Tetrahedron Letters,Vol.30,No.37,pp 4983-4984,1989	0040-4039/89 $3.00 + .00
Printed in Great Britain	Pergamon Press plc

CHIRALITY TRANSFER IN THE 1,5-HYDRIDE SHIFT OF A STANNYL COMPOUND HAVING CATIONIC CENTER AT δ-POSITION

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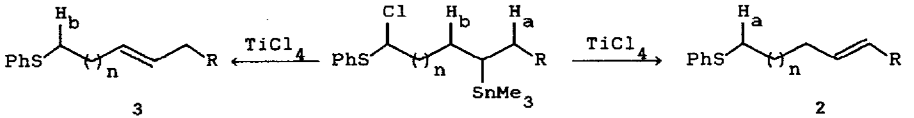
Chirality transfer with 7 : 1 selectivity was realized in the I_2/AgOTf-induced 1,5-hydride shift of 2-methyl-5(R)-trimethylstannyl-1-hexene to 6-iodo-5(S)-methyl-1-hexene.

Some time ago, we reported$^{1)}$ that the treatment of **1** with $TiCl_4$ induced an elimination of chloride anion with concomitant hydride shift, resulting in the olefin formation (eq 1). Notably, only H_a-shift was observed with the substrates of n = 1 or 2, producing **2**, while only H_b-shift was observed when n = 3 or 4, producing **3**. The reaction was also noted for its high trans selectivity.

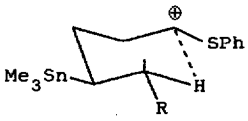


(1)

3 **1** **2**

H_b-shift, n=3 or 4	H_a-shift, n=1 or 2

These facts induced us to propose a reaction scheme involving a cyclic transition state **4**, in which the trimethylstannyl group and migrating hydrogen atom occupy the anti-periplanar position.$^{2)}$ With a view to prove the scheme, as well as to extend the scope of the reaction, we envisioned to achieve a chirality transfer from the tin-bearing carbon to the cationic center. For this purpose, the creation of a prochiral cationic center is requisite, and we manipulated a reaction system shown in eq 2.



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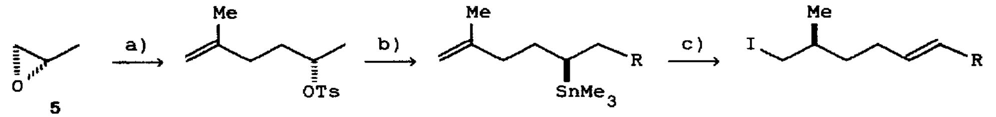
The optically active **7** was prepared from (S)-methyloxirane **5** through a reaction sequence shown in eq 2. We assigned (R)-configuration for **7** because the reaction of a tosylate with Me_3SnLi is known to proceed with



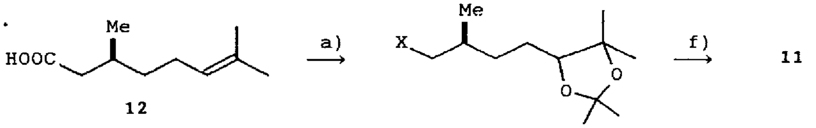
(2)

5 **6** **7**: R = H **8**: R = Me (racemic) **9**: R = H **10**: R = Me (racemic)

a) i) 2-methyl-2-propenylmagnesium bromide, ii) TsCl/Py; b) Me_3SnLi; c) I_2/AgOTf;

complete inversion.³⁾ When treated with I_2/AgOTf in CH_2Cl_2 at −78 °C, **7** underwent the 1,5-hydride shift to afford terminal olefin **9** in about 70% yield. In order to evaluate the optical purity, the iodide **9** was converted to a diastereomeric mixture of the corresponding L-menthyl ether **11**, and the diastereomeric ratio was determined on a capillary gas chromatography. Two peaks with area ratio of 7 to 1 were observed, while the ratio was 1 to 1 in case of the menthyl ether derived from racemic **7**.

The absolute stereochemistry of the newly-created chiral center of the major product was assigned as (S), since the product was identical with the authentic **11**, prepared from (S)-citronellic acid **12** (eq 3), on GLC and NMR analyses.

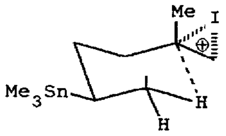


(3)

$$\text{X: NCO} \xrightarrow{b)} \text{NHAc} \xrightarrow{c)} \text{N(NO)Ac} \xrightarrow{d)} \text{OAc} \xrightarrow{e)} \text{L-menthoxy}$$

a) i) H_2O_2/HCOOH, 40 °C; ii) acetone/$ZnCl_2$; iii) ClCOOEt/Et_3N/NaN_3/acetone, −5 ~ 0 °C; iv) reflux/toluene; b) reflux/AcOH; c) $NaNO_2$/AcOH-Ac_2O, 0 °C; d) reflux/hexane; e) i) NaOH/EtOH-H_2O, reflux; ii) TsCl/Py, 0 °C; iii) L-menthol/Na/toluene, reflux; f) i) HCl/EtOH-H_2O, rt; ii) $NaIO_4$/dioxane-H_2O, rt; iii) $Ph_3P(Br)Me$/n-BuLi/Et_2O, rt.

The results show that the reaction proceeds through a cyclic transition state **13**, in which trimethylstannyl and iodonium π-complex moieties occupy quasi-equatorial positions. The introduction of a chiral center at a position remote from any chiral functionality is one of the challenging problems in organic synthesis. Although the remote chirality transfer is observed in sigmatropic rearrangement, only few cases⁴⁾ are known with non-conjugated system.



13

The I^+-induced 1,5-hydride shift was also attained with (±)-**8**, which gave (±)-**10** in 71% yield. The typical procedure is as follows. To a mixture of AgOTf (0.5 mmol) and **7** or **8** (0.4 mmol) in CH_2Cl_2 (4 ml), was added a solution of iodine (0.5 mmol) in CH_2Cl_2 (4 ml) at −78 °C under nitrogen, and the mixture was stirred for 2 h at this temperature. The crude material, after washing with $NaHCO_3$ aq, and treating with a short column of silica gel, gave the product as an almost pure sample.

Financial support from the Asahi Glass Foundation is acknowledged.

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(Received in Japan 26 June 1989)