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Anti Stereochemistry in $\underline{S}_E$'' Reaction of an Optically Active 2,4-Dienylsilane[1)]

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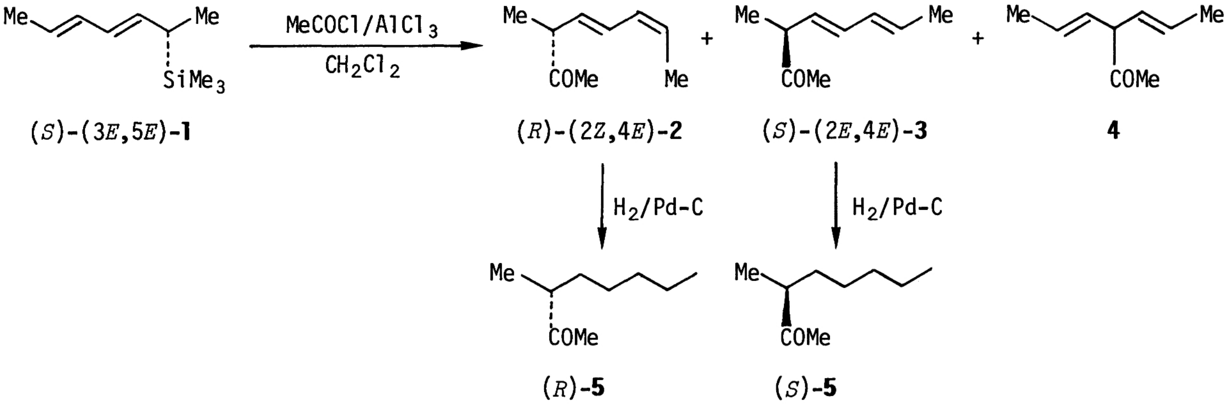
The $\underline{S}_E$'' reaction of (S)-(3E,5E)-2-(trimethylsilyl)hepta-3,5-diene with acetyl chloride and aluminum chloride in dichloromethane proceeded with anti stereochemistry to give (2Z,4E)-6-methylocta-2,4-dien-7-one of R configuration and its (2E,4E) isomer of S configuration.

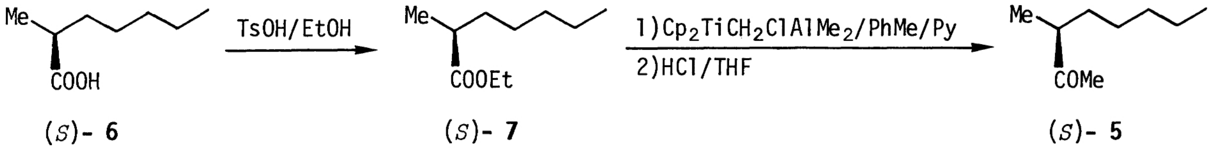
The stereochemistry of electrophilic reactions ($\underline{S}_E$') of allylsilanes giving γ-substituted products has been extensively studied with several types of allylsilanes including optically active ones, and it is now recognized that electrophiles attack the double bond selectively anti with respect to the leaving silyl group.[2-6)] Here we report the first observation of the stereochemistry in electrophilic ε-substitution reaction ($\underline{S}_E$'') of a 2,4-dienylsilane, which has attracted considerable mechanistic interest.[7-9)]

An optically active dienylsilane, (S)-(3E,5E)-2-(trimethylsilyl)hepta-3,5-diene (1) ($[\alpha]_D^{20}$ -14.6° (c 5.1, benzene), 32% ee),[10)] which was prepared by



Scheme 1.

