Tetrahedron Letters, Vol.31, No.43, pp 6137-6140, 1990
Printed in Great Britain

0040-4039/90 \$3.00 + .00
Pergamon Press plc

# A NEW STEREOSELECTIVE SYNTHESIS OF (Z)-VINYLSILANE ALLYLIC ALCOHOLS†

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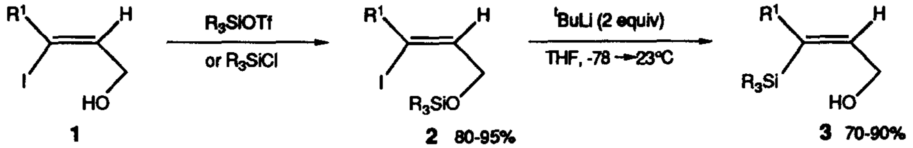
Summary: A new, highly stereoselective method for the synthesis of (Z)-vinylsilane allylic alcohols 3 is described. This approach to such γ-silylated allylic alcohols employs a novel 1,4-O→sp$^2$C silyl rearrangement of appropriate silyl ether precursors 2.

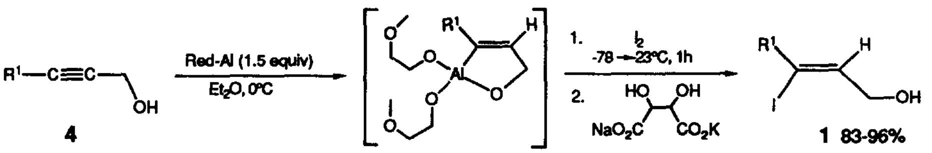
Vinylsilanes are now being recognized as versatile synthetic reagents since their carbon silicon bond can be readily cleaved by various electrophiles in a regio- and stereoselective manner.[1] In particular, γ-silylated allylic alcohols have been employed as efficient precursors of various carbonyl compounds,[2] allylsilanes,[3] and stereochemically homogeneous epoxides.[4] While a few useful methods for the synthesis of (E)- and (Z)-vinylsilane allylic alcohols have been recorded,[2b,5,6] almost invariably these syntheses start from trimethylsilyl substituted alkynes, a feature that may be scope-limiting with regard to silicon substitution.[2d,6]

We wish to report a general and stereoselective synthesis of (Z)-vinylsilane allylic alcohols 3 which relies on the discovery of a 1,4-O→C silyl migration as shown in eq 1 ($SiR_3$=TMS, TBDMS, TIPS). It is well known that trialkylsilyl groups have a proclivity to participate in anionic 1,n-O→C rearrangements[7] and in fact three examples of 1,4-O→sp$^3$C silyl shifts[8] have been recorded involving phosphonamide stabilized,[9a] pyramidal unstabilized,[9b] and 1-azaallyl[9c] carbanions as intermediates. However, the process described herein represents a novel example of 1,4-O→sp$^2$C silyl migration that proceeds through a vinyl carbanion.[10]



(1)

The required (Z)-vinyl iodides 1 were prepared from propargylic alcohols 4 by the Denmark modification[5a] of the Corey reductive iodination ($LiAlH_4$, $NaOCH_3$; $I_2$)[11] of ethynyl carbinols (eq 2). In turn, reaction of alcohols 1 with $(TMS)_2NH$ (TMS-Cl, Py), TBDMS-Cl



(2)

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† Dedicated to Professor Francis Johnson on the occasion of his 60th birthday.

(cat.DMAP, $Et_3N$; $CH_2Cl_2$, 0→23°C), and TIPS-OTf (2,6-lutidine; $CH_2Cl_2$, 0→23°C) provided the silyl ether precursors 2 (eq 1). The following, general procedure was used for the preparation of (Z)-vinylsilane allylic alcohols 3 (1-5 mmol scale). A ~0.2 M solution of the appropriate silyl ether 2 in THF was cooled to -78°C under an atmosphere of dry, oxygen-free argon and 2.0-2.1 equiv of t-BuLi in pentane (1.7 M; Aldrich) was added dropwise via syringe over a 5-min period. Reaction was allowed to proceed for 30 min at -78°C and then the pale yellow solution was warmed (~30 min) to room temperature (23°C) and stirred for another 30 min before being poured into saturated aqueous $NH_4Cl$ and extracted twice with ether. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to provide crude 3 (eq 1, Table).

