42 (t), 33.96 (t), 36.86 (d), 49.44 (t), 52.51 (t), 120.38 (d), 140.95 (s), 210.32 (s).

(16) For **10b**: 360-MHz ^1H NMR ($CDCl_3$) δ 0.896 (d, 6 H, *J* = 6.5 Hz), 0.923 (d, 3 H, *J* = 6.1 Hz), 5.375 (br dd, 1 H, *J* = 0.7, 5.5 Hz); 90.56-MHz ^{13}C NMR ($CDCl_3$) δ 19.83 (q), 21.66 (q), 23.88 (q), 24.61 (d), 25.81 (t), 28.67 (d), 31.60 (t), 33.96 (t), 36.86 (d), 49.29 (t), 52.43 (t), 120.25 (d), 140.95 (s), 210.32 (s).

equiv)/BF_3·OEt_2 (1.25 equiv)/AcOH/CH_2Cl_2 at −15 °C proceeded smoothly in 88% and 95% yields, respectively, without epimerization at C-7, judging by 90.56-MHz ^{13}C NMR spectroscopy. However, desulfurization to methylenes with W-2 Raney nickel under various conditions led to a serious loss (~15%) of diastereomeric purity at C-7 in both cases, albeit in excellent chemical yields. Therefore, the diketo esters **15a** and **15b** were first reduced with $NaBH_4$ in MeOH to the hydroxy esters **16a** (95%) and **16b** (93%). Formation of the phenyl thionocarbonates of both **16a** and **16b**, followed by reduction with $(n\text{-Bu})_3SnH$,[17] proceeded in high yields, but the products were found to have epimerized at C-7 to the extent of about 15%. This problem of partial epimerization at C-7 was circumvented by $LiAlH_4$ reduction (Et_2O, 0 °C to room temperature, 2 h) of the dimesylates of **16a** and **16b**. The reduction products were contaminated to a minor extent with olefinic compounds. These were removed via epoxidation with *m*-chloroperoxybenzoic acid in CH_2Cl_2 followed by silica gel flash column chromatography[18] to provide the optically pure C_{15} alcohols **7a**[19] ($[\alpha]^{23}_D$ +3.35° (*c* 0.955, $CHCl_3$)) and **7b**[20] ($[\alpha]^{23}_D$ +3.56° (*c* 1.805, $CHCl_3$)) in 54% and 66% yields from **16a** and **16b**, respectively. High-field (90.56 MHz) ^{13}C NMR analysis of these alcohols and their racemic 50:50 diastereomeric mixture, obtained from methyl farnesoate (1. H_2/Pd, 2. $LiAlH_4$), showed the alcohols **7a** and **7b** to be over 98% diastereomerically pure. This was further confirmed by comparison of the high-field ^{13}C NMR spectra of the methyl esters derived from **7a** and **7b** (1. Jones reagent, 2. CH_2N_2) with those of the corresponding racemic esters.[21]

The approach described herein provides *highly efficient and totally stereocontrolled* syntheses (12 steps) of the optically pure 3*R*,7*R* vitamin E side-chain alcohol **7a** and its thus far unreported C-7 epimer **7b** (3*R*,7*S*) from the readily available (+)-pulegone in 12.6% and 11.7% overall yields, respectively. It should be noted that (−)-pulegone is also easily accessible via a number of efficient syntheses.[22] Therefore, the synthesis of all four stereoisomers having 1,5-dimethylated acyclic chains (1) should be attained by a minimal modification of the method described herein.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. AM30025) for the support of this research and to the National Science Foundation for its contribution to the purchase of a Bruker 360-MHz NMR spectrometer. We thank Professor B. M. Trost for the high-field ^{13}C NMR spectra of the methyl esters derived from **7a** and **7b**.

Supplementary Material Available: Experimental details including physical properties, spectral data, and analyses (17 pages). Ordering information is given on any current masthead page.

[†] Celanese Graduate Fellow, 1982–1983.

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(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(19) For **7a**: 360-MHz ^1H NMR ($CDCl_3$) δ 0.847 (d, 3 H, *J* = 7.5 Hz), 0.866 (d, 6 H, *J* = 6.6 Hz), 0.896 (d, 3 H, *J* = 6.7 Hz), 3.69 (m, 2 H); 90.56-MHz ^{13}C NMR ($CDCl_3$) δ 19.77* (q), 22.63 (q), 22.71 (q), 24.45 (t), 24.84 (t), 28.04 (d), 29.73 (d), 32.89 (d), 37.39* (t), 37.47 (t), 37.62* (t), 39.48 (t), 40.15* (t), 61.31 (t). The ^{13}C NMR peaks of **7a** and **7b** (ref 20) with an asterisk indicate those diagnostic for diastereomeric distinction. Reported optical rotation for **7a**: $[\alpha]^{25}_D$ +3.16 ($CHCl_3$; concentration not given).[5b] This alcohol was derived from the degradation of (+)-phytol.

(20) For **7b**: 360-MHz ^1H NMR ($CDCl_3$) δ 0.843 (d, 3 H, *J* = 6.6 Hz), 0.866 (d, 6 H, *J* = 6.6 Hz), 0.894 (d, 3 H, *J* = 6.6 Hz), 3.68 (m, 2 H); 90.56-MHz ^{13}C NMR ($CDCl_3$) δ 19.72* (q), 22.63 (q), 22.71 (q), 24.45 (t), 24.84 (t), 28.04 (d), 32.89 (d), 32.47* (t), 37.47 (t), 37.48 (t), 37.58* (t), 39.48 (t), 40.22* (t), 61.31 (t).

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