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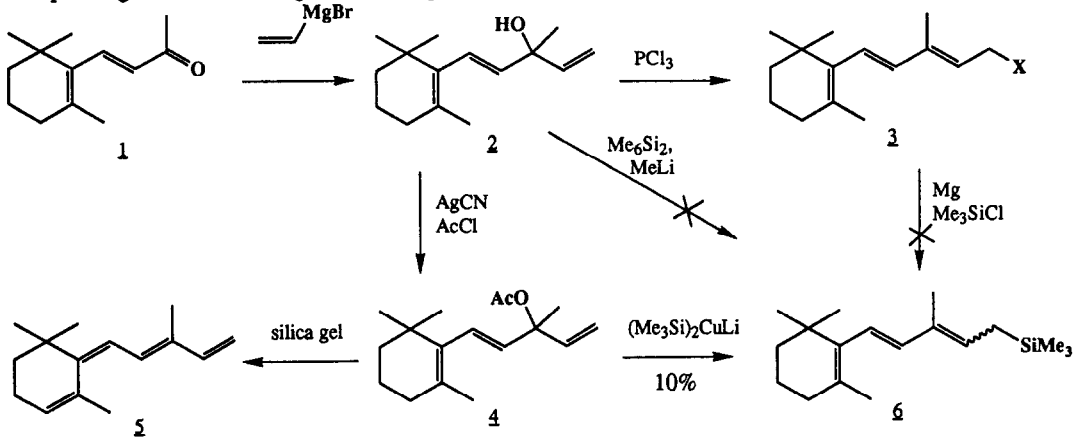
A Novel Regioselective Synthesis of Allylsilanes.

T.H. Chan and D. Labrecque*
Department of Chemistry, Mc Gill University, Montreal, Quebec, Canada H3A-2K6.

Summary: The anions derived from allyl sulfones were silylated in the α-position. Reductive desulfonylation gave the desired allylsilanes regioselectively.

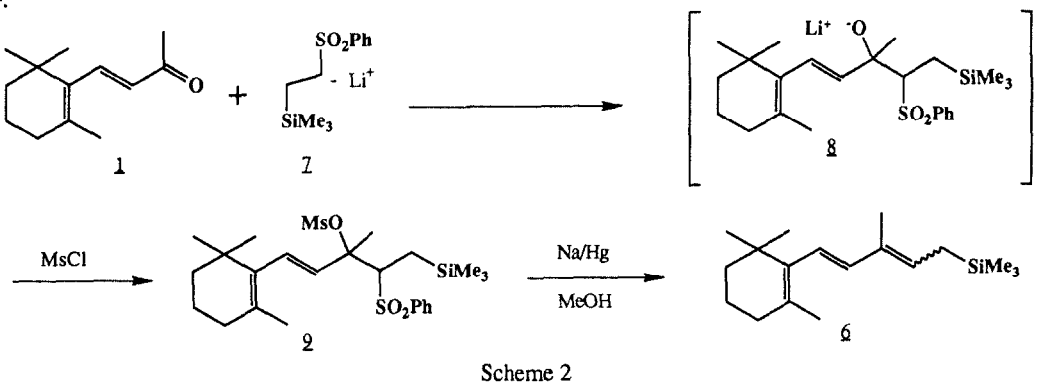
Allylsilanes have become useful reagents in organic synthesis[1]. A number of methods have been developed for their preparation [2-5]. A major concern in the synthesis of allylsilanes is the control of regiochemistry[6] as well as the stereochemistry of the double bond. As part of our general research in the use of silylallyl anion in organic synthesis[7], we became interested in the synthesis of polyenylsilane **6**. Because of the conjugated polyenic structure and the possible regio- and stereoisomers, the synthesis of **6** is particularily challenging. We attempted a number of the reported general methodologies and none proved to be satisfactory (Scheme 1).



