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REGIO- AND STEREOSELECTIVE SYNTHESIS OF ALLYLTRIMETHYLSILANES VIA KRIEF-REICH ELIMINATION IN β-SELENO-γ-SILYL ALCOHOLS

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Summary : The synthesis of (E)-allyltrimethylsilanes by regio- and stereocontrolled pathways is described based on the preference for Krief-Reich elimination over silicon-controlled rearrangement in β-seleno-γ-silyl alcohols, readily available from α-selenoaldehydes, 10 - 12. Usefulness of this protocol for the introduction of the allylsilane function α to the carbonyl group in cycloalkanones as well as for the preparation of unsymmetrically substituted allylsilanes is also reported.

Introduction

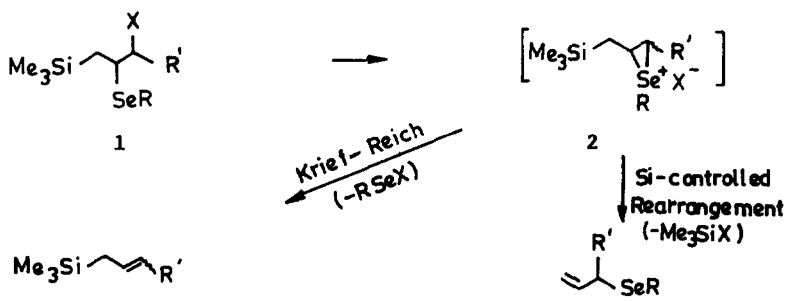
Allylsilanes[1,2] occupy a pre-eminent place in the organic chemist's arsenal of selective carbon-carbon bond forming reagents and a number of methods[3] for their synthesis have been developed over the past several years. Nevertheless, interest in the development of newer and more efficacious routes to these species continues unabated. In particular, the problem of regio- and stereocontrol still remains and, therefore, further development of highly regio- and stereocontrolled routes to allylsilanes is required to reply to their synthetic potentiality.[4]

We have recently reported[5] a new method for synthesizing terminal (E)-allylsilanes from the α-selenoaldehyde 10 and alkyl/aryl halides or cycloalkanones by making use of Krief-Reich reaction[6,7] in the crucial olefin forming step. Herein, we report on the full details of that work together with the application to the synthesis of unsymmetrically substituted allyltrimethylsilanes.

1. Strategy

In 1976 Warren et al[8] showed that exposure of 3-trimethylsilyl-2-phenylthio substituted alcohols to acids leads to specific allylic sulfides by silicon-controlled rearrangement. In 1982 Itoh et al[9] 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 et al[10] 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

Scheme - I



1 2 3 4

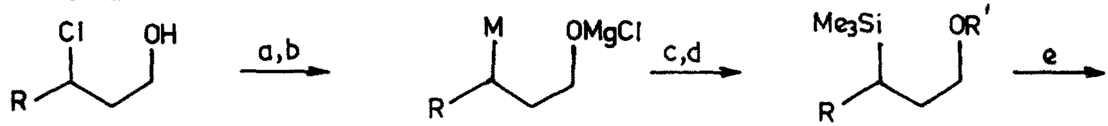
olefination processes, e.g., 1→2→3 and 1→2→4 are conceivable under Krief-Reich élimination[6,11] conditions (Scheme-I). As will be discussed shortly, the former mode of reactivity was found to be the exclusive[11a] pathway under a given set of conditions thus providing a general route to allyltrimethylsilanes.

It was envisaged that the requisite β-seleno-γ-silyl alcohols 1(X = OH) would be available by addition of Grignard reagents or aldol reaction on α-selenoaldehydes 1(X, R' = O). In the first phase of this work, therefore, the development of an efficient route to these aldehydes was taken up.

2. *Preparation of α-selenoaldehydes*

Three different α-selenoaldehydes, 10-12, were used in this study. For a large-scale preparation of 10, the most convenient starting material appeared to be the enolsilane 9. In fact, a high-yield and one-pot synthesis of 9(E-isomer only) was reported by Picard et al[12] by reductive silylation of acrolein. Unfortunately, several attempts to reproduce this preparation[13] gave in our hands a consistently poor yield (~10%) of 9 contaminated[14] with other unidentified materials. We, therefore, resorted to an alternate synthesis of 9 starting from the commercially available alcohol 7[15,16a] which was prepared in about 80% yield by quenching of the Normant's Grignard reagent 6[16b] (prepared from 5) (Scheme-II) with trimethylsilyl chloride and hydrolysis of the silyl ether 7 (R = H; R' = $SiMe_3$) with aqueous acid. Swern oxidation[17] of 7 and enolsilylation of the aldehyde 8[12,18] under the conditions described by Miller et al[19] gave 9 as a predominantly (Z)-isomer (contaminated with about 10% E-isomer,[12] from ^{1}H-NMR). Finally, treatment of 9 with phenylselenyl bromide[20] at a low temperature gave the desired reagent 10. Incidentally, a direct preparation of 10 from 8 under the conditions described by Sonoda et al[21] resulted in a very poor yield (~10%) of 10. Following an identical protocol, 11 and 12 were prepared as mixtures of diastereomers from the known intermidiates 13[16a] and 19.[22] 13[16a] was made either via 17a (prepared from 15[16a] via 17) or via 16 (prepared via lithiation[23] of 17) and exposure of these species to trimethylsilylchloride followed by hydrolysis. 19[22] was made from methyl 3-phenyl-3-(trimethylsilyl) propanoate[24] by LAH reduction to 18 and Swern oxidation of the latter.

