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Regioselectivity of inter- and intramolecular hydrosilylation of the vinyloxy group

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Abstract

The addition of dialkylethoxysilanes to divinyl ether in the presence of chloroplatinic acid occurs at the terminal carbon atom whereas the regioselectivity of intramolecular hydrosilylation of dialkyl(2-vinyloxyethyl)silanes depends on the substituents at silicon. The effect of the oxygen and sulfur atoms on the competing formation of five- and six-membered cyclic products is discussed.

Introduction

Intramolecular hydrosilylation of (4-pentenyl)hydrosilanes, $HX_2SiCH_2CH_2CH_2CH=CH_2$ ($X_2 = Me_2$, $ClCH_2Me$, MePh, MeCl, EtCl, ^iPrCl) in the presence of transition metal catalysts has been studied in detail. The reaction affords a mixture of isomeric five- and six-membered cycles, the ratio of which depends on the catalyst used and substituents at silicon [1–4]. However in all cases the five-membered cycle is the predominant product.

So far, very little is known about the heteroatom effect on the ring closure regioselectivity. The cyclization of dimethyl(3-butenyloxy)silane * and its derivatives catalysed by chloroplatinic acid leads to five- and six-membered 1-oxa-2-silacycloalkanes, the former prevalent [5].

Earlier we found that diethyl(2-vinylthioethyl)silane undergoes ring closure in the presence of Speier's catalyst to form a five-membered cyclic product [7]. Now we have examined a similar intramolecular hydrosilylation involving the vinyloxy group.

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* In an earlier paper, the formation of only the six-membered cycle from this compound was reported [6]. However these data look doubtful because there is no structural assignment.

Results and discussion

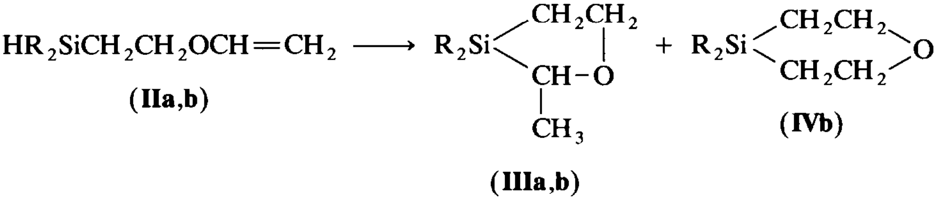
The syntheses of the appropriate starting compounds were carried out by hydrosilylation of divinyl ether. Previously we have shown that divinyl sulfide adds diethylsilane in the presence of chloroplatinic acid to give a mixture of terminal and non-terminal mono-adducts [7]. Our attempt to carry out a similar reaction with divinyl ether was unsuccessful. Instead of mono-addition, only polyaddition resulting in viscous products was observed. Therefore we chose the sequence of reactions shown in eq. 1.

$$\begin{tikzcd} R_2(EtO)SiH + CH_2{=}CHOCH{=}CH_2 \arrow[r] & R_2(EtO)SiCH_2CH_2OCH{=}CH_2 \\ & \textbf{(Ia,b)} \quad \arrow[d, "LiAlH_4"] \\ & HR_2SiCH_2CH_2OCH{=}CH_2 \\ & \textbf{(IIa,b)} \end{tikzcd}$$

(R = Et in (**a**) and Me in (**b**)) (1)

Diethylethoxysilane and dimethylethoxysilane were added easily to divinyl ether upon heating in the presence of platinum catalyst to give only terminal mono-adducts in good yield. The marked differences in selectivity of hydrosilylation of divinyl ether and divinyl sulfide are consistent with the polarization of the vinyloxy group opposite to that of the vinylthio group and cause a principal difference in the behavior of the oxygen and sulfur atoms. The former acts as a π-donor-σ-acceptor and the latter as a π,σ-acceptor [8]. Thus, the regioselectivity of the intermolecular addition of the silicon–hydrogen bond to the vinyloxy and vinylthio group largely depends on the electronic factors.

