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INTRAMOLECULAR HYDROSILATION OF ACETYLENES: REGIOSELECTIVE FUNCTIONALIZATION OF HOMOPROPARGYL ALCOHOLS[1]

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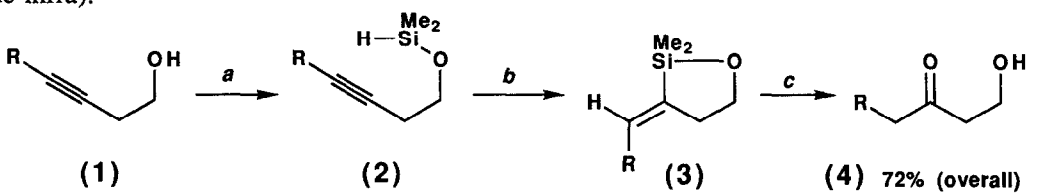
Summary: Platinum-catalyzed intramolecular hydrosilation of hydrodimethylsilyl ethers of homopropargyl alcohols proceeds regioselectively in a 5-*exo-dig* mode. The resulting vinylsilanes can be transformed into 3-alkanon-1-ol and 3-bromo-3-alken-1-ol derivatives by H_2O_2 oxidation and bromine cleavage, respectively.

Although hydrosilation of acetylenes has frequently been used for the preparation of vinylsilanes as versatile synthetic intermediates,[2] it suffers from the rather low regioselectivity, in particular in the case of unsymmetrical internal acetylenes.[3] One fascinating result has been reported by Stork and his co-workers, who observed a functional group directed, regioselective hydrosilation of the pivalate ester of 2-butyn-1-ol; the silicon moiety attaches to the proximal carbon atom.[4]

We report herein intramolecular hydrosilation[5] of homopropargyl alcohols as a new tool for regioselective functionalization of unsymmetrical internal acetylenes. Representative transformations are shown in Scheme 1. Homopropargyl alcohol **1** was thus converted into the hydrodimethylsilyl ether **2** by treatment with $(HMe_2Si)_2NH$. Platinum-catalyzed intramolecular hydrosilation proceeded smoothly at room temperature exothermically. Bulb-to-bulb distillation gave cyclic vinylsilane **3** as a sole volatile product in ca. 70% yield.[6] It should be noted that no other regio- and stereo-isomers were detected. The result is consistent with the favorable 5-*exo-dig* ring closure[7] (or 6-*exo-dig* mode in the Pt-containing intermediates[5]) and with the cis hydrosilation to acetylene.[3] The stereochemistry of the vinylsilane moiety was also confirmed by bromine-cleavage (vide infra).

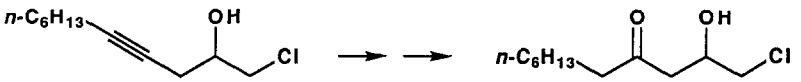


[a] $(HMe_2Si)_2NH$.
[b] H_2PtCl_6 $6H_2O$ (0.1 mol%) / CH_2Cl_2 / room temp. / 0.5 h.
[c] 30% H_2O_2 / KF / $KHCO_3$ / MeOH / THF / 30 °C / overnight.
[d] (1) Br_2 / 0 °C. (2) KHF_2 / MeOH / room temp. / overnight.

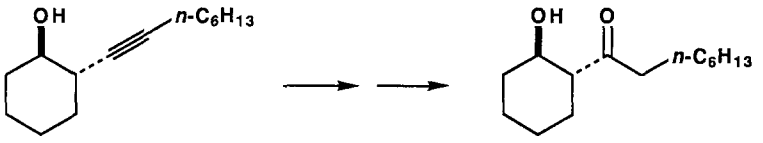
Scheme 1

The cyclic vinylalkoxysilane **3** could be transformed into the corresponding β-hydroxy ketone **4** by hydrogen peroxide oxidation.[8] Noteworthily, no dehydration of the product was observed under the basic oxidation condition. The vinylsilane **3** was also converted into (*Z*)-3-bromo-3-decen-1-ol (**5**)[6] by a sequence of bromination and debromosilylation with net inversion of olefin geometry.[9] The stereochemistry of **5** was confirmed by debromination with retention of configuration by treatment with *t*-BuLi (3 equiv) followed by hydrolysis, giving (*E*)-3-decen-1-ol.

Two further examples of preparation of β-hydroxy ketones from homopropargyl alcohols are shown below.



76% (overall)



67% (overall)

The results demonstrate that intramolecular hydrosilation of homopropargyl alcohols has provided a new procedure for regio- and/or stereo-selective functionalization of unsymmetrical internal acetylenes.[10,11,12] Further applications of cyclic vinylsilanes thus obtained are now under investigation.

References and Notes

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6) ^{1}H NMR (δ, ppm): **3** (200 MHz, $CDCl_3$) 0.170 (s, 6H), 0.868 (t, J = 6.5 Hz, 3H), 1.2-1.45 (m, 8H), 2.084 (dt, J = 7.1 and 6.9 Hz, 2H), 2.40-2.50 (m, 2H), 3.965 (t, J = 6.5 Hz, 2H), 5.796 (tt, J = 2.6 and 6.8 Hz, 1H); **5** (100 MHz, CCl_4) 0.8-1.15 (m, 3H), 1.38 (br.s, 8H), 2.18 (q, J = 7.0 Hz, 2H), 2.63 (t, J = 6.5 Hz, 2H), 2.88 (s, 1H), 3.73 (t, J = 6.5 Hz, 2H), 5.79 (t, J = 7.0 Hz, 1H).
7) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).
8) K. Tamao, M. Kumada, and K. Maeda, *Tetrahedron Lett.*, **25**, 321 (1984).
9) K. Tamao, M. Akita, K. Maeda, and M. Kumada, *J. Org. Chem.*, **52**, 1100 (1987).
10) In contrast, a propargyl alcohol derivative, 2-nonyn-1-ol, gave only polymeric materials under a similar intramolecular hydrosilation condition; attempted distillation gave a trace amount of volatile product. A longer-chain analog, 4-undecyn-1-ol, underwent intramolecular hydrosilation to give a cyclic product, but in less than 50% yield, together with polymeric materials.
11) Utimoto reported a palladium-catalyzed, regioselective cyclization of homopropargyl alcohols where the oxygen functionality was introduced onto the distal acetylene carbon atom (5-*endo*-*dig* mode), complementarily to the present method: K. Utimoto, *Pure Appl. Chem.*, **55**, 1845 (1983).

12) We thank the Ministry of Education, Japan, for a Grant-in-Aid, No. 63550644.

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