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β-HYDROXY α-SILYL SELENIDES AS VERSATILE INTERMEDIATES IN ORGANIC[1] SYNTHESIS.

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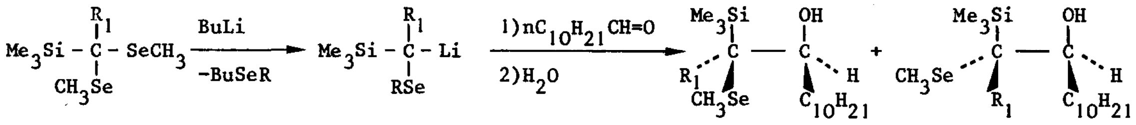
We recently reported[1,2] the first synthesis of β-hydroxy α-silyl selenides 3 from easily available α-lithio α-silyl selenides and aldehydes. We found during this work that both stereoisomers (3', 3") generally obtained, present a very different behaviour by TLC (SiO_2), allowing their easy separation by chromatography technics (Scheme I).

SCHEME I



		3'	3"
R_1 : H	3a : 54 %	3'a : 35 % (0.60)*	3"a : 65 % (0.45)*
R_1 : CH_3	3b : 50 %	3'b : 60 % (0.72)*	3"b : 40 % (0.62)*

We present now our preliminary results for their selective transformation to a large variety of compounds including vinyl selenides, vinyl silanes, vinyl bromide, tridecanone and 3-hydroxy 2-tridecanone. The reactions which lead to vinyl selenides and vinyl silanes are higly stereoselective and allow us (vide infra) to propose the structures 3' and 3" for the two stereoisomers of 3 (see scheme I).

Let's now consider the reactivity of these highly functionalized derivatives.

We first observed that compounds 3 are easily transformed to vinyl selenides 4 when reacted with potassium t.butoxide in THF[16a]. These transformations are highly stereoselective (>95) and allow for the first time the synthesis of di- and trisubstituted vinyl selenides[3] of high stereochemical purity (N.M.R. and V.P.C. analysis on SE.30 capillary column HL) from each stereoisomer of β-hydroxy α-silyl selenides 3a or 3b (scheme II).

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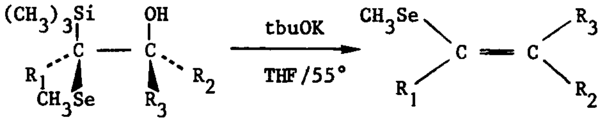
* (refer to rf on TLC (Thin Layer Chromatography) (SiO_2, Merck) using ether / pentane : 10/90 as eluant).

SCHEME II



3 4

	R_1	R_2	R_3	Yield
3'a	H	H	$C_{10}H_{21}$	4'a 74 %
3"a	H	$C_{10}H_{21}$	H	4"a 78 %
3'b	CH_3	H	$C_{10}H_{21}$	4'b 89 %
3"b	CH_3	$C_{10}H_{21}$	H	4"b 70 %

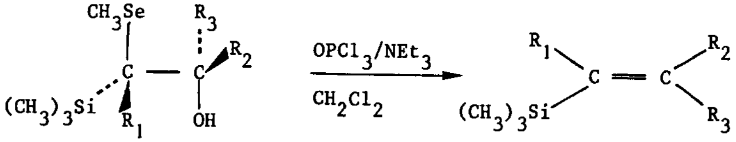
The NMR spectra of 4'a, 4"a and 4'b, 4"b are clearly different and as expected the value of the coupling constant between the two olefinic protons is greater in the E isomer 4"a (J_{H-H}:15 Hz) than in the Z one 4'a (J_{H-H}: 9 Hz). These results can be related to the well known Peterson-Olefin synthesis[4] from β-hydroxy silanes which occurs,in basic media, by syn elimination[5] of hydroxyl and silyl moieties.

β-Hydroxy α-silyl selenides were also cleanly transormed to vinyl silanes when reacted with phosphorus oxychloride/triethyl amine in methylene chloride[6,16b] or thionyl chloride/triethyl amine in the same solvant[7a](scheme III).