Compounds **Ia** and **Ib** are reduced easily to **IIa** and **IIb** by the reaction with lithium aluminum hydride (eq. (1)). Heating of **IIa** with chloroplatinic acid results in the formation of 2-methyl-3,3-diethyl-1-oxa-3-silacyclopentane (**IIIa**, eq. 2).



(**IIa,b**) (**IIIa,b**) (**IVb**)

(2)

The minor content of the second product (less 5%) does not allow its isolation from the reaction mixture and assignment as an isomeric six-membered cycle. Consequently, the regioselectivity of intramolecular ring closure of HEt_2SiCH_2-$CH_2ECH{=}CH_2$ (E = S, O) does not change significantly upon replacement of the sulfur atom by the oxygen atom.

A slightly different result is obtained for the cyclization of **IIb**, which transforms to a mixture of five-membered (**IIIb**) and six-membered (**IVb**) cycles upon heating in the presence of platinic catalyst. The five-membered cycle is the prevailing reaction product, the ratio of **IIIb**/**IVb** being about 2:1.

From the above and from the results of other studies of a similar catalytic intramolecular hydrosilylation, it follows that the distribution of the five-membered and six-membered cyclic products is dependent on the nature of the heteroatom attached to the vinyl group. However in most cases regioselectivity is mainly controlled by thermodynamic factors which favor primary formation of the platinum-containing six-membered cyclic intermediate resulting in the five-membered cyclic product.

It should be noted that these reactions have allowed the first synthesis of 1-oxa-3-silacyclopentane and 1-oxa-4-silacyclohexane derivatives.

Experimental

Analytical gas chromatography (GLC) was carried out on a LCHM-8MD instrument with a catharometer having a stainless steel 2.0 m × 3 mm column packed with 10% Lukopren G-1000 on 45–60 mesh Chromaton N-AW-HMDS. ^1H NMR spectra were recorded on a Jeol FX 90Q spectrometer using $CDCl_3$ as solvent and HMDS as internal standard.

Hydrosilylation of divinyl ether

(a) *With diethylethoxysilane.* A mixture of 1.32 g (0.01 mol) of diethylethoxysilane, 1.40 g (0.02 mol) of divinyl ether and 5 drops of a chloroplatinic acid solution (0.1 *N* in isopropyl alcohol) was heated in a sealed glass tube at 100°C for 10 h. Direct distillation of the reaction mixture afforded 1.80 g (59%) of diethylethoxy(2-vinyloxyethyl)silane, b.p. 80°C (18 Torr), n_D^{25} 1.4342 [lit. [9]: b.p. 87°C (22 Torr), n_D^{20} 1.4370]. ^1H NMR: δ 0.67 (m, 6H, CH_2Si), 0.97 (m, 6H, CH_3CSi), 1.18 (t, 3H, CH_3CO), 3.73 (q, 2H, CH_2OSi), 3.86 (t, 2H, CH_2O), 3.97, 4.15 (dd, 2H, $=CH_2$), 6.44 (dd, 1H, CH=).

(b) *With dimethylethoxysilane.* Under the above conditions, 0.93 g (53%) of dimethylethoxy(2-vinyloxyethyl)silane (**Ib**) was obtained from 1.04 g (0.01 mol) of dimethylethoxysilane and 1.40 g (0.02 mol) of divinyl ether, b.p. 71°C (26 Torr), n_D^{20} 1.4235. ^1H NMR: δ 0.14 (s, 6H, Me_2Si), 1.09 (t, $SiCH_2$), 1.18 (t, 3H, CH_3CO), 3.66 (q, 2H, CH_2OSi), 3.80 (t, 2H, CH_2O), 3.95, 4.13 (d d, 2H, $=CH_2$), 6.42 (dd, 1H, CH=). Anal. Found: C 55.15, H 10.42, Si 16.16. $C_8H_{18}SiO_2$ calc.: C 55.12, H 10.41, Si 16.10%.