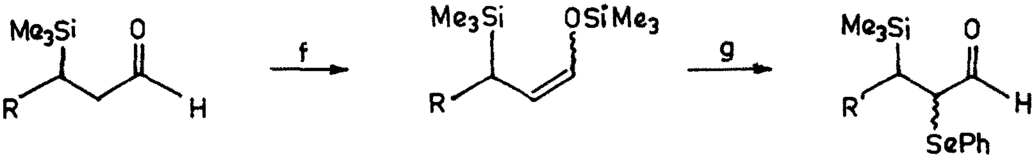
Scheme-II



5, R = H
15, R = Me

6, R = H; M = MgCl
16, R = Me; M = Li
17, R = Me; M = Cl
17a, R = Me; M = MgCl

7, R = R' = H
13, R = Me; R' = H
18, R = Ph; R' = H



8, R = H
14, R = Me
19, R = Ph

9, R = H
20, R = Me
21, R = Ph

10, R = H
11, R = Me
12, R = Ph

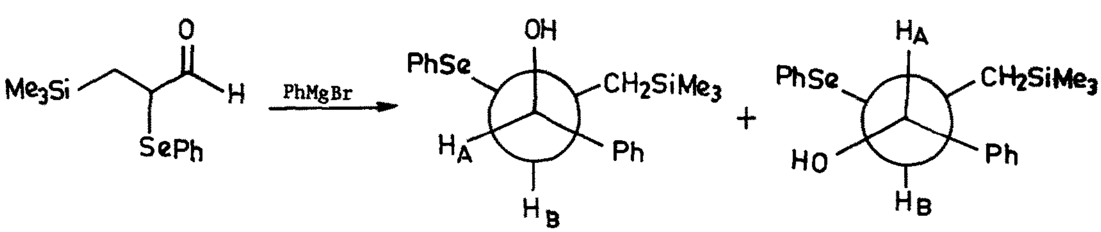
a) $^{i}BuMgCl$; b) Mg <u>or</u> Li; c) Me_3SiCl; d) H_3O^+; e) $(COCl)_2/DMSO/Et_3N$; f) $Me_3SiI/HN(SiMe_3)_2$; g) PhSeBr

3. Preparation of β-seleno-γ-silyl alcohols

The alcohols 22a-g were prepared in good yields (40-90%) by the addition of 10 to the respective Grignard reagents in THF or ether as shown in the Table. In all cases, the l-diastereomer[25] was stereoselectively formed.

Interaction of 10 with phenylmagnesium bromide gave a mixture of two diastereomeric alcohols 22e and 23 (l:u = 92:8) which were separated by chromatography (Scheme-III). The major diastereomer was identified as l - 22e by ^{1}H-NMR from the coupling constant ($J_{H_AH_B} \sim 2.4$ Hz) between H_A & H_B. The minor isomer u-23 was also characterized by ^{1}H-NMR ($J_{H_AH_B} \sim 7.2$ Hz).

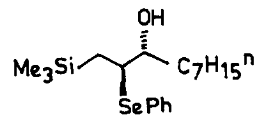
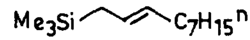
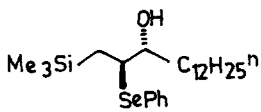
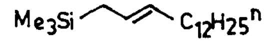
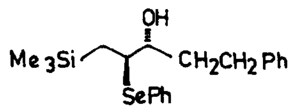
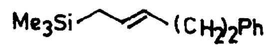
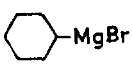
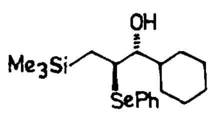
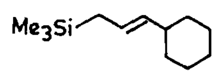
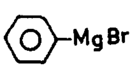
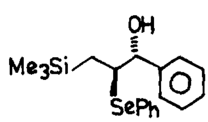
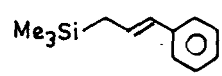
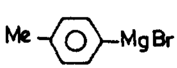
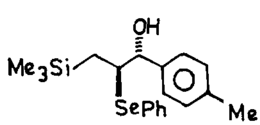
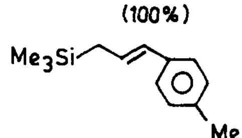
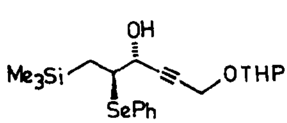
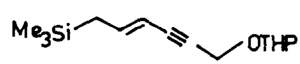
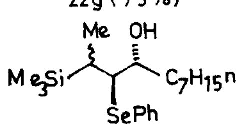
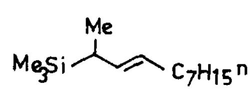
Scheme - III

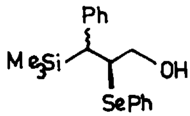
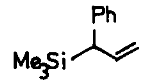


10   *l*-22e   u-23

Interaction of 10, on the other hand, with aliphatic Grignard reagents (RMgX, R = $^nC_3H_7$-, $PhCH_2CH_2$-, etc.) produced only one diastereomer in each case which were tentatively assigned the l-configuration. The homogeneity of the crude products on TLC(silica gel) indicated their absence from the u-isomers as β-seleno alcohols are usually separable[6e] under these conditions. Confirmation of stereochemical assignments to these alcohols came later through their stereospecific conversion into pure (E)-allylsilanes.

Table

Reagent	Alcohol (Yield, %)	Method[a]	Allylsilane (Yield, %)
n-$C_7H_{15}MgBr$	 22a (85%)	A	 24a (80%)
n-$C_{12}H_{25}MgBr$	 22b (60%)[b]	B	 24b (90%)
$PhCH_2CH_2MgBr$	 22c (90%)	A B	 24c (80%) (92%)
	 22d (40%)[b]	B	 24d (90%)
	 22e (80%)	A B	 24e (90%) (100%)
	 22f (81%)	B	 24f (90%)
$THPOCH_2C \equiv CMgBr$	 22g (75%)[b]	B	 24g (92%)
n-$C_7H_{15}MgBr$	 22h (72%)	B	 24h (86%)

LiAlH4  22i (94%) B  24i (68%)

(a) Method A : MsCl/Et_3N/25°C, 1h; Method B : O=C(Im)$_2$/toluene/115°C, 3h; (b) this Grignard reaction was run in THF; all others were run in ether

The high diastereoselectivity in the Grignard addition step can be rationalized in terms of Felkin-Anh's rule[26] (the PhSe-group behaves as the largest group to which the incoming neucleophile approaches in an antiperiplanar relationship). Several examples of such high asymmetric induction in α-heterosubstituted carbonyl compounds have been described in the literature.[27]

The lower yield in the case **22d** is due to the formation of a substantial amount of a by-product, e.g., phenylselenocyclohexane **25a** ($C_6H_5SeC_6H_{11}$) formed by attack of the Grignard reagent on **10**. The diastereoselectivity in the acetylenic Grignard reagent (BrMgC≡CH_2OTHP) addition to **10** was somewhat poorer in comparison to the cases with phenyl and aliphatic Grignard reagents. The product alcohol **22g** was a mixture of l-and u-isomers which could not be separated by chromatography. The diastereomeric ratio (l:u = 87:13) in this case was ascertained from ^{1}H-NMR by integration of the TMS resonances.