Scheme 1

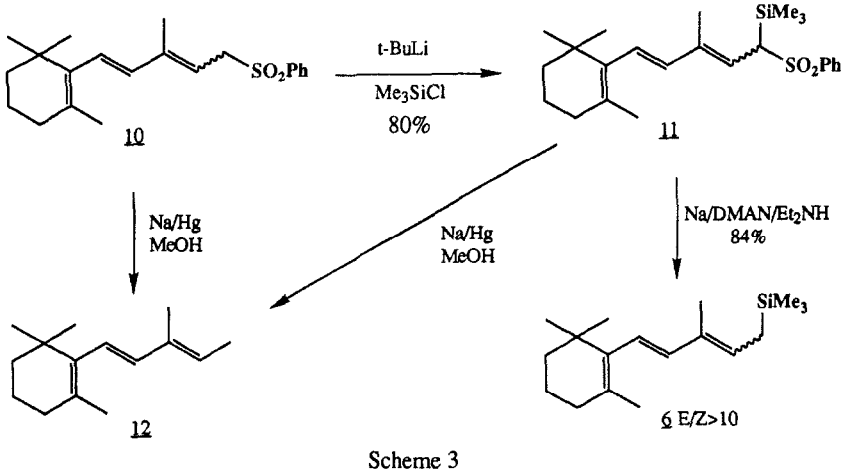
A common method for the synthesis of allylsilanes is to couple allyl halides with trimethylchlorosilane via the corresponding organometallics. The bromide or chloride **3**, prepared[8] from vinyl-β-ionol **2**, on reaction with Mg and trimethylchlorosilane according to the procedure of Calas et al[3] did not give **6**. Complex mixture of uncharacterisable compounds were obtained. An alternative approach, using the "counterattacking principles" for the silylation of allylic alcohol, **2** was equally unsuccessful in our hands. The vinyl alcohol **2**, on treatment with Me_6Si_2/MeLi in THF at 60 °C gave only recovered **2** and none of the desired **6** ; more stringent reaction conditions led to decomposition of starting material. A variation on the same theme is the displacement of an allylic function

with silylmetallics. Thus, compound **2** was acetylated[9] with AcBr/AgCN to give the allylic acetate **4**. Treatment of **4** with the silyl cuprate reagent[10] $Li_2Cu(SiMe_3)_2$ did give the desired compound **6**, as a 1:2 E:Z mixture , however only in 10% yield. The low yield may be attributed to the fact that compound **4** was not purified before use, since it was not particularly stable and decomposed on standing or on column chromatography to give the elimination product **5**[11].



Scheme 2

Alternative approaches to the synthesis of **6** were sought. The organolithium compound **7**, generated from the precursor β-trimethylsilylethylphenyl sulfone[12], reacted with β-ionone to give the adduct **8** which was quenched with methanesulfonyl chloride to give the mesylate **9** in good yield. Reductive elimination[13] of **9** using sodium amalgam gave the desired **6**. again as a mixture of isomers in 2:1 E:Z ratio. The low yield (7 %) was however unsactisfactory (Scheme 2). Nevertheless, the possibility of using sulfone chemistry in the preparation of allylsilanes prompted us to examine the following approach.



Scheme 3

The vinyl-β-ionol **2** was converted to the sulfone **10** folowing a procedure by Julia[13]. Treatment of **10** (1.00 g) with t-BuLi (1.2 eq.) in 50 ml of a 1:1 mixture of THF and ether at -78 °C generated the anion which

reacted with trimethylchlorosilane(3 eq) to give the silylated sulfone **11** as brown cristals which could be recrystallized in hexanes , giving 0.96 g (80%) of pale yellow crystals (m.p.:113-114 °C). Sodium amalgam reduction of **11** in methanol gave the desilylated and desulfonylated hydrocarbon **12**. The formation of **12** was attributed to the cleavage of carbon-silicon bond by methoxide ion which was formed under the reduction conditions. Indeed, treatment of **11** with sodium methoxide in methanol gave the starting sulfone **10** in good yield. Sulfone **10** was also reduced under sodium amalgam conditions to give the hydrocarbon **12**. Selective cleavage of the sulfone function was eventually achieved under non-nucleophilic conditions. Sodium/dimethylaminonaphthalene (DMAN) reduction of sulfur containing compounds, developed by Bank[14a] and Ley[14b] succesfully reduced **11** to the desired **6** in 70% yield. The silane **6** was formed as a mixture of E and Z isomers (7:1) with the all-trans compound predominating. The two isomeric compounds were purified by flash column chromatography but could not be separated from each other.