Particularly spectacular is the absence of vinyl selenides in these reactions although under the last conditions both β-hydroxy selenides[7] and β hydroxy silanes[8] have been transformed into olefins.

These reactions are again highly stereoselective (>95%) producing the disubstituted vinyl silanes 5'a or 5"a respectively from 3'a or 3"a and the trisubstituted ones 5'b or 5"b respectively from 3'b or 3"b (scheme III).

SCHEME III



3 5

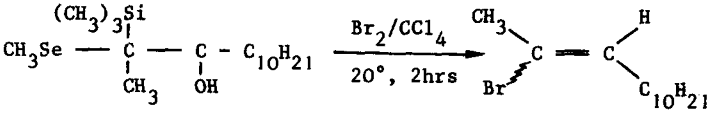
	R_1	R_2	R_3	Yield
3'a	H	H	$C_{10}H_{21}$	5'a 83 %
3"a	H	$C_{10}H_{21}$	H	5"a 75 %
3'b	CH_3	H	$C_{10}H_{21}$	5'b 81 %
3"b	CH_3	$C_{10}H_{21}$	H	5"b 80 %

The stereochemical purity and the assignement of configuration of theses silanes have been deducted from their ^{1}H NMR spectra and by comparison of our results with the ones described in the literature for di[11a,b] and trisubstituted[11c] vinyl silanes of known stereochemistry.

These stereochemical results clearly agree with an anti elimination of the hydroxyl and selenyl moieties, already observed on β-hydroxy selenides[7].

Otherwise 2-bromo 2-tridecene 6 (80%) is obtained[16c] when compound 3b and bromine are stirred together in CCl_4 at 20°C for 2hr (scheme IV).

SCHEME IV

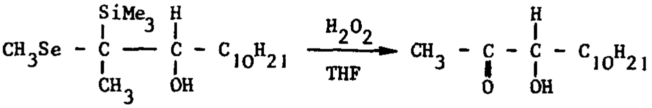


3b 6

80%

β-hydroxy α-silyl selenides have also been found valuable precursors of carbonyl compounds. For example 3-hydroxy tridecane 2-one 7 is obtained in 50 % yield, along with unidentified products, when compound 3b is reacted with hydrogen peroxyde in THF under conditions which are described to produce carbonyl compounds from simple α silyl selenides[2,12],(scheme V).

SCHEME V



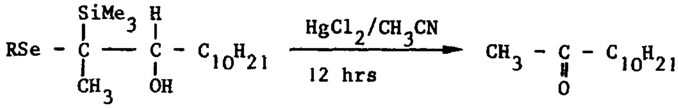
$$CH_3Se-\underset{CH_3}{\overset{SiMe_3}{C}}-\underset{OH}{\overset{H}{C}}-C_{10}H_{21}\xrightarrow[THF]{H_2O_2}CH_3-\underset{\underset{O}{\|}}{C}-\underset{OH}{\overset{H}{C}}-C_{10}H_{21}$$

3b 7

Unfortunately only a few percent of 2-hydroxy dodecanal is produced when 3a is reacted under similar experimental conditions.

Finally we would like to report the spectacular transformation of 3-hydroxy 2-trimethyl silyl 2-selenomethyl tridecane 3b and its selenophenyl analog 3c to tridecane-2-one (75% and 70 yield respectively)[16d] when heated with mercuric chloride in acetonitrile for 12 hrs (scheme VI).

SCHEME VI



$$RSe-\underset{CH_3}{\overset{SiMe_3}{C}}-\underset{OH}{\overset{H}{C}}-C_{10}H_{21}\xrightarrow[12\ hrs]{HgCl_2/CH_3CN}CH_3-\underset{\underset{O}{\|}}{C}-C_{10}H_{21}$$

3	R	Yield in 8	8
3b	CH_3	75%	
3c	C_6H_5	70%	

In the first case we also observe the formation of 2-tridecene in 8% overall yield and this olefin is formed in much higher yield (30%) when the reaction is carried out in THF instead of acetonitrile[13].