Similarly, **22h** was obtained as a mixture of diastereomers by the addition of the appropriate Grignard reagent to **11**. Incidentally, addition of Grignard reagents (e.g., MeMgI) to **12** led to a product[36] devoid of either SePh or $SiMe_3$ moieties and presumably formed by rapid 1,4-silyl shift (C→O)[38] in the initially formed Grignard addition product followed by elimination[28] of the phenylseleno group and hydrolysis of the silyl ether. In this case change of reaction conditions (Grignard addition/quench at lower temperatures) did not, however, result in any of the desired product. On the other hand, LAH reduction of **12** at -20°C proceeded without event to give **22i** as a diastereomeric mixture.

4. Krief-Reich elimination of β-Hydroxyselenides

The Krief-Reich reaction[6,7] involves stereoselective conversion of β-hydroxyselenides, e.g., **1**(X = OH) to olefins (Scheme-I) by elimination of the elements of RSeOH. For success of Krief-Reich elimination in the system 1, the following conditions were deemed to be important :

a) the reactions should be run under neutral or mildly basic conditions to prevent protodesilylation of the acid labile allylsilanes.
b) the counter ion (X-) should be non-silicophilic so as to reduce the possibility of desilylation leading to allylselenides, e.g., **4**.
c) since the crucial olefin forming step (1⇌2⇌3) is reversible, fast disposal of the active electrophile (RSeX) is a must for success of the reaction.

An ideal choice seemed to be a combination of methanesulfonyl chloride an triethylamine introduced by Reich et al[6b]. It involves a relatively non-silicophilic methane sulfonate ion and the sulfone, e.g., CH_2SO_2[6b] formed from the excess reagent (MsCl/Et_3N) plays th role of a scavenger to remove the active electrophile (RSeX) from the system.

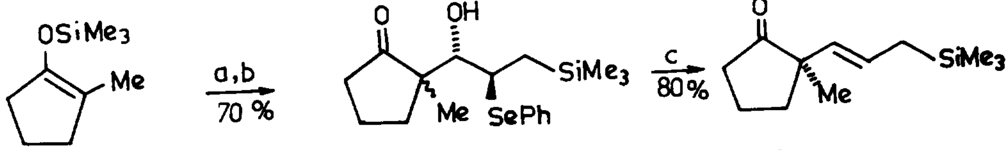
In the event when **22e** was exposed to excess methanesulfonyl chloride/triethyl amine,[6b] the allylsilane **24e** was cleanly formed in very good yield (90%) (Table). The isomeri purity of **24e** was checked by capillary GLC and high-field ^{1}H-NMR. Also no trace of any allylsele-nide could be detected in the crude reaction product by ^{1}H-NMR. Under similar conditions, 22 gave the allylsilane **24c**. Capillary GLC, reverse phase HPLC (on $AgNO_3$ impregnated column) an GC-MS of **24c** indicated the presence of (E)- and (Z)- isomers in the ratio 99:1, respectively This also confirms the high diastereoselectivity in the Grignard addition step (**10→22c**) Similarly, other β-seleno-γ-silyl alcohols (Table) resulted in the exclusive[37] formation of th allylsilanes **24a-g** in very good yields (≥ 80%) and high isomeric purity (> 98% E). Anothe reagent, e.g., N,N'-carbonyldiimidazole[6c] in hot tolune is also effective for this purpose. number of allylsilanes were prepared by this method. The yield of allylsilanes are excellent i every case (and, in fact, somewhat better than in the MsCl/Et_3N cases) and the work-up procedur is also very simple. The TMS-signals of (E)- and (Z)-allylsilanes resonate at different fields.[2] Hence, the isomeric purity and characterization of these species could be done by ^{1}H-NMR. Th (E)-allylsilanes in this work have been characterized by their olefinic splitting pattern an coupling constants(^{1}H-NMR).

Incidentally, **24h** was obtained contaminated with about 10% of the corresponding Z-isomer as revealed from ^{1}H-NMR. Also treatment of **22i** with N,N'-carbonyldiimidazole[6e] gave (E)-1-phenyl-3-(phenylseleno)-1-propene **25b**(E-$C_6H_5SeCH_2CH{=}CHC_6H_5$ {20%}, rather surprisingly, in addition to the expected allylsilane **24i** (68%). This is the only case where we observed evidence of the alternative silicon-controlled rearrangement pathway, e.g., **1→4** (Scheme-I) leading to an allylselenide.

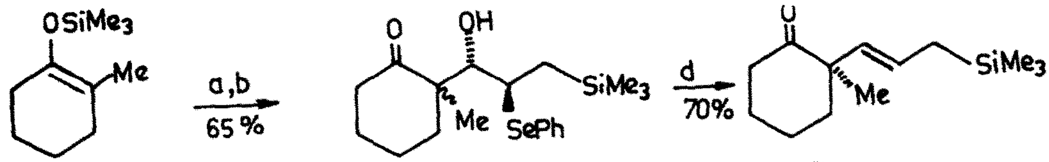
5. *Introduction of allylsilane function α to Ketones*

The usefulness of the new method is further documented by the introduction of th allylsilane function α to the carbonyl group[30] in two different systems (Scheme-IV) in predictable fashion. Diastereoselective aldol condensation[31] of **26a** with α-selenoaldehyde **1** gave two diastereomeric alcoholic products **27a** & **27b**, separable by column chromatography. Eac isomer on treatment with N,N'-carbonyldiimidazole gave the same allylsilane **28a**. Similarly, th condensation product **27c** (a 1:3 mixture of diastereomeric alcohols, as revealed from ^{1}H-NMR) obtained from **26b** and **10**, gave a single allylsilane **28b**. The olefin geometry of **28b** is tenta tively assigned to be (E).

