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SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS. 30.[1]
INTRAMOLECULAR HYDROSILATION OF ALKENYL ALCOHOLS: A NEW APPROACH TO THE REGIOSELECTIVE SYNTHESIS OF 1,2- AND 1,3-DIOLS

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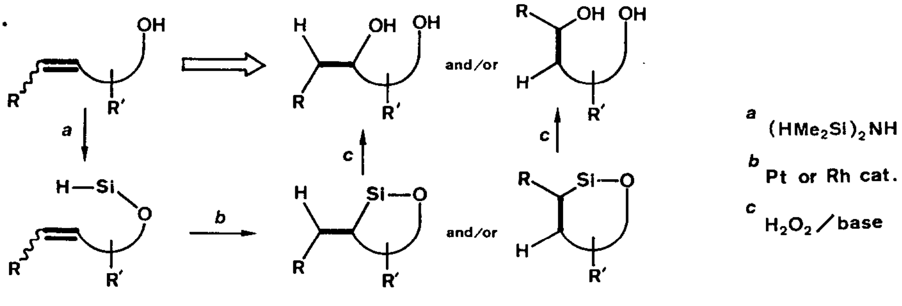
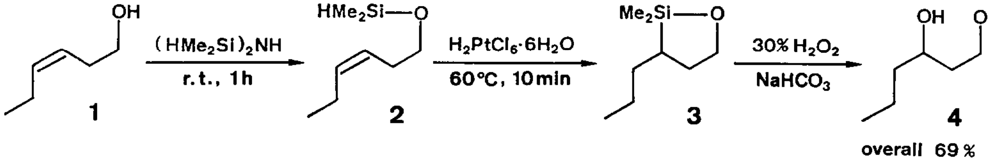
Summary: Intramolecular hydrosilation of allyl and homoallyl alcohols and the subsequent oxidative cleavage of the resultant carbon-silicon bond have provided a new approach to the regio-controlled synthesis of 1,2- and/or 1,3-diols.

We have recently developed a new methodology for the anti-Markownikoff hydration of terminal olefins by a sequence of hydrosilation[2] with $HSiMe(OEt)_2$ and the oxidation of the resultant carbon-silicon bond.[3] This procedure may be synthetically useful as an alternative to the existing hydrometallation-oxidation processes, in view of the simplicity, wider functional group compatibility, and high terminal-regioselectivity. Unfortunately, this procedure however has been applicable essentially only to mono-substituted terminal olefins, because of the low reactivity or the almost inertness of the more-substituted olefins toward the usual intermolecular hydrosilation; under drastic conditions internal olefins give also the terminal adducts via concomitant isomerization of the double bond.[4,5] We have now developed an intramolecular hydrosilation to overcome these difficulties and to enhance the synthetic utility of hydrosilation.[6] As shown in Scheme 1, the intramolecular hydrosilation may be attained with a hydrosilyl group anchored to a neighboring hydroxy group in the presence of transition metal catalysts such as platinum and rhodium, where the regio- and stereo-chemistry should be controlled during the addition of a transition metal-hydride to olefin,[4] and the final oxidative cleavage of the resultant carbon-silicon bond should form the regio- and stereo-defined diols.

As shown representatively in eq. 1, a hydrodimethylsilyl group was introduced onto a hydroxy group in homoallyl alcohol 1 by treatment with 1,3-dihydrotetramethyldisilazane $(HMe_2Si)_2NH$[7] (0.6-1 molar equiv) to form the hydrosilyl ether 2. After removal of the excess

Scheme 1.



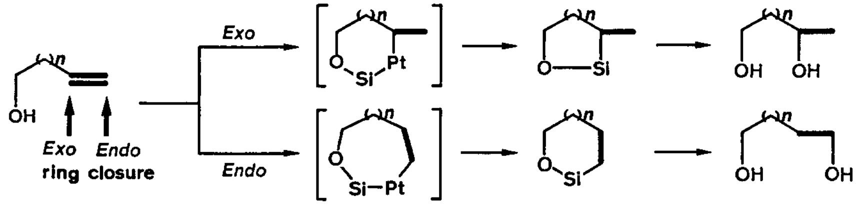


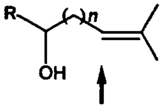
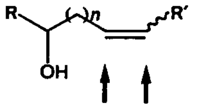
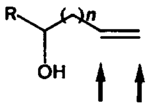
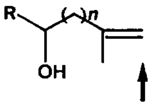
(1)

disilazane, the hydrosilation of 2 in the presence of $H_2PtCl_6 \cdot 6H_2O$ (0.1 mol%)[8] was completed at 60°C within 10 min to give a five-membered cyclic product 3 solely (92% isolated yield), which was then oxidized with 30% H_2O_2 in the presence of $NaHCO_3$[9] to form 1,3-diol 4 in high overall yield.[10] Intermolecular hydrosilation of the related system did not occur at all even under more drastic conditions. The dramatic acceleration of the intramolecular hydrosilation is noteworthy. The above result presents virtually the first example of the direct hydrosilation of internal olefin under such mild conditions without olefin isomerization and with a high regioselectivity.[5]

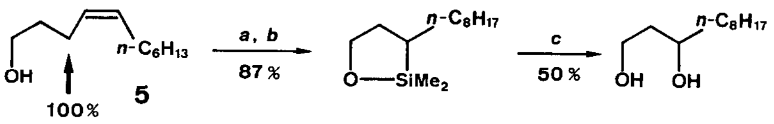
The regioselectivity and the reactivity were examined with various types of allyl and homoallyl alcohols in the presence of $H_2PtCl_6 \cdot 6H_2O$ (0.1-1 mol%, r.t.-60°C, 1-20 h).[11] Results summarized in Table 1 show the following trends. (1) With the internal olefins, an Exo-ring closure[12] occurred exclusively or predominantly in both the allyl and homoallyl alcohols (allyl/Exo and homoallyl/Exo). (2) With the terminal olefins, an Endo process took place highly selectively in allylic cases (allyl/Endo), while an Exo-ring closure predominated in homoallyl alcohols (homoallyl/Exo). (3) With the vinylidene type olefins, an Endo process occurred exclusively in both cases (allyl/Endo and homoallyl/Endo). (4) In no case, tertiary alkyl-silicon bond formation was observed at all. These regioselectivities may be controlled mainly by two factors: the ring size of the Pt-containing metallacycle intermediates[6d,e] and the relative stability of the primary and secondary alkyl-transition metal bond therein.