The yield and the selectivity were increased (Scheme 3) by adding diethylamine together with **11** to the Na/ DMAN reducing agent. The radical anion Na/DMAN was not quenched by diisopropylamine or diethylamine under the condition in which the reaction were carried out. Moreover the isomeric ratio in **6** appeared to be dependent on the proton source used to protonate the intermediate allyl anion.

Typical procedure for the reduction of allylsulfonylsilanes: A solution containing 0.100 g of sulfone **11** dissolved in 1.0 ml of anhydrous THF [with 0.5 ml diethyl amine for the improved method] was added under an argon atmosphere at -85°C to a previously prepared solution of Na /DMAN (4 eq.). This solution was prepared by stirring sodium (8 eq.) in 20 ml of THF with DMAN at -10 °C under argon for 3 hours. Immediatelly after addition of the allyl sulfone to this solution at -85°C, 1 ml of distilled water was added and then followed up by the addition of 20 ml of hexanes (at this point the excess sodium was removed from the reaction mixture). The resulting solution was extracted with 20 ml water and twice with 20 ml HCl 10% to remove the DMAN. The organic solvents were evaporated and the residue was purified by flash chromatography using hexanes as eluent affording 0.044 g (70%) [0.056 g (84 %) improved method] of **6** as a clear oil (b.p.= 110 °C at 0.4 mm/Hg.)

To our knowledge, the synthesis of **6** via an allylsulfone represents a completely new way of access to allylsilanes. The regiochemical control is ensured by the sulfonyl group which directs the electrophile to the α-position of the allylic system. We demonstrated the generality of the approach by the synthesis of other allylsilanes and one allylstannane as represented in Table 1.

Acknowledgement: Financial support by NSERC and FCAR is gratefully acknowledged.

1. H. Sakurai, *Pure appl. Chem.*, **1982**, 154, 1; G. Majetich, in Organic Symthesis, Theory and applications, T. Hudlicky, Ed.,Jai Press, Inc., Greenwich, CT.,1989.
2. T.H. Chan and I. Fleming, *Synthesis*, **1979**, 761.
3. R. Calas, J. Dunogues, J.P. Pillot, *Tetrahedron Lett.*, **1976**, 22, 1871.
4. J. R. Hwu, L.C. Lin, B.R.Liaw, *J.Am.Chem.Soc.*, **1988**, 110, 7252.
5. I.Fleming and A.P. Thomas,*J.Chem.Soc.Chem. Commun.*, **1985**, 411.
6. Compare, for example, the syntheses of the two regioisomers of geranyltrimethylsilane by two different methods. B.M. Trost, J. Yosilida and M. Lautens, *J.Am.Chem.Soc.*, **1983**, 105, 4494; D. Wang and T.H. Chan, *J. Chem.Soc. Chem. Commun.*, **1984**, 1274.