Scheme-IV



26a **27a, 27b** **28a**



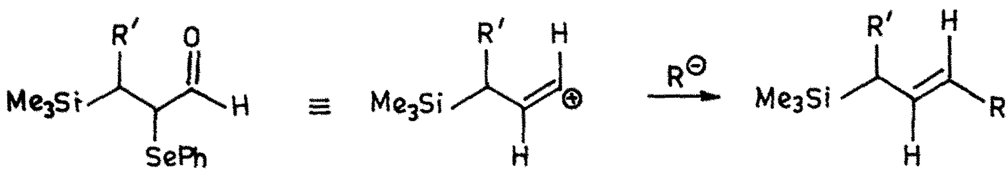
26b 27c 28b

a) MeLi; b) 10; c) O=C(Im)$_2$; d) MsCl/Et$_3$N

6. *Conclusion*

In conclusion, a simple and efficient synthesis of (E)-allylsilanes has been developed based on the α-selenoaldehydes 29(R'=H) which serves as the hitherto unknown synthetic equivalent of 30 (R'= H) (Scheme-V).

Scheme-V



29 30 24

Extension of this protocol to the preparation of unsymmetrically substituted allylsilanes is possible, although, the process is attended with somewhat lower stereoselectivity. Finally, the special attractive feature of this method is the ease with which an allylsilane function is introduced α to the carbonyl group in cycloalkanones.

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EXPERIMENTAL

General details :

Solvents were dried by distillation from drying agents as follows : diethylether, THF (sodium benzophenone ketyl), methylene chloride (P_2O_5), petroleum ether, benzene, toluene (Na-metal), DMSO (CaH_2). Column chromatography and TLC were carried out on silica gel (BDH, 120-200 mesh and 60 HF$_{254}$, respectively). Boiling and melting points are uncorrected. Unless otherwise specified, gas liquid chromatography (GLC) were carried out on Shimadzu GC-7A, fitted with flame ionization detector and glass column. Infrared spectra (IR) were recorded on Perkin-Elmer (Model 783) Infrared spectrophotometer or Perkin-Elmer (Model 283) Grating spectrometer. The absorption frequencies (ν_{max}) are expressed in wave number (cm^{-1}). Proton magnetic resonance spectra (^{1}H-NMR) were recorded on 60 MHz Varian A-60A, 90 MHz Varian EM-390, 100 MHz FT JEOL, 200 MHz Varian XL 200, 300 MHz Nicolet, 360 MHz Bruker, 500 MHz Bruker spectrometers using deuterochloroform ($CDCl_3$) or carbon tetrachloride (CCl_4) as solvent. Tetramethylsilane (TMS) was used as internal standard (δ0.00 ppm) for compounds having no trimethylsilyl group, otherwise the trimethylsilyl (TMS)-signal from the compounds was taken as δ0.00 ppm. Mass spectra (MS) were recorded on Jeol JMS-D 300, Shimadzu OP 1000, VG Micromass 7070F, Finnigan 1020 automated GC-MS instruments and spectral data (MS) are given as m/z (rel%) For selenium containing compounds, along with the fragment ion containing ^{80}Se, the mass spectrum also contains the peaks M+2, M+1, M-1, M-2, M-3, M-4 of the parent fragment ion M according to the abundance ratio of selenium isotopes, which are not mentioned in the mass spectrum details.

3-(Trimethylsilyl)-1-propanol 7

To a solution of 3-chloro-1-propanol 5 (66.2g, 0.7 mol) in dry THF (750 ml) at -20°C under nitrogen was added with stirring a solution of isobutylmagnesium chloride (250 ml, 2.8 M in THF) in THF over a period of 1 h. After the addition was over, the mixture was stirred at room temperature for 0.5 h and then heated under reflux for 15 min to drive out all the butane gas. After cooling to room temperature, magnesium turnings (30 g, 1.25 g.atom) were added followed by 1,2-dibromoethane (0.5 ml) and the mixture was warmed gently on a water bath with stirring until a vigorous reaction set in. The mixture was heated under reflux with stirring for 9 h and the Normant's Grignard reagent 6 thus formed was transferred under nitrogen into a flask with the aid of a cannula so as to separate it from the unreacted magnesium metal. To this was added dropwise with stirring at 0°C under nitrogen trimethylsilyl chloride (177 ml, 1.4 mol) during 1 h. The resulting white semi-solid mass was heated under reflux for 2 h and quenched with saturated aqueous ammonium chloride solution (100 ml). Sufficent ice-water was added to dissolve the precipitated salt. The resulting two phases were separated and the aqueous phase was extracted with ether (4 x 200 ml). The combined organic extract containing 7 (R=H; R'=$SiMe_3$) was treated with 10 ml concentrated HCl, heated under reflux for 0.5 h and left overnight at room temperature. The mixture was washed with saturated aqueous sodium bicarbonate (3 x 100 ml), brine (100 ml), dried ($MgSO_4$) and concentrated to afford a colourless liquid 7 (74g, 80%) : b.p. 67°C /10 torr (lit[15] b.p. 111-112°C/ 96 torr); ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.40-0.77 (m, 2H), 1.27-1.77 (m, 2H), 3.53 (t, 2H, J=5.8 Hz), 4.13 (bs, 1H).

