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PHENYLSELENODESILYLATION OF ALLYLSILANES AND REGIOSPECIFIC TRANSFORMATION OF ALLYLSILANES TO ALLYLIC ALCOHOLS VIA ALLYLSELENIDES

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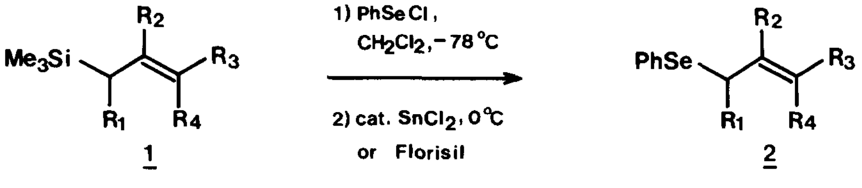
Abstract: Allylsilanes were converted regiospecifically to allylselenides by reaction with phenylselenenyl chloride and subsequent treatment with anhydrous tin(II) chloride or florisil. Oxidative work-up of these allylselenides gave the corresponding allylic alcohols regiospecifically.

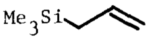
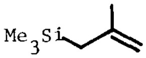
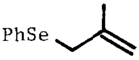
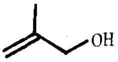
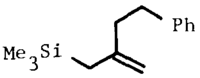
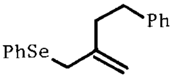
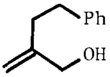
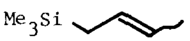
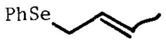
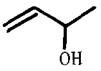
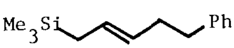
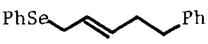
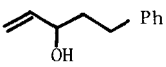
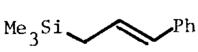
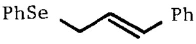
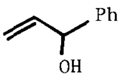
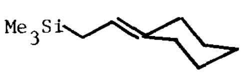
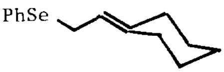
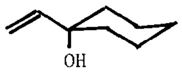
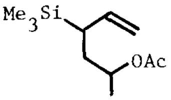
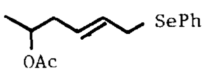
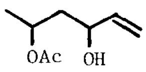
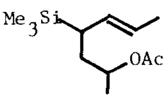
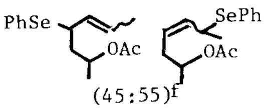
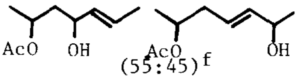
Allylsilanes react with a wide range of electrophiles and are particularly useful to organic synthesis.[1] Addition or substitution of allylsilanes with many electrophiles takes place at the γ-position of an allylic system. We wish to describe here a reaction of allylsilanes and phenylselenenyl chloride[2], and a regiospecific transformation of allylsilanes to allylic alcohols.

Addition of a dichloromethane solution of phenylselenenyl chloride to a solution of allylsilane 1 in dichloromethane at -78 °C afforded the corresponding adduct, which was subsequently converted to allylselenide (2a-2i) in good yield by treatment of a catalytic amount of anhydrous tin(II) chloride or passing through a short column of florisil[3] (Table 1). Trimethylsilyl group was unexpectedly displaced at the less substituted position by phenylselenenyl group (Entry 4-8).



Further experiments showed that the reaction of deuterated allylsilane 4[5] with phenylselenenyl chloride afforded the mixture of α- and γ-positional isomers (5:6 = 46:54, total 82%)[6], whereas that with phenylsulfenyl chloride[7] gave only γ-substituted product 7 (82%)[6]. Almost complete scrambling in the

Table 1 Phenylselenodesilylation of Allylsilanes and Transformation to Allylic Alcohols.[a]

Entry	Allylsilane[b] 1	Selenide 2 (yield,%)[c]		Allylic Alcohol 3 (yield,%)[d]	
1			2a (90)		3a (87)[e]
2			2b (87)		3b (81)[e]
3			2c (87)		3c (92)
4			2d (91)		3d (82)[e]
5			2e (97)		3e (91)
6			2f (89)		3f (44)
7			2g (80)		3g (84)
8			2h (80)		3h (68)
9		 (45:55)[f]	2i (65)	 (55:45)[f]	3i (61)