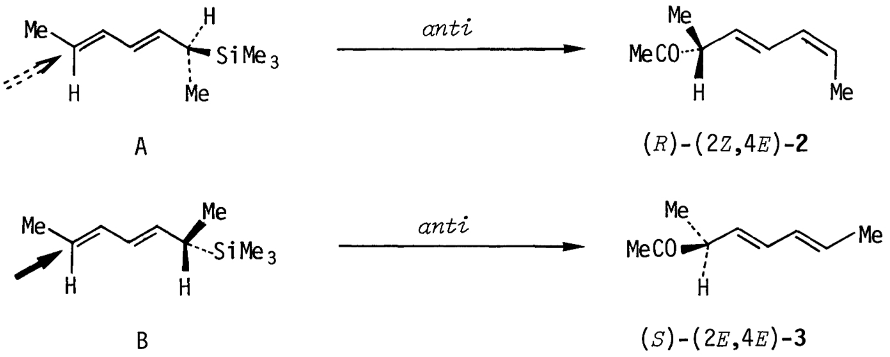
asymmetric cross-coupling of 1-(trimethylsilyl)ethylmagnesium chloride with (*E*,*E*)-1-bromo-1,3-pentadiene in the presence of a chiral palladium catalyst,[10)] was allowed to react with 2.0 equiv. of acetyl chloride and 1.0 equiv. of aluminum chloride in dichloromethane at -78 °C for 2 min. Aqueous work-up followed by preparative TLC on silica gel (pentane/ether = 5/1) gave 67% yield of S_E'' products consisting of (2*Z*,4*E*)-6-methylocta-2,4-dien-7-one (**2**)[11)] and its (2*E*,4*E*) isomer (3)[12)] in a ratio of 2 : 1, and 3% yield of an S_E' product, 4-acetylhepta-2,5-diene (**4**). The S_E'' products (2*Z*,4*E*)-**2** ($[\alpha]_D^{20}$ -48.3° (*c* 1.1, pentane)) and (2*E*,4*E*)-3 ($[\alpha]_D^{20}$ +46.2° (*c* 0.9, pentane)) which were separated isomerically pure by HPLC (Develosil 60-5, hexane/ethyl acetate = 96/4) were hydrogenated (140 atm at 60 °C) in the presence of palladium charcoal to give 6-methyloctan-7-one (5) with the specific rotation of $[\alpha]_D^{20}$ -0.6° (*c* 1.0, CCl_4) and $[\alpha]_D^{20}$ +0.9° (*c* 0.9, CCl_4), respectively (Scheme 1). The configuration of methyl ketone **5** was correlated with that of known (*S*)-2-methylheptanoic acid (**6**)[13)] (Scheme 2). Thus, ethyl ester (*S*)-(+)-7 obtained by esterification (EtOH/TsOH) of the optically active acid (*S*)-(+)-**6** ($[\alpha]_D^{20}$ +4.1° (neat))[14)] was converted into methyl ketone **5** by methylenation with $Cp_2TiCH_2ClAlMe_2$ followed by acidic hydrolysis. The rotation of (*S*)-**5**, whose enantiomeric purity was confirmed to be 17% ee by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$, was $[\alpha]_D^{20}$ +2.4° (*c* 2.1, CCl_4). It follows that the S_E'' product **2** is an (*R*) isomer of at least 4% ee (13% stereoselective) and 3 is an (*S*) isomer of at least 7% ee (20% stereoselective).



Scheme 2.

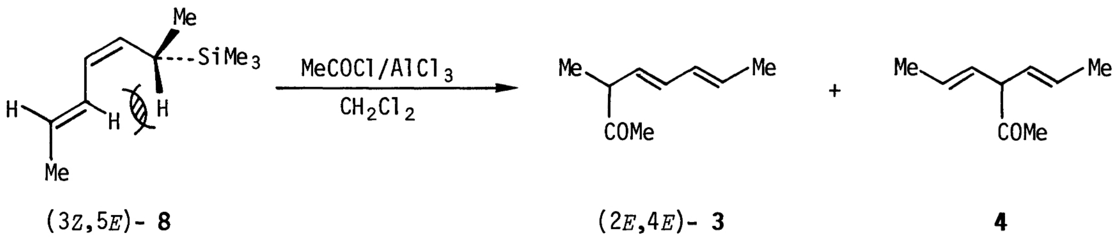
The stereochemical course of the S_E'' reaction is illustrated in Scheme 3. The dienylsilane, (*S*)-(3*E*,5*E*)-**1**, is expected to exist in the conformation A or B where the C-Si linkage is nearly perpendicular to the plane of the C-C double bond[15)] and the two double bonds are in a transoid manner (Scheme 3). Other possible conformations with cisoid dienes which would suffer a disadvantageous steric repulsion can be excluded because the formation of S_E'' products bearing

(4Z) geometry was not observed. The products (2Z,4E)-2 and (2E,4E)-3 should arise from A and B, respectively, and their configurations ((R) for **2** and (S) for **3**) indicate that the electrophilic attack on the ε carbon occurred preferentially anti to the silyl group either in A or B. Thus, the stereochemical course of the S_E'' reaction was determined to be anti. The low stereoselectivity may be ascribed to the difficulty in transmitting electronic or steric information owing to the long distance between the chiral carbon center and the reaction site.



Scheme 3.

In the acetylation of (3Z,5E)-2-(trimethylsilyl)hepta-3,5-diene (8), 30% of the S_E' product **4** was formed together with 20% of the S_E'' product (2E,4E)-3 (Scheme 4). It is likely that the steric repulsion between the hydrogens at α and δ positions prevents coplanarity of the diene system and consequently the ε attack of the electrophile becomes less feasible.



Scheme 4.

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11) ^{1}H NMR (400 MHz in C_6D_6) for (2Z,4E)-2: δ 1.160 (d, J = 6.8 Hz, 3H), 1.669 (dd, J = 1.7 and 7.1 Hz, 3H), 1.831 (s, 3H), 2.925 (quint, 1H), 5.463 (dq, J = 10.8 and 7.1 Hz, 1H), 5.556 (dd, J = 15.4 and 8.7 Hz, 1H), 6.060 (tq, J = 10.8 and 1.7 Hz, 1H), 6.458 (dd, J = 15.4 and 10.8 Hz, 1H).

12) ^{1}H NMR (400 MHz in C_6D_6) for (2E,4E)-3: δ 1.162 (d, J = 6.8 Hz, 3H), 1.668 (d, J = 7.2 Hz, 3H), 1.849 (s, 3H), 2.893 (quint, 1H), 5.448 (dd, J = 8.6 and 14.6 Hz, 1H), 5.576 (dq, J = 14.3 and 6.8 Hz, 1H), 6.004 (dd, J = 14.3 and 10.5 Hz, 1H), 6.061 (dd, J = 14.6 and 10.5 Hz, 1H).

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