3-(Trimethylsilyl)-1-butanol 13

(a) To a solution of 17 (prepared from 1.5 g of 3-chloro-1-butanol[16a], following the same procedure as described for 6, R = H; M = Cl, above) in THF at -40°C under argon was added lithium powder (400 mg, 0.057 g. atom) and the mixture stirred at the same temperature for 1h. This was slowly brought to ~ 5°C and stirred at the same temperature for 10h and then filtered through a G-3 filter. To the filtrate was added at 0°C trimethylsilyl chloride (3.7 ml, 0.029 mol), heated under reflux for 2h and then worked-up as described for 7 to afford a colourless liquid, 13 (0.8 g 40%) : b.p. 67-69°C/3 torr; IR (film) 3340, 1250 Cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H) 0.93 (d, 3H) 0.60-1.90 (m, 3H), 3.34-3.67 (m, 2H), 3.91 (bs, 1H); MS, m/z No M^+, 131, 129, 128, 127, 115, 73.

(b) Following the same procedure described for 7, from 3-chlorobutane 1-ol[16a] (10.85 g, 0.1 mol.), Magnesium turning (12 g., 0.5 g-atom) and Trimethylsilylchloride (25.5 ml., 0.2 mol.) was obtained 13 as a colourless liquid (8.9 g, 61%). 3,5-dinitrobenzoate of 13 : m.p. 62-63°C ; Anal. Calcd. for $C_{14}H_{20}N_2O_6Si$; C, 49.41 ; H, 5.82 ; N, 8.24 ; Found C, 49.41; H, 5.92 ; N, 8.30 :

3- Phenyl-3-(Trimethylsilyl)-1-propanol 18

18 was obtained by $LiAlH_4$ reduction in ether of methyl 3-phenyl-3-(trimethylsilyl)propanoate[24] as a white crystalline solid : m.p. 55-56°C ; IR (KBr) 3230 (b), 1600, 1490, 1450, 1245 Cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 1.80-2.33 (m, 3H), 2.75 (bs, 1H), 3.18-3.66 (m, 2H), 6.92-7.36 (m, 5H); MS, m/z 208 (M^+,0), 193 (2.6), 176 (1.0), 175 (1.6), 165 (1.5), 147 (1.1), 145 (1.4), 137 (11.0), 135 (2.5), 118 (100.0), 115 (7.8), 105 (7.3), 104 (5.2), 103 (9.4), 92 (4.8), 91 (14.6), 77 (7.0), 75 (42.0), 73 (100.0).

3-(Trimethylsilyl)propanal 8

To a solution of oxalyl chloride (15 ml, 0.17 mol) in methylene chloride (400 ml) at -60°C was added over a period of 0.5 h a solution of DMSO (25.5 ml, 0.36 mol) in methylene chloride (30 ml). After stirring for 5 min the alcohol 7 (22g, 0.17 mol) in methylene chloride (30 ml) was added during 10 min. Stirring was continued for an additional 15 min and triethylamine (110 ml, 0.78 mol) was added. After 10 min the reaction mixture was allowed to attain room temperature. Water (600 ml) was added and the aqueous phase extracted with methylene chloride (300 ml). The methylene chloride extract was washed successively with 5% aqueous HCl, saturated aqueous sodium bicarbonate, brine and dried ($MgSO_4$). After removal of the solvent, the residue was distilled to afford a colourless liquid 8 (17.2 g, 86%) : b.p. 71-73°C/79 torr (lit[12,18] b.p. 58°C/30 torr); ^{1}H-NMR (90 MHz, CCl_4) : δ 0.00 (s, 9H), 0.60-0.94 (m, 2H), 2.17-2.47 (m, 2H), 9.66 (t, 1H).

3-(Trimethylsilyl)butanal 14

The experimental procedure for the preparation of 14 was same as that described for 8. From 13 (2.2 g, 15.06 mmol) was obtained 14 (1.6 g, 74%) : b.p. 85°C/25 torr (lit[22] b.p. 90°C/25 torr); ^{1}H-NMR (90 MHz CCl_4) δ 0.00 (s, 9H), 0.83-1.50 (m, 1H), 0.95 (d, 3H), 2.05-2.65 (m, 2H), 9.70 (t, 1H).

3-phenyl-3-(Trimethylsilyl)propanal 19

The experimental procedure for the preparation of 19 was same as that described for 8. From 18 (4.16 g, 0.02 mol) was obtained 19 (3.8 g, 90%) : b.p. 84-85°C/0.3 torr (lit [22] b.p. 110°C/2 torr) ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 2.50-3.00 (m, 3H), 6.96-7.36 (m, 5H), 9.63 (t, 1H).

(Z)-1-(Trimethylsilyloxy)-3-(trimethylsilyl)-1-propene 9

To a stirred mixture of aldehyde 8 (17 g, 131 mmol) in dry petroleum ether (40-60°C) (1.5 lit) and hexamethyldisilazane (35 ml, 166 mmol) at -20°C under nitrogen was added freshly prepared trimethylsilyl iodide[32] (20 ml, 141 mmol over a period of 15 min. The reaction mixture was stirred under the same condition for 20 min, at room temperature for 2.5 h and quenched with ice-cold saturated aqueous sodium bicarbonate solution (200 ml). The organic phase was thoroughly washed with water, brine, dried ($MgSO_4$) and concentrated to give 9 (13.2 g, 50%) : b.p. 75-77°C/12 torr ; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.17 (s, 9H), 1.46 (dd, 2H, J=8 & 1.4 Hz), 4.40 (dt, 1H, J=8 & 6 Hz), 6.10 (td, 1H, J=6 & 1.4 Hz).

(Z)-1-(Trimethylsilyloxy)-3-(trimethylysilyl)-1-butene 20

The experimental procedure for the preparation of 20 (Z-isomer only) was same as that described for 9. From 14 (1.35 g, 9.3 mmol) was obtained 20 (1.1 g, 55%) : b.p. 85°C/5 torr; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.198 (s, 9H), 0.97 (d, 3H, J=7.5 Hz), 1.77-2.16 (m, 1H), 4.20 (dd, 1H, J=6 & 7.5 Hz), 5.97 (d, 1H, J=6 Hz).

