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SILICON-CONTROLLED REARRANGEMENT VERSUS KRIEF-REICH REACTION IN β-SELENO-γ-SILYL ALCOHOLS : A NEW STEREOSELECTIVE SYNTHESIS OF TERMINALLY-SUBSTITUTED ALLYLSILANES

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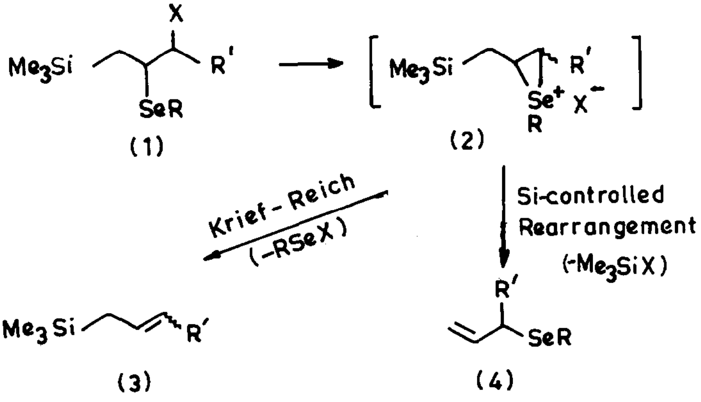
Summary : A new and efficient route to terminally-substituted (E)-allylsilanes is described based on the preference for Krief-Reich elimination in several β-seleno-γ-silyl alcohols, readily available by diastereoselective addition of various Grignard reagents or aldol reaction on 2-(phenylseleno)-3-(trimethylsilyl)propanal(9).

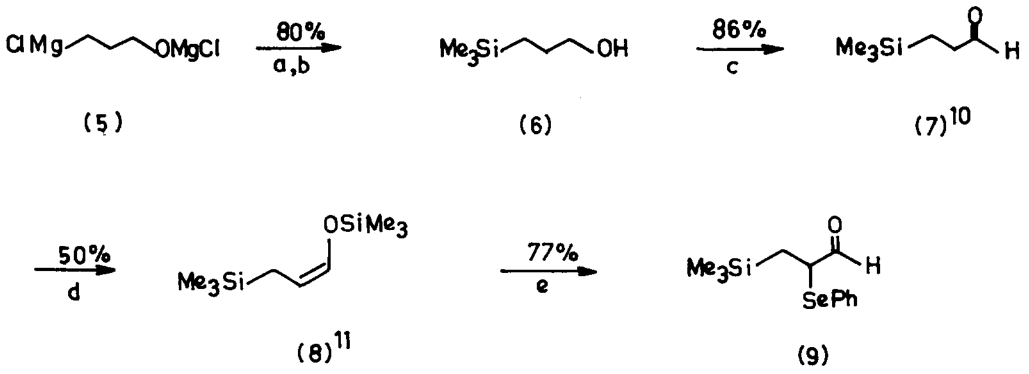
In 1976 Warren and co-workers[1,2] showed that exposure of 3-trimethylsilyl-2-phenylthio substituted alcohols to acids leads to specific allylic sulfides by silicon-controlled rearrangement. In 1982 Itoh and co-workers[3] made the observation that 2-hydroxy-3-trimethylsilylpropyl selenides on treatment with tin(II) chloride give mainly allylic selenides, while a novel rearrangement to β-trimethylsilylpropanals predominates when silver nitrate-Celite is used instead of tin(II) chloride. These reports and the observations of Krief and co-workers[4] that 1-hydroxy-2-silyl-2-seleno species can be induced to undergo a stereoselective anti-elimination of the hydroxy and selenyl moieties leading to substituted vinylsilanes prompted us to investigate the chemistry of the related 3-trimethylsilyl-2-phenylseleno substituted alcohols where two competing modes of olefination processes, $1 \rightarrow 2 \rightarrow 3$ and $1 \rightarrow 2 \rightarrow 4$, are conceivable under Krief-Reich elimination[5,6] conditions (Scheme -I). We wish to report here that the former mode of reactivity is the exclusive pathway under a given set of conditions thus providing a general route to terminally-substituted allylsilanes.[7]

Scheme-I



The preparation of the β-seleno-γ-silyl alcohols was achieved by diastereoselective[8] addition of various Grignard reagents to (9) (Table) which in turn was made from the readily available carbinol (6)[9] as illustrated in Scheme-II.

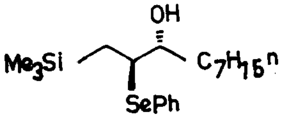
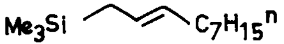
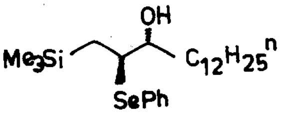
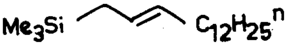
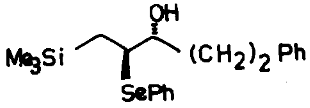
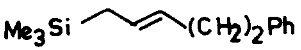
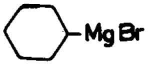
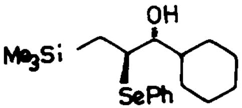
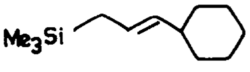
Scheme-II[12]

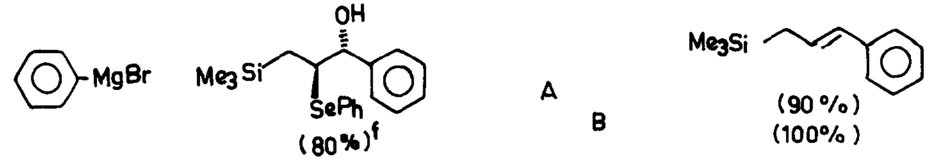


a) Me_3SiCl; b) H_3O^+; c) $(COCl)_2/DMSO/Et_3N$,-60°C; d) $Me_3SiI/HN(SiMe_3)_2$,-20°C→r.t.; e)PhSeBr,-80°C.