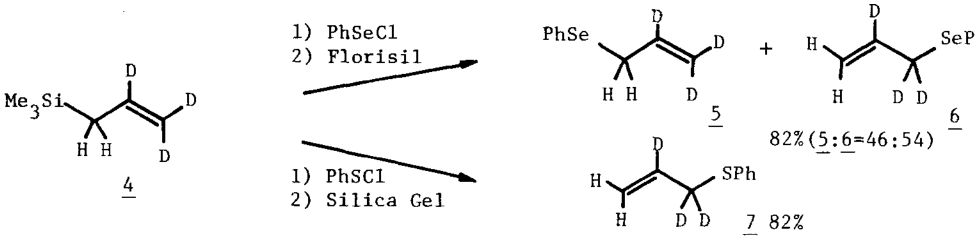
a. After stirring a dichloromethane solution (ca. 5 ml/mmol) of allylsilane (1.2 equiv. of PhSeCl) and PhSeCl at -78 °C for 10 min., the reaction temperature was raised to 0 °C, then anhydrous $SnCl_2$ (10 mol% of PhSeCl) was added. The mixture was stirred for 1.5 hr. and treated with aqueous $NaHSO_4$. After extraction with CH_2Cl_2 and following concentration, almost pure selenide was obtained. Further purification was performed by florisil column chromatography. Alternatively, the selenide was also isolated directly by passing the concentrated reaction mixture through florisil column (small amounts of diphenyldiselenide was obtained as a forerunner). The selenide was subsequently treated with 15%-H_2O_2 (10 equiv.) and pyridine (2 equiv.) in CH_2Cl_2 at 0 °C for 20 min. to give the allylic alcohol.

b. For preparation of allylsilanes, see ref. 4.

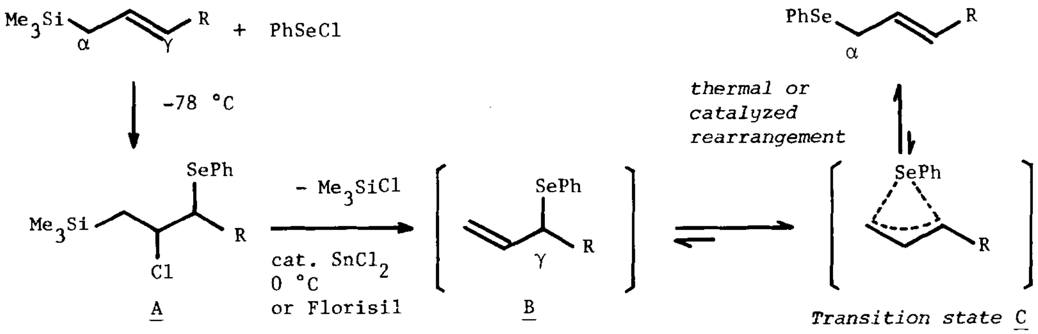
c. Isolated yield. d. Isolated yield based on PhSeCl starting from allylsilane.

e. Determined by GLPC. f. Determined by ^1H-NMR.

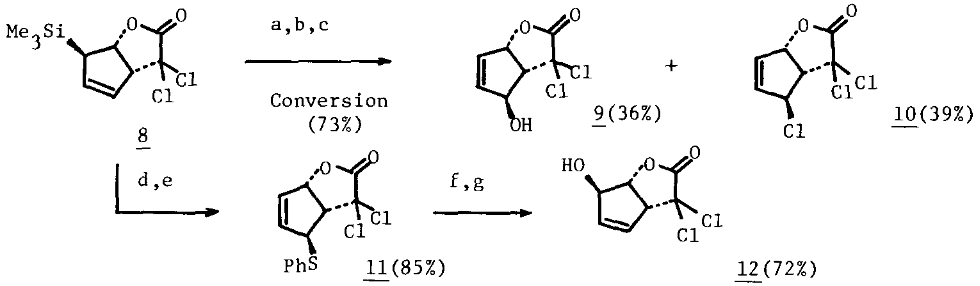
phenylselenodesilylation is interpreted in terms of the transition state C, which may be equivalent to that of [1,3] shift of allylselenides.[8]



The mechanism is considered illustratively as follows. The reaction at -78 °C gave the adduct A,[9] which caused dechlorosilylation by the treatment with tin(II) chloride at 0 °C or by florisil column chromatography to form the normal γ-substituted product B. The rearrangement of B took place immediately in the reaction medium to give the less substituted allylselenide.