(E)- & (Z)-3-phenyl-1-(Trimethylsilyloxy)-3-(trimethylsilyl)-1-propene 21

The experimental procedure for the preparation of 21 (1:9 E,Z - mixture) was same as that described for 9 . From 19 (4g, 19.5 mmol) was obtained 21 (3.8 g, 70%) : b.p. 95°C/0.3 torr; ^{1}H-NMR (90 MHz, $CDCl_3$) for Z-isomer : δ 0.00 (s, 9H), 0.198 (s, 9H), 3.56 (d, 1H, J=12 Hz), 5.00 (dd, 1H, J=6 & 12 Hz), 5.56 (t, 1H, J=12 Hz), 6.33 (d, 1H, J=6 Hz), 7.09-7.59 (m, 5H); for E-isomer : δ 0.00 (s, 9H), 0.198 (s, 9H), 2.84 (d, 1H, J=12 Hz), 5.56 (t, 1H, J=12 Hz), 6.33 (d, 1H, J=12 Hz), 7.09-7.59 (m, 5H).

2-(Phenylseleno)-3-(trimethylsilyl)propanal 10

To a solution of 9 (9 g, 45 mmol) in dry ether (75 ml) at -80°C under nitrogen was added with stirring a solution of phenylselenyl bromide [45.6 mmol, prepared from diphenyl diselenide (7.116 g , 22.8 mmol) and bromine (3.56 g, 23 mmol) in dry ether (125 ml)] in ether over a period of 1 h. After the addition was over the pale brown solution was quenched into a saturated aqueous solution of sodium bicarbonate (100 ml) and extracted with ether (3 x 100 ml). The combined ethereal extract was washed with brine, dried ($MgSO_4$) and concentrated. The crude product on chromatography over silica gel and elution with ethyl acetate-petroleum ether (60-80°C) (2:98) afforded 10 (9.7 g, 76.4%) as a pale yellow oil. This compound was sufficiently pure for all synthetic purposes. An analytical sample was obtained by distillation at reduced pressure : b.p. 65-68°C (bath)/0.01 torr ; IR (film) 1705 (s), 1575, 1250 (s) cm^{-1}; ^{1}H-NMR (100 MHz, CCl_4) δ 0.00 (s, 9H), 0.81-1.31 (m, 2H), 3.62-3.82 (m, 1H), 7.18-7.62 (m, 5H), 9.24 (d, 1H, J=4 Hz); MS, m/z 286 (M^+, 0.5), 271 (1.0), 231 (1.8), 216 (4.7), 214 (2.56), 198 (3.0), 158 (13.0), 130 (95), 73 (100).

2-(Phenylseleno)-3-(trimethylsilyl)butanal 11

The experimental procedure for the preparation of 11 was same as that described for 10 From 20 (1 g, 4.6 mmol) was obtained 11 (880 mg, 64%) (1:1 mixture of diastereomers) as an oil : IR (film) 1705, 1580, 1475, 1440, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.03 (s, 9H), 1.18 (d, 3H x 2), 0.73-1.64 (m, 1H x 2), 3.30-3.37 (m, 1H x 2), 7.06-7.45 (m, 5H x 2), 9.22 (d, 1H, J=4.3 Hz), 9.3 (d, 1H, J=4.8 Hz); MS, m/z 300 (M^+, 2.6), 285 (1.2), 234 (1.3), 232 (1.3), 228 (2.0), 226 (1.0), 217 (1.2), 216 (1.0), 215 (5.6), 213 (3.0), 212 (1.3), 211 (1.1), 158 (3.7), 157 (3.2), 155 (5.0), 143 (45.0), 77 (11.3), 75 (19.2), 73 (100.0).

3-Phenyl-2(phenylseleno)-3-(trimethylsilyl)propanal 12

The experimental procedure for the preparation of 12 was same as that described for 10. From 21 (3.03 g, 10.9 mmol) was obtained 12 (1.5 g, 38%) (1:1 mixture of diastereomers) as an oil : IR (film) 1710, 1600, 1580, 1500, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.137 (s, 9H), 2.60 (d, 1H, J=12 Hz), 2.66 (d, 1H, J=12 Hz), 4.23 (dd, 1H, J=5 & 12 Hz), 4.18 (dd, 1H, J=6 & 12 Hz), 7.00-7.85 (m, 20H), 9.19 (d, 1H, J=6 Hz), 9.46 (d, 1H, J=5 Hz); MS, m/z 362 (M^+), 347, 294, 293, 292, 217, 216, 215, 213, 205, 158, 157, 73.

Addition of Grignard Reagents (RMgX) to α- Selenoaldehydes. A General Procedure

To a solution of the Grignard reagent (3 mmol, in ether or THF) at -95°C under nitrogen was added with stirring a solution of the aldehyde 10 or 11 (2 mmol) in ether or THF (1 ml) during 15 min. After the addition was over the reaction mixture was stirred under the same condition for 2.5 h and then at -60°C for 0.5 h. The reaction mixture was quenched at -60°C (in the case of 22h, the reaction mixture was brought to 0°C in 1 h and quenched) with saturated aqueous NH_4Cl solution (2 ml) and allowed to attain room temperature. After addition of sufficient water to dissolve the precipitated salt, the organic matter was extracted with ether (4 x 20 ml). The combined organic phase was washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated. The crude product on chromatography over silica gel and elution with ethyl acetate-petroleum ether (60-80°C) (5:95) gave the desired alchohol as a colourless thick oil.

ℓ-2-(Phenylseleno)-1-(trimethylsilyl)-3-decanol 22a

IR (film) 3450 (b), 3070, 1590, 1490, 1450, 1260 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.60-0.95 (m, 5H), 1.00-1.45 (bs, 13H), 3.05-3.42 (m, 2H), 7.00-7.50 (m, 5H); MS, m/z 386 (M^+, 1.0), 369 (2.6), 313 (1.0), 312 (1.2), 300 (1.9), 299 (1.7), 258 (1.0), 257 (1.3), 229 (21.6), 213 (65.0), 158 (18.0), 157 (19.1) 139 (20.7), 97 (38.2), 91 (24.1), 83 (78.8), 75 (41.8), 73 (100.0).

ℓ-2-(Phenylseleno)-1-(trimethylsilyl)-3-pentadeacnol 22b

IR (film) 3450, 1590, 1490, 1260 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.56-0.90 (m, 5H), 0.92-1.40 (bs, 22H), 3.00-3.40 (m, 2H), 6.96-7.50 (m, 5H); MS, m/z No M^+, 439, 299, 282, 231, 158, 157, 73.