As shown in the Table, exposure of the alcohols to methanesulfonyl chloride under the conditions described by Reich[5b] resulted in the exclusive formation of the allylsilanes in very good yields and high isomeric purity (>98% E-isomer). No trace of any allylselenide could be detected in the crude reaction products by ^1H NMR. Yet another reagent which also brings about this transformation in very high yields was found to be N,N'-carbonyldiimidazole[5e,13] in hot hydrocarbon solvents (Table).

Table. Stereoselective synthesis of terminally-substituted allylsilanes

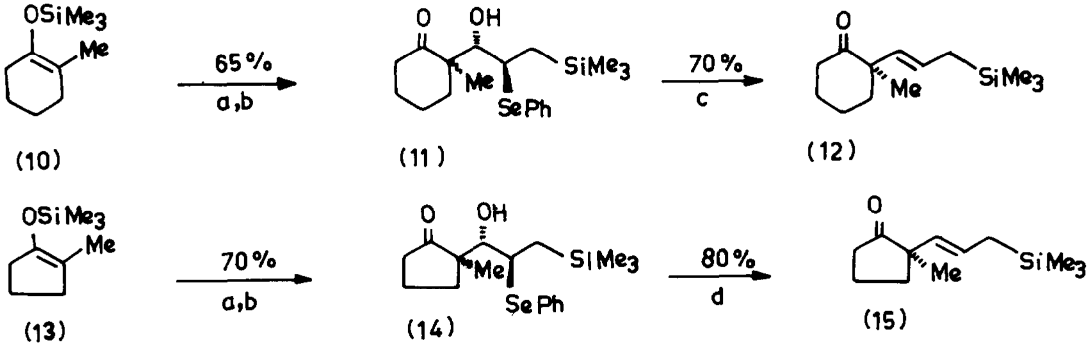
Reagent	Alcohol (Yield, %)^{a,b,c}	Method^d	Allylsilane (Yield, %)^b
n-$C_7H_{15}MgBr$	 (85%)	A	 (80%)
n-$C_{12}H_{25}MgBr$	 (60%)	B	 (90%)
$PhCH_2CH_2MgBr$	 (90%)	A B	 (80%) (92%)
	 (40%)^e	B	 (90%)



(a) The alcohols were obtained by the addition of (9) to the ethereal solution of the respective Grignard reagents at -95°C(2.5h), then at -60°C(1/2 h) followed by aq. NH_4Cl quench. (b) See ref. 12 (c) The crude alcohols were homogeneous on TLC. (d) Method A : $MsCl/Et_3N/25\,^{\circ}C$, 1h. Method B: $O{=}C(Im)_2$/toluene/115°C, 2h. (e) The low yield in this case is due to the readily separable by-product, $C_6H_{11}SePh$ (20%) formed by attack of the Grignard reagent on selenium in (9). (f) The other minor diastereomer (8%) was separated by chromatography.

The usefulnes of the new method in further documented by the introduction of the allylsilane function α to the carbonyl group[14] in two different systems (Scheme-III) in a predictable fashion.

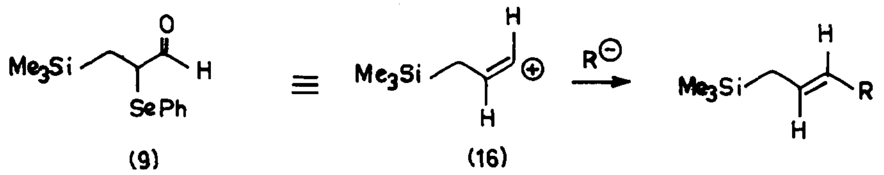
Scheme-III [12]



a) MeLi, ether, 25°C; b) (9),-80°C; c) $MsCl/Et_3N$,25°C, 2h; d) $O{=}C(Im)_2$, tol, 115°C,3h.

In conclusion, we have developed a simple and efficient synthesis of terminally-substituted (E)-allylsilanes based on the α-selenoaldehyde (9) which serves as the hitherto unknown synthetic equivalent of (16) (Scheme-IV). Furthermore, the new method makes use of a relatively unexplored commercially available reagent[9,15] and should find use in organic synthesis.[16]

Scheme-IV



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11. (a) Contaminated with ~10% (E)-isomer. (b) Picard etal (Picard, J.-P.; Ekouya, A.; Dunogues, J.; Duffant, N.; Calas, R. J. Organometal Chem. **1975**, 93, 51) described a one-pot synthesis of the (E)-isomer of (8) by reductive silylation of acrolein. We, however, experienced difficulty in reproducing this preparation.

12. Yields refer to material purified by chromatography on silica gel. All compounds reported were homogeneous by TLC analysis and showed ^{1}H NMR, IR and mass spectra consistent with the assigned sturctures.

13. Results were unsatisfactory with trifluoroacetic anhydride/triethylamine (see: ref. 5c). Details will be reported in a full paper.

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16. Extension of this work using the stannyl analog of (9) is currently under investigation. For a recent synthesis of allyl-and homoallyl-stannanes by selenoxide elimination, see: Jephcote, V.J.; Thomas, E.J. Tetrahedron Lett. **1985**, 26, 5327.

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