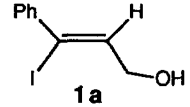
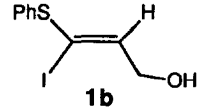
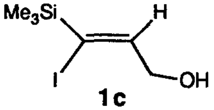
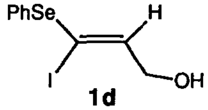
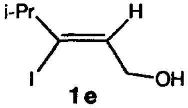
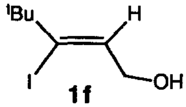
The efficiency of the present method, as indicated by the rather high yields of TMS, TBDMS, and TIPS vinylsilane alcohols 3 (eq 1, Table), is particularly owed to the intramolecular delivery of the trialkylsilyl groups rendering not only protection and deprotection steps unnecessary, but also the potential use of an inseparable isomeric mixture of γ-halo allylic silyl ether precursors feasible.[2b] For instance, reaction of 1a ($R^1$=Ph) with dihydropyran (PPTS, 23°C) followed by lithium-iodine exchange (t-BuLi, -78°C), quenching of the resultant vinyllithium with TMS-Cl, and deprotection (PTSA; MeOH, 23°C) gave 3a ($R^1$=Ph, $SiR_3$=TMS) in rather low yield.[12] Furthermore, reaction of a 1:1 mixture of 2b ($R^1$=SPh, $SiR_3$=TBDMS) and its (E)-isomer[13] with t-BuLi (THF, -78→23°C) provided alcohol 3b ($R^1$=SPh, $SiR_3$=TBDMS) and the easily separable TBDMS ether of cis-3-phenylthio-2-propenol.

Although reaction of the (E)-isomer of 2b ($R^1$=SPh, $SiR_3$=TBDMS)[13] with 4-trimethylsilyl-3-butyn-2-one or acetone under specified conditions (t-BuLi, THF, -78°C; $CeCl_3$, -78°C; addition of ketone)[13] furnished tertiary alcohol products, treatment of 2b ($R^1$=SPh, $SiR_3$=TBDMS) under identical conditions gave rise only to 3b ($R^1$=SPh, $SiR_3$=TBDMS). This set of experiments pointed out the intramolecular nature of the silyl migration. Confirmation of intramolecularity[10c] was obtained by a crossover experiment. Specifically, treatment of an equimolar mixture of 2a ($R^1$=Ph, $SiR_3$=TMS) and 2c ($R^1$=TMS, $SiR_3$=TBDMS) with t-BuLi (-78→23°C) gave rise only to 3a ($R^1$=Ph, $SiR_3$=TMS) and 3c ($R^1$=TMS, $SiR_3$=TBDMS).

The lower yield of product 3d (Table, entry 4; $R^1$=SePh, $SiR_3$=TIPS) is tentatively attributed to a combination effect (thermodynamic and/or kinetic)[14] involving the relative stability (lower reactivity) of the phenylseleno vinylanion and the steric bulk of the triisopropyl group.[9a] Interestingly, $t_{1/2}$ (<15 min at -78°C) for the rearrangement of the vinylanion corresponding to 2e ($R^1$=iPr, $SiR_3$=TBDMS) was found to be shorter than that (~45 min at -78°C)[15] of 2b ($R^1$=SPh, $SiR_3$=TBDMS). The presumed intermediacy[7b,9b,16] of a pentacoordinate anionic silicate[17] thereby establishing an effective equilibrium between vinyl carbanion and γ-silylated allylic alkoxide should await experimental verification.

Further applications of the intramolecular delivery concept[18] on related nonracemic γ-silylated allylic alcohols ($R^2$≠H, see Graphical Abstract) as well as efficient asymmetric synthesis of their precursors are the subject of current studies.

**Table.** Synthesis of (Z)-Vinylsilane Allylic Alcohols[a]

| | | % Yield[c] | | $\underline{3}$ % Yield[d] | |
|---|---|---|---|---|---|
| Entry | γ - Iodoallylic Alcohols[b] | $\underline{1}$ | TMS[e] | TBDMS[f] | TIPS[g] |
| 1. |  **1a** | 88 | 75 | 84 | 80 |
| 2. |  **1b** | 85 | 70 | 80 | |
| 3. |  **1c** | 96 | 85 | 88 | |
| 4. |  **1d** | 92 | 82 | 76 | 50 |
| 5. |  **1e** | 83 | 72 | 81 | 86 |
| 6. |  **1f** | 91 | 78 | 90 | |

[a] All vinylsilane products exhibited spectral properties ($^1$NMR, IR, and/or MS) in accordance with the assigned structures. [b] Stereoselectivities of the hydroalumination/iodination sequence were determined to be >10 : 1 by $^1$NMR (270 MHz) integration. [c] Isolated yield after flash chromatography. [d] Overall from $\underline{1}$, isolated yield after preparative TLC or molecular distillation (100% isomeric purity). [e] Trimethylsilyl. [f] tert-Butyldimethylsilyl. [g] Triisopropylsilyl.

## Acknowledgement

Financial support from the donors of the Petroleum Research Fund administered by the American Chemical Society (20811-G1) and from the American Cancer Society (Institutional Research Grant #IN-181) is gratefully acknowledged. Professors Kung K. Wang and William R. Moore of this department are thanked for helpful discussions.

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(Received in USA 18 June 1990)