ℓ-2-(Phenylseleno)-5-phenyl-1-(trimethylsilyl)-3-pentanol 22c

IR (film) 3450, 1610, 1585, 1500, 1480, 1255 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.80-0.96 (m, 2H), 1.40-1.76 (m, 2H), 2.06 (bs, 1H), 2.23-2.83 (m, 2H), 3.10-3.53 (m, 2H), 6.90-7.50 (m, 10H); MS, m/z No M^+, 375, 317, 236, 232, 219, 158, 157, 91, 73.

ℓ-1-Cyclohexyl-2-(phenylseleno)-3-(trimethylsilyl)-1-propanol 22d

IR (film) 3460, 1590, 1485, 1260 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.60-2.20 (bm, 14H), 2.86 (bd, 1H), 3.17-3.40 (m, 1H), 6.95-7.45 (m, 5H); MS, m/z No M^+, 353, 232, 213, 197, 158, 157, 123, 82, 73.
^{1}H-NMR (90 MHz, CCl_4) of 25a : δ 1.06-2.10 (bm, 10H), 2.93-3.36 (m, 1H), 7.03-7.60 (m, 5H).

ℓ- & u- 1-Phenyl-2-(phenylseleno)-3-(trimethylsilyl)-1-propanol 22e

IR (film) 3450, 1590, 1490, 1260 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) of ℓ-22e : δ 0.00 (s, 9H), 0.60-1.00 (m, 2H), 2.70 (d, 1H, J ~ 2.4 Hz), 3.33-3.56 (m, 1H), 4.60 (t, 1H), 7.00-7.50 (m, 10H); ^{1}H-NMR (90 MHz, CCl_4) of u-23 : δ 0.00 (s, 9H), 0.80-1.02 (m, 2H), 2.85 (bs, 1H), 3.15-3.46 (m, 1H), 4.32 (d, 1H, J ~ 7.2 Hz), 7.05-7.50 (m, 10H) ; MS, m/z 364 (M^+), 347, 314, 312, 259, 234, 232, 230, 157, 117, 77, 73.

ℓ-1-(4'-Methylphenyl)-2-(phenylseleno)-3-(trimethylsilyl)-1-propanol 22f

IR (film) 3450, 1580, 1510, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.60-0.92 (m, 2H), 2.33 (s, 3H), 2.50 (bs, 1H), 3.30-3.60 (m, 1H), 4.57 (d, 1H , J ~ 2.5 Hz), 6.90-7.70 (m, 9H); MS, m/z 378 (M^+), 361, 258, 257, 221, 206, 205, 157, 132, 131, 121, 116, 115, 91, 77, 75, 74, 73.

ℓ- & u-2-(Phenylseleno)-6-(tetrahydropyranyloxy)-1-(trimethylsilyl)-hex-4-yne-3-ol 22g

IR (film) 3420, 1580, 1480, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H, from ℓ-isomer), 0.01 (s, 9H , from u-isomer), 1.00-1.23 (m, 2H), 1.27-2.00 (bm, 6H), 2.85 (d, 1H, J ~ 6 Hz), 3.15-3.95 (m, 3H), 4.13 (d, 2H, J ~ 1.5 Hz), 4.13-4.43 (m, 1H), 4.76 (bs, 1H), 7.10-7.75 (m, 5H); MS, m/z No M^+, 411, 389, 343, 327, 257, 236, 181, 169, 158, 157, 85, 73.

3-(Phenylseleno)-2-(trimethylsilyl)-4-undecanol 22h

IR (film) 3460, 1580, 1480, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00-0.10 (3s, 9H), 0.76-1.76 (m, 19H), 3.23-3.694 (m, 3H), 7.07-7.60 (m, 5H); MS, m/z No M^+, 383, 371, 369, 243, 231, 230, 229, 228, 227, 158, 157, 155, 73.

3-Phenyl-2-(phenylseleno)-3-(trimethylsilyl)-1-propanol 22i

To a solution of 12 (210 mg, 0.58 mmol) in dry ether (5 ml) at - 21°C under argon was added with stirring a solution of $LiAlH_4$ (0.75 ml of 1 M solution, 0.75 mmol) in THF. The resulting mixture was stirred for another 4 h and then decomposed with saturated aqueous sodium sulfate solution at the same temperature and worked-up. The crude product was chromatographed over silica gel and eluted with ethyl acetate - petroleum ether (60-80°C) (5:95) to give 22i as a colourless thick oil (200 mg, 94%); IR (film) 3440, 1600, 1580, 1490, 1250 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.00-0.06 (2s, 9H), 2.42 (d, 1H, J = 9 Hz), 3.10-3.35 (m, 1H), 3.38-3.83 (m, 2H), 6.85-7.58 (m, 10H).

2-Methyl-2-[1'-hydroxy-2'-(phenylseleno)-3'-(trimethylsylyl)-propyl]-cyclopentanone 27a, 27b

To a solution of methyl lithium (3 ml, 1 M in ether) was added with stirring at room temperature under nitrogen a solution of 2-methyl-1-(trimethylsilyloxy)-1-cyclopentene[33] (475 mg, 3 mmol) in ether (1 ml) during 45 min. The mixture was cooled to -78°C and a solution of 10 (572 mg, 2 mmol) in ether (1 ml) was added over a period of 1 min. The mixture was stirred under that condition for 7 min, quenched with saturated aqueous ammonium chloride solution (2 ml) and allowed to attain room temperature. The mixture was extracted with ether (3 x 15 ml), washed with brine (1x10 ml), dried ($MgSO_4$) and concentrated to afford a pale yellow oil. It was chromatographed over silica gel (40 g) and eluted with ethyl acetate - petroleum ether (60-80°C) (3:97) to afford 27a (326 mg, 42.5%) as major product and another minor product 27b (210 mg, 27.5%). ^{1}H-NMR (90 MHz, CCl_4) of 27a : δ 0.00 (s, 9H), 0.83 (s, 3H), 0.8-1.20 (m, 2H), 1.40-2.40 (bm, 6H), 2.90 (bs, 1H), 2.93-3.30 (m, 1H), 3.40-3.65 (m, 1H), 6.95-7.50 (m, 5H); ^{1}H-NMR (90 MHz, CCl_4) of 27b : δ 0.00 (s, 9H), 0.54 (s, 3H), 0.60-0.90 (m, 2H), 1.20-2.50 (m, 6H), 2.60 (bs, 1H), 3.16-3.43 (m, 1H), 3.65 (bs, 1h), 6.95-7.50 (m, 5H).