It should be attractive to explain the ketone production via a protonated epoxysilane, (which can be produced by interaction of the soft mercuric chloride with the soft selenium atom) and which is known to rearrange into ketone[11a]. However our preliminary results related to the behaviour of an authentic sample of 2,3-epoxy 2-trimethylsilyl tridecane under similar conditions (HCl, $HgCl_2$) are not in full agreement with the previous observation.

Work is now in progress to understand the mechanism of the ketone formation and to generalize such reactions.

References.

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   c) J. Remion and A. Krief, Tet. Lett. 3743 (1976)
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8) T.H. Chan and E. Chang, J. Org. Chem. 39, 3264 (1974)
9) However when the isomer 3'a is reacted with sulfuric acid in THF[7a] at 60°C,vinyl silane 5'a is obtained in 60% yield along with tridecanone (20%) probably arising from the corresponding vinyl selenide 4'a[10].
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   b) P.F. Hudrlik, D. Peterson, R.J.Rona, J. Org.Chem.40, 2263(1975)
   c) K.Utimoto, M.Obayashi, H.Nozaki, J. Org.Chem. 41, 2940 (1976)
12) a) K.Sachdev and H.X. Sachdev, Tet. Lett. 4223 (1976)
   b) H.J. Reich and S.K. Shah, J. Org. Chem. 42, 1773 (1977)
13) 2(Z)-tridecene is stereoselectively (95%) formed from 3'b whereas 2(E)-tridecene is obtained stereoselectively (95 %) from 3"b :
   hese olefins could arise from the reaction of the corresponding vinyl silanes 5'b and 5"b (probably formed in the medium beside the ketone), with hydrochloric acid present in the medium. This suggestion is supported by the independant transformation of 5'b to 2(E)-tridecene[14] by gazeous HCl in THF (20°, 8h).
14) For similar reactions of vinyl silanes with iodhydric acid : K.Utimoto, M.Kitai and H.Nozaki, Tet. Lett. 2825 (1975).
15) Silicon in organic synthesis, E.W. Colvin, Chem. Soc.Reviews, 7, 15 (1978)
16) *Typical experiments.*
   a) Vinyl selenide synthesis tBu/OK (1.5 10^{-3}m) is added at 0°C to a solution of β-hydroxy α-silyl selenide (1.10^{-3}m) in THF (3ml). The mixture is then stirred for 3-4 hr at 20°. Usual work up followed by PLC of the crude mixture (SiO_2, pentane as eluant) affords the pure vinyl selenide. (PLC : preparative layer chromatography).
   b) Vinyl silane synthesis:to a solution of β-hydroxy α-silylselenide (1.10^{-3}m) and triethylamine (1ml) in CH_2Cl_2 (10ml) is added at 0°C phosphorous oxychloride (0.4ml). After 3-4 hr at 20°C, the mixture is cooled to 0°C and water (1ml) is slowly added. Usual work up followed by PLC of the crude mixture (SiO_2, pentane as eluant) gives the pure vinyl silane.
   c) Synthesis of 2-bromo-2-tridecene.
   Bromine (1.1 10^{-3}m) and β-hydroxy α-silyl selenide (1.10^{-3}m) are stirred for 2hr at 20°C in CCl_4(4ml). The mixture is washed with aqueous thiosulfate, bicarbonate and water and dried. PCL of the crude mixture gives 2-bromo-2-tridecene in 80% yield. (SiO_2, pentane as eluant).
   d) Ketone synthesis. β-hydroxy α-silyl selenide (1.10^{-3}m) and mercuric chloride (Merck, dried under vacuum for 12hr) (1.5 10^{-3}m) in dry acetonitrile (10 ml) are heated under N_2 at 50-55°C for 15hr. The solid which formed during the reaction is filtered off and washed with ether (3x10 ml). After usual work-up of the filtrate, the ketone is isolated from the crude mixture by PLC (SiO_2, ether / pentane:1 / 9).

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