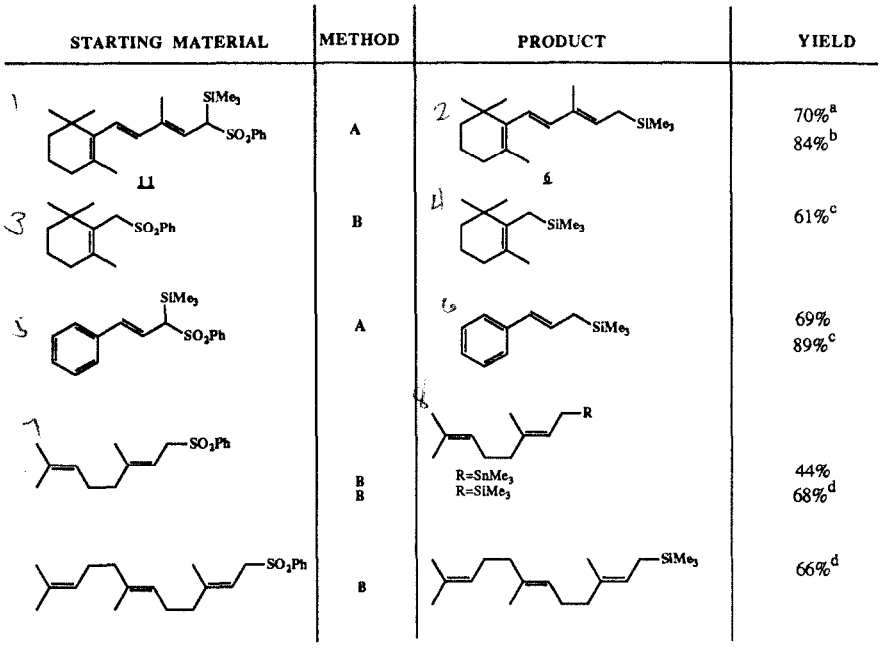


Table 1: Method A) as described in text, Method B) the allyl sulfonyl silane was formed in situ and the resulting solution was added to the Na /DMAN as described in the text, a) 7:1 E:Z at C-9, ref.15,16 b) By adding diethylamine as internal anion quencher the yield and selectivity were improved to > 10: 1 E:Z at C-9, c) The corresponding sulfone was recrystallyzed in ethyl acetate from product synthesized using procedure described in reference 17, d) same as in b but selectivity was already good, e) contaminated with 10 % of the corresponding vinylsilane.

7. P.W.K Lau and T.H. Chan, *Tetrahedron Lett.* **1978**, 27, 2383; T.H. Chan and K. Koumaglo, *J. Organomet. Chem.*, **1985**, 285, 109; R.F. Horvath and T.H. Chan, *J.Org.Chem.* **1989**, 54, 317.
8. D. Arnould, P. Chabardes, G.Farge and M.Julia, *Bull.Soc.Chim.Fr.* **1985**, 2, 130.
9. S.Takimoto, J. Inanaga, T.Katsuki, M.Yamaguchi. *Bull.Chem.Soc.Jpn*, **1976**, 49, 2335.
10. E.Azzari, C.Faggi, N.Gelsomini and M.Taddei, *Tetrahedron Lett.*, **1989**, 30, 6067.
11. P.S. Manchand, M. Rosenberger, G.Saucy, P.A. Wehdi, H. Wong, L. Chambers, M.P. Ferro, W.Jackson. *Helv.Chim.Act.* **1976**, 59, 387.
12. C.-N. Hsiao and H.Shechter, *J.Org.Chem.*, **1988**, 53, 2688.
13. M.Julia and D.Arnould, *Bull.Soc.Chim. Fr.* **1973**, 2, 746.
14. a) S. Bank, M. Platz; *Tetrahedron Lett.* **1973**, 23, 2097. b) S.V. Ley, B. Lygo, F. Sternfeld, A. Wonnacott, *Tetrahedron* **1986**, 42, 4333.
15. Spectroscopic data of **6**: ^{1}H nmr($CDCl_3$): 5.93(dd, 16 Hz, 2H), 5.46(t, 9 Hz, 1H), 1.98(m, 2H), 1.71(s, 3H), 1.67(s, 3H), 1.57(d, 9 Hz, 2H), 1.57(m, 2H), 1.43(m, 2H), 0.99(s, 6H), -0.01(s, 9H); ^{13}Cnmr($CDCl_3$): 138.3, 138.0, 131.9, 127.9, 127.7, 122.3, 39.6, 34.2, 33.0, 28.9, 21.7, 19.9, 19.4, 12.2, 1.6.
16. Assignment of stereochemistry of **6** was based on comparison with similar compounds in the literature. See G. Englert, *Helv.Chim.Acta* **1975**, 58, 8, 2367; B. D. Sykes, R.Rowan, *J.Am.Chem. Soc.* **1974**, 96, 7000; J.Pugmire, D.M. Grant, D.K. Dalling, S.Berger, R.S. Becker, *J.Am.Chem.Soc.*,**1974**, 96, 7008.
17. S. Torii, K. Uneyama, M. Isihara, *Chemistry Letters*, **1975**, 479.
Spectroscopic data of the allyl silane: ^{1}H nmr($CDCl_3$): 1.9(m, 2H), 1.6(m, 2H), 1.5(s, 3H), 1.4(m, 2H), 0.95(s, 6H), 0.1(s, 9 H). ^{13}C nmr($CDCl_3$): 135.5, 123.1, 39.8, 34.6, 32.6, 28.7, 21.3, 19.6, 17.9, 0.3 .

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