2-Methyl-2-[1'-hydroxy-2'-(phenylseleno)-3'-(trimethylsilyl)-propyl]-cyclohexanone 27c

Phenylselenoaldehyde 10 (513 mg, 1.8 mmol) was converted into the title keto alcohol 27c following the same procedure as described for the mixture 27a & 27b by using methyllithium (2 ml, 1.1 M in ether) and 2-methyl-1-(trimethylsilyloxy)-1-cyclohexene 26b[33] (370 mg, 2 mmol). The crude product was chromatographed over silica gel (30 g) and eluted with ethyl acetate - petroleum ether (60-80°C) (3:97) to afford 27c (465 mg, 65%) : ^{1}H-NMR (90 MHz, CCl_4) δ 0.00 (s, 9H), 0.15 (s, 9H), 0.70-1.14 (m, 5H), 1.14-2.10 (m, 6H), 2.12-2.60 (m, 2H), 3.10 (bs, 1H), 3.30-3.78 (m, 1H), 3.96 & 4.10 (two broad singlets, 1H), 7.10-7.70 (m, 5H).

Reductive Elimination of β-Hydroxyselenides . A General Procedure

(Procedure A)

To a solution of β-phenylseleno alcohol (1 mmol), and triethylamine (0.7 ml, 5 mmol) in methylene chloride (5 ml) at -20°C under nitrogen was added with stirring a solution of methanesulfonyl chloride (0.35 g, 3 mmol) in methylene chloride (3 ml) during 15 min. After the addition was over, the mixture was slowly allowed to attain room temperature and stirred for 1 h. This was quenched with cold saturated aqueous sodium bicarbonate solution (5 ml) and extracted with ether (3 x 20 ml). The combined organic phase was successively washed with water (10 ml), brine (10 ml), dried ($MgSO_4$) and finally concentrated to afford a red oil which on preparative layer chromatography over silica gel (developed with petroleum ether, 60-80°C) afforded the pure allylsilane as oil.

(Procedure B)

To a solution of β-phenylseleno alcohol (0.5 mmol), in toluene (4 ml) was added N,N'-carbonyldiimidazole (162 mg, 1 mmol) and the mixture heated to reflux with stirring for 3h. After cooling to room temperature the reaction mixture was filtered through a silica gel bed to remove the tarry residue and excess N,N'-carbonyldiimidazole. Removal of solvent followed by preparative layer chromatography over silica gel (developed with petroleum ether, 60-80°C) gave the pure allylsilane as oil.

(E)-1-(Trimethylsilyl)-2-decene 24a

IR (film) 3010, 2955, 2925, 2860, 1250 (s), 1155, 965 (s), 850 cm^{-1}; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 0.00 (s, 9H), 0.90 (t, 3H, J ~ 7 Hz), 1.28 (bs, 10H), 1.41 (d, 2H, J ~ 7.5 Hz), 1.93-2.03 (m, 2H), 5.27 (td, 1H, J ~ 7.5 & 15 Hz), 5.38 (td, 1H, J ~ 7.5 & 15 Hz); MS, m/z 212 (M^+, 1.0), 138 (1.0), 99 (1.8), 81 (1.0), 73 (100.0).

(E)-1-(Trimethylsilyl)-2-pentadecene 24b

IR (film) 3040, 2990, 2960, 2880, 1260 (s), 1165, 965 (s), 850 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9H), 0.90 (t, 3H, J ~ 7 Hz), 1.29 (bs, 20H), 1.40 (d, 2H, J ~ 7.5 Hz), 1.90-2.00 (m, 2H), 5.24 (td, 1H, J ~ 7.5 & 15 Hz),

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REGIO- AND STEREOSELECTIVE SYNTHESIS OF ALLYLTRIMETHYLSILANES VIA KRIEF-REICH ELIMINATION IN β-SELENO-γ-SILYL ALCOHOLS

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Summary : The synthesis of (E)-allyltrimethylsilanes by regio- and stereocontrolled pathways is described based on the preference for Krief-Reich elimination over silicon-controlled rearrangement in β-seleno-γ-silyl alcohols, readily available from α-selenoaldehydes, 10 - 12. Usefulness of this protocol for the introduction of the allylsilane function α to the carbonyl group in cycloalkanones as well as for the preparation of unsymmetrically substituted allylsilanes is also reported.

Introduction

Allylsilanes[1,2] occupy a pre-eminent place in the organic chemist's arsenal of selective carbon-carbon bond forming reagents and a number of methods[3] for their synthesis have been developed over the past several years. Nevertheless, interest in the development of newer and more efficacious routes to these species continues unabated. In particular, the problem of regio- and stereocontrol still remains and, therefore, further development of highly regio- and stereocontrolled routes to allylsilanes is required to reply to their synthetic potentiality.[4]

We have recently reported[5] a new method for synthesizing terminal (E)-allylsilanes from the α-selenoaldehyde 10 and alkyl/aryl halides or cycloalkanones by making use of Krief-Reich reaction[6,7] in the crucial olefin forming step. Herein, we report on the full details of that work together with the application to the synthesis of unsymmetrically substituted allyltrimethylsilanes.

1. Strategy

In 1976 Warren *et al*[8] showed that exposure of 3-trimethylsilyl-2-phenylthio substituted alcohols to acids leads to specific allylic sulfides by silicon-controlled rearrangement. In 1982 Itoh *et al*[9] 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 *et al*[10] 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

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