Table 1. Regioselectivity of Intramolecular Hydrosilation of Allyl and Homoallyl Alcohols Catalyzed by $H_2PtCl_6 \cdot 6H_2O$

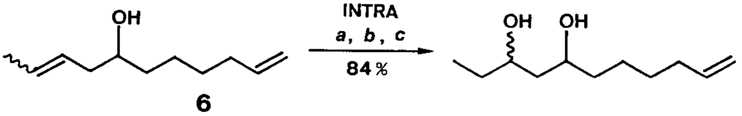


	internal olefin		terminal olefin	
				
Allyl; *n*=0	100%[a]	80~95% 20~5%[b]	35% 65%[c]	100%[d]
Homoallyl; *n*=1	100%[e]	100%[f]	90% 10%[g]	100%[h]

[a] R = *n*-Bu. [b] R = H; R′ = *n*-C_6H_{13}. [c] R = Ph. [d] R = *n*-Bu, *i*-Pr, *t*-Bu, Ph.
[e] R = H, *i*-Pr, Ph. [f] R = H, *n*-C_5H_{11}; R′ = Et, *n*-C_5H_{11}. [g] R = Ph. [h] R = *i*-Pr.



(2)



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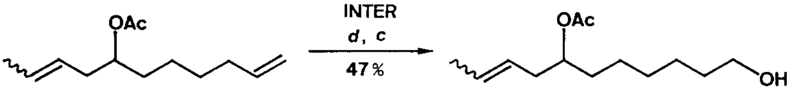

(4)

[a] $(HMe_2Si)_2NH$ / r.t. / 1 h. [b] H_2PtCl_6 $6H_2O$ (0.1 mol%) / 60°C / 3 h.
[c] 30% H_2O_2 / $NaHCO_3$ (or KF / $KHCO_3$) / MeOH / THF / r.t.-60°C / 12 h.
[d] $HSiMe(OEt)_2$ / $RhCl(PPh_3)_3$ (0.1 mol%) / 100°C / 1 h.

The "allyl/Endo" and "homoallyl/Exo" reactions seemed to proceed most readily, some of them, especially the vinylidene type, being even highly exothermic. While all of the five- and six-membered cyclic hydrosilation products were isolable and the final 1,3- and 1,4-diols were obtained in 50-85% yields, the four-membered ones anticipated from the "allyl/Exo" reaction were not obtained, but the subsequent oxidation of the resulting polymeric viscous materials afforded the 1,2-diols in 30-40% yields.[13]

The one-carbon higher homologs took different reaction courses. Thus, the internal olefin counterpart **5** did undergo the intramolecular hydrosilation smoothly, but the final product was a 1,3-diol only, arising from the concurrent olefin isomerization; the anticipated 1,4- or 1,5-diol was not obtained at all (eq. 2). With the terminal olefin analog $PhCH(OH)CH_2CH_2CH{=}CH_2$, the intramolecular hydrosilation was no longer the main reaction course, but polymeric, intermolecular hydrosilation products were mostly formed (86%); oxidation gave almost pure 1,5-diol.

Further characteristic feature of the intramolecular hydrosilation may be shown by the reaction of dienol **6**: the intramolecular hydrosilation did occur on the internal olefin, leaving the otherwise much more reactive terminal olefin intact (eq. 3 vs. eq. 4).

The intramolecular hydrosilation thus provides a new methodology for the regioselective synthesis of 1,2- and/or 1,3-diols from certain allyl and homoallyl alcohols. We will report the stereochemical aspects and applications soon.[14,15]

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7 (HMe$_2$Si)$_2$NH is commercially available: an air-stable but moisture-sensitive liquid, bp. 99-100°C.

8 A 0.05 *M* solution of H$_2$PtCl$_6$·6H$_2$O in THF was conveniently used.

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10 The following two precautions should be taken for the success. (1) The excess disilazane (catalyst poison) should be removed either by distillation (up to ca. 50°C/100 mmHg) through a short distillation head for volatile substrates or in vacuo at room temperature for less volatile ones. (2) Since the platinum species induce undesirable rapid decomposition of hydrogen peroxide in the next oxidation step, it may be removed from the reaction mixture by flash distillation, by treatment with crystalline EDTA·2Na·2H$_2$O followed by filtration or by passing through a very short alumina column.

11 Intramolecular hydrosilation was also catalyzed by rhodium complexes such as RhCl(PPh$_3$)$_3$ and [RhCl(COD)]$_2$ at 80-100°C. The results were not largely different from those obtained with the Pt catalyst, with a few exceptions. Details will be reported in due course.

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13 The other part of the product in these cases consisted of a mixture of unsaturated and saturated monools.

14 K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi and Y. Ito, to be submitted.

15 We thank Professor Emeritus M. Kumada for encouragement and Shin-etsu Chemical Industrial Co., Ltd. for a gift of organosilicon compounds and (*Z*)-3-hexen-1-ol.

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