*Reduction of **Ia***

A solution of 4.90 g (0.028 mol) of **Ia** in 5 ml diethyl ether was added to a suspension of 0.60 g (0.016 mol) of lithium aluminum hydride at room temperature. The reaction mixture was allowed to reflux for 9 h, decanted from the precipitate and treated with a minimum amount of saturated aqueous NH_4Cl. Drying ($MgSO_4$) and distillation of the ether solution gave 2.17 g (49%) of diethyl(2-vinyloxyethyl)silane (**IIa**), b.p. 93°C (49 Torr), n_D^{20} 1.4393. ^1H NMR: δ 0.66 (m, 6H, CH_2Si), 1.00 (m, 6H, CH_3CSi), 3.65 (s, 1H, HSi), 3.72 (t, 2H, CH_2O), 3.97, 4.15 (dd, 2H, $=CH_2$), 6.44 (dd, 1H, CH=). Anal. Found: C 60.20, H 11.63, Si 17.65. $C_8H_{18}SiO$ calc.: C 60.69, H 11.41, Si 17.74%.

*Reduction of **Ib***

Dimethyl(2-vinyloxyethyl)silane (**IIb**) was obtained (33%) by reaction of **Ib** (3.00 g, 0.017 mol) with $LiAlH_4$ (0.40 g, 0.011 mol) as described above, b.p. 122°C, n_D^{20} 1.4240. ^1H NMR: δ 0.13 (d, 6H, Me_2Si), 1.09 (dt, 2H, $SiCH_2$), 3.65 (s, 1H, SiH), 3.81 (t, 2H, CH_2O), 3.97, 4.16 (dd, 2H, $=CH_2$), 6.44 (dd, 1H, CH=). Anal. Found: C 55.53, H 10.82, Si 21.17. $C_8H_{14}SiO$ calc.: C 55.32, H 10.83, Si 21.56%.

Cyclization of ***IIa***

1.3 g (0.008 mol) of **IIa** and 4 drops of chloroplatinic acid solution were heated in a glass sealed tube for 4 h at 100°C. Distillation and purification of the crude product by preparative GLC (20% polyoxyphenylene on Chromaton N-AW-HMDS, 125°C) gave pure 2-methyl-3,3-diethyl-1-oxa-3-silacyclopentane (0.58 g, 45%), n_D^{20} 1.4540. ^1H NMR: δ 0.70 (m, 6H, CH_2Si), 0.95 (m, 6H, CH_3CSi), 1.31 (d, 3H, CH_3), 3.33 (q, 1H, CH), 3.62 (m, 2H, CH_2O). Anal. Found: C 61.00, H 11.62, Si 17.73. $C_8H_{18}SiO$ calc.: C 60.69, H 11.46, Si 17.74%. No detectable amount of the isomeric 4,4-diethyl-1-oxa-4-silacyclohexane was observed in ^1H NMR analysis of the crude product.

Cyclization of ***IIb***

Heating (80°C, 6 h) of 2.06 g (0.016 mol) of **IIb** in the presence of 3 drops of chloroplatinic acid solution afforded a 2.3 : 1 mixture of 2,3,3-trimethyl-1-oxa-3-silacyclopentane (**IIIb**) and 4,4-dimethyl-1-oxa-4-silacyclohexane (**IVb**). The reaction mixture was evaporated under reduced pressure (65–4 Torr) to give 1.04 g (50% total yield) of a fraction condensed in a trap cooled with liquid N_2. **IIIb** and **IVb** were separated by preparative GLC (conditions as described above). **IIIb**: n_D^{20} 1.4415. ^1H NMR: δ 0.12, 0.17 (s, 3H, s, 3H, Me_2Si), 0.94 (dd, CH_2^XSi), 1.26 (d, 3H, CH_3), 3.21 (q, 1H, CH), 3.58, 4.03 (AB spectrum each component of which is split into a triplet, OCH_2^{AB}), $^3J(CH_3-CH) = 7.6$ Hz, $^3J(A-X) = 6.3$ Hz, $^3J(B-X) = 7.8$ Hz, $^2J(AB) = 10.3$ Hz. Anal. Found: C 54.72, H 10.76, Si 20.96. $C_6H_{14}SiO$ calc.: C 55.32, H 10.83, Si 21.56%. **IVb**: n_D^{20} 1.4432. ^1H NMR: δ 0.04 (c, 4H, Me_2Si), 0.76 (t, 4H, $SiCH_2$), 3.79 (t, 4H, OCH_2).

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