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STEREOSELECTIVE SYNTHESIS OF (2E,4Z)-DIEN-1-OLS; KEY INTERMEDIATES FOR SYNTHESIS OF SEX PHEROMONES OF SILK WORM AND OF GRAPE VINE MOTH

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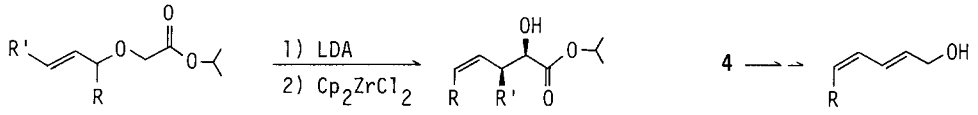
Summary: Two (2E,4Z)-dien-1-ols, synthetic key intermediates for the insect pheromones with a (E,Z)-diene system, were synthesized stereoselectively by using a combination of zirconium-mediated [2,3]Wittig rearrangement reaction and Peterson reaction as key steps.

A conjugated (E,Z)-diene system is often encountered in natural products, and the biological activity highly specific to the diene geometry as observed in some lepidopteran pheromones has prompted the stereocontrolled synthesis of the system.1) Recently, we developed a zirconium-mediated [2,3]Wittig rearrangement of (E)-α-alkenyloxyacetic acid esters (**1**) to (2,3-syn,4Z)-3-alkyl-2-hydroxy-4-alkenoic acid esters (**2**) with high stereoselectivity (Scheme 1).2) When the C3 alkyl group (R') of starting **1** is replaced by a Me_3Si group, the reaction is considered to provide a new stereoselective route to (E,Z)- (**5**) or (Z,Z)-diene derivatives (**10**) because the rearranged products (**4**) are nice substrates for the Peterson elimination.3,4,5)



1 R'= Me
3 R'= Me_3Si

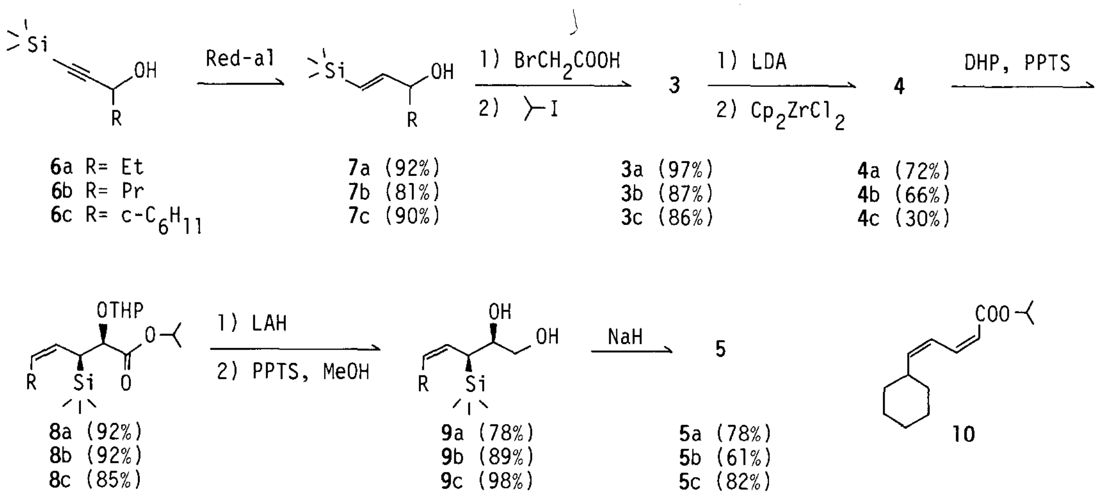
2 R'= Me
4 R'= Me_3Si

5

Scheme 1

Here, we describe the practicability of the above approach and its application to the synthesis of (2E,4Z)-2,4-hepta- (**5a**) and (2E,4Z)-2,4-octadienol (**5b**), which are the synthetic intermediates of sex pheromones, (7E,9Z)-dodeca-7,9-dien-1-yl acetate6) (grape Vine moth) and bombykol7) (silk worm), respectively (Scheme 2).

The trimethylsilylpropargylic alcohols (**6**) prepared from respective aldehydes and trimethylsilylacetylene were first converted to **3** by reduction with Red-al8) followed by treatment of the resulting allylic alcohols (**7**) with bromoacetic acid.9) The zirconium-mediated [2,3]-Wittig rearrangement of **3** gave the rearranged products (**4**), each of which was a single isomer in ^{1}H NMR (90 MHz).10) The products (**4**) were further converted to the desired dienols (**5**) by a sequence; i) protection of the hydroxyl group as a THP ether (DHP, PPTS, CH_2Cl_2, rt),11) ii) LAH reduction, iii) deprotection of the THP ether (PPTS, MeOH, 50 °C),11) and iv) Peterson elimination of the resulting diols (**9**) (NaH, THF, rt). The configurations of the dienols were assigned to be 2E,4Z from the respective coupling constants of vinylic protons ($J_{2,3}$= 15-16Hz, $J_{4,5}$= 10-12Hz).12)



Scheme 2

For an example of a transformation to (Z,Z)-diene structure, **4c** (R= cyclo-C_6H_{11}) was transformed ($BF_3.OEt_2$, CH_2Cl_2, rt, 6 h) into the (2Z,4Z)-dienoate (**10**) ($J_{2,3}$= 10.7Hz, $J_{4,5}$= 10.8Hz) in 75% yield.13)

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10) Bulky R seemed to retard the rearrangement from **3** to **4** as can be seen in the yield of **3c** to **4c** though the stereoselectivity was not affected. Further example: R= n-C_7H_{15}, 30%.
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12) **5a**: ^{1}H NMR, δ ($CDCl_3$), 0.92(3H, t, J= 7.0Hz), 1.38(1H, m), 2.18(1H, m), 4.24(2H, d, 6.5Hz), 5.32 6.00(2H, m), 6.01(1H, dd, J= 11.8Hz, J= 11.8Hz), 6.56(1H, dd, J= 11.8Hz, J= 16.0Hz). **5b**: ^{1}H NMR, δ ($CDCl_3$), 0.98(3H, t, J= 6.4Hz), 2.19(1H, dq, J= 6.4Hz, J= 7.5Hz), 4.18(2H, d, J= 5.7Hz), 5.37 5.80(2H, m), 5.94(1H, dd, J= 10.8Hz, J= 11.6Hz), 6.54(1H, dd, J= 11.6Hz, J= 15.5Hz). **5c**; ^{1}H NMR, δ ($CDCl_3$), 0.72 1.77(10H, m), 2.39(1H, m), 4.14(2H, d, J= 5.7Hz), 5.23(1H, dd, J= 9.9Hz, J= 9.9Hz), 5.73(1H, dt, J= 5.7Hz, J= 15.8Hz), 5.83(1H, dd, J= 10.3Hz, J= 11.1Hz), 6.50(1H, dd, J= 11.1Hz, J= 15.8Hz).
13) **10**: ^{1}H NMR, δ ($CDCl_3$), 1.08 1.75(10H, m), 1.27(6H, d, J= 7.3Hz), 2.55(1H, m), 5.06(1H, m), 5.62(1H, d, 10.7Hz), 5.73(1H, dd, J= 9.8Hz, J= 10.8Hz), 6.92(1H, dd, J= 10.8Hz, J= 11.7Hz), 7.17(1H, dd, J= 10.7Hz, J= 11.7Hz).

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