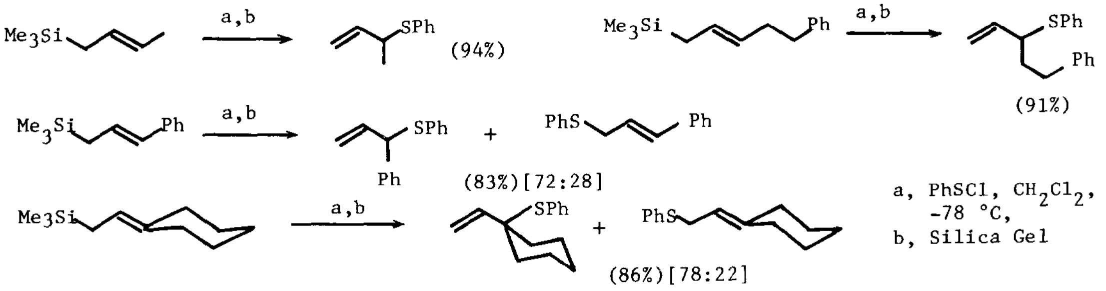
This regiospecific formation of allylselenides was applied to the preparation of allylic alcohols by well known oxidative rearrangement of allylselenides with hydrogen peroxide (viz., 2,3-sigmatropic rearrangement of allylselenoxides).[10] After the preparation of allylselenide, the crude product was treated with hydrogen peroxide (15%) and pyridine in dichloromethane at 0 °C for 20 minutes to afford the allylic alcohol having hydroxy group at the more substituted site (Table 1). Regiospecific transformation of allylsilanes to allylic alcohols has been reported but is fairly difficult to select the adequate reaction conditions.[11] Our method gave allylic alcohols from allylsilanes with high regiospecificity under more convenient condition. As a further application, a comparative transformation of Fleming's prostaglandin intermediate 8[12] to isomeric allylic alcohols 9 and 12 was demonstrated in the following scheme.



a, PhSeCl, r.t.; b, Florisil; c, H_2O_2, Py; d, PhSCl, -30 °C; e, Silica Gel; f, $NaIO_4$, MeOH, r.t., 1 day; g, $P(OMe)_3$, MeOH, r.t., 1 day.

References and Notes

1. (a). T.H. Chan and I.Fleming, Synthesis, 761 (1979). (b). A. Hosomi, A. Shirahata, and H. Sakurai, Tetrahedron Lett., 3043 (1978). (c). A. Hosomi, M. Sato, and H. Sakurai, Tetrahedron Lett., 355 (1980). (d). T. Tsunoda, M. Suzuki, and R. Noyori, Tetrahedron Lett., 71 (1980) and references therein.
2. Phenylselenenyl chloride was freshly prepared by Sharpless' method from PhSeSePh and sulfryl chloride. (a). K.B. Sharpless, R.F. Lauer, and A. Teranishi, J. Am. Chem. Soc., 95, 6137 (1973). (b). K.B. Sharpless and R.F. Lauer, J. Org. Chem., 39, 429 (1974).
3. Florisil; Merck, Art 12518 ($MgO:SiO_2$=15:85, 60-100 mesh).
4. See ref. 1.(a),P.775-782.
5. Trimethylallylsilane-d_3 4 was prepared by the cross-coupling reaction of trimethylsilylmethyl Grignard reagent and vinyl bromide-d_3 in the presence of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$ as a catalyst. [See, K. Tamao, et at., Bull. Chem. Soc. Jpn., 49, 1958 (1976).]
   4: ^{1}H-NMR($CDCl_3$, $CHCl_3$ as a internal standard)δ ppm, 0.03(s, 9H, CH_3Si), 1.54(broad s, 2H, CH_2Si).
6. ^{1}H-NMR($CDCl_3$, TMS), 5:δ 3.37(s, 2H, $SeCH_2CD{=}CD_2$) ppm; 6:δ 4.81(broad s, 2H, $SeCD_2CD{=}CH_2$) ppm; 7:δ 5.1(broad s, 2H, $SCD_2CD{=}CH_2$) ppm.
7. γ-Substitution of allylsilane with phenylsulfenyl chloride was reported. See ref. 12. We demonstrated other examples as follows with some exceptions. Silica gel was effective for dechlorodesilylation from the corresponding adducts. [1,3] Shifts were a little observed in the case of tertiary and benzyl at the γ-carbon of the allylic system.



a, PhSCl, CH_2Cl_2, -78 °C,
b, Silica Gel

8. K.B. Sharpless and R.F. Lauer, J. Org. Chem., 37, 3973 (1972).
9. The formation of these adducts was confirmed by ^{1}H-NMR and IR at room temperature. Without $SnCl_2$ or florisil, these adducts were not converted to the allyl selenides.
10. H.J. Reich, J. Org. Chem., 40, 2572 (1975).
11. R.F. Hudrlik and G.P. Withers, Tetrahedron Lett., 29 (1976) and references therein.
12. B. -W. Au-Yeung and I. Fleming, J. Chem. Soc ., Chem. Comm., 79 (1977).

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