

## 291. 1,1-Disilyl-2-Alkenes: Preparation and Some Synthetic Applications

Preliminary communication<sup>1)</sup>

by **Hansjürg Wetter**

Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, CH-8092 Zürich

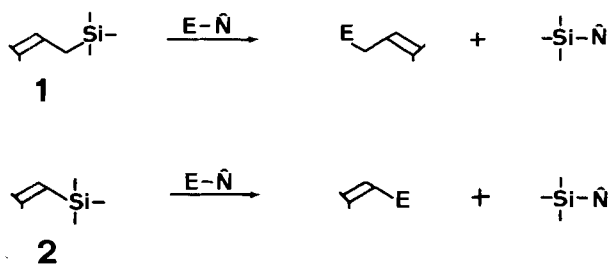
(30.X.78)

### Summary

Allyl sulfides and a selenide are metallated and silylated with chloro(penta-methyl)disilane. Treatment of the resulting disilanylmethyl sulfides **4** with trimethyloxonium tetrafluoroborate furnishes 1,1-disilyl-2-alkenes **5** in good yields. Some synthetic possibilities of **5** are outlined.

The synthetic utility of allylsilanes **1** and vinylsilanes **2** has been amply demonstrated [1] (*Scheme 1*). Whereas there are convenient methods to prepare vinylsilanes<sup>2)</sup>, routes to allylsilanes<sup>3)</sup> are mostly complicated and often leading to mixtures. We describe an easy way to convert allyl sulfides **3** and an allyl selenide *via* the corresponding disilanes **4** to substituted 1,1-disilyl-2-alkenes **5**. Based on the observation by *Kumada* of a facile disilane-disilylmethane rearrangement<sup>4)</sup> the

*Schéma 1*



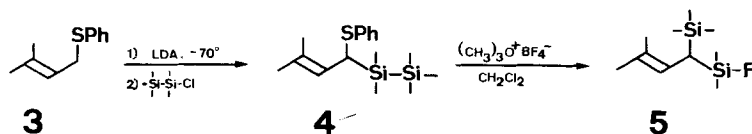
<sup>1)</sup> Part of these results were presented at the Fall Meeting of the Swiss Chemical Society, October 20<sup>th</sup>, 1978.

<sup>2)</sup> From ketones [2a], from alkynes [2b].

<sup>3)</sup> For a general method using 2-(trimethylsilyl)ethylidene(triphenyl)phosphorane [3]; hydrosilylation of cyclopentadiene [4]; allylmagnesium compounds and chlorosilanes [5]; by cycloadditions [6].

<sup>4)</sup>  $\text{CH}_3\text{O}-\text{Si}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{Si}-\text{Cl} \xrightarrow{\text{BCl}_3} \text{CH}_3\text{O}-\text{Si}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-\text{Si}-\text{Cl}$  [7].

Scheme 2



approach of *Scheme 2* was developed. Metallation of the allyl compounds **3** [8] with lithium diisopropylamide at  $-70^\circ$  for 30 min and quenching the resulting lithium compounds with chloro (pentamethyl)disilane [9] at  $-70^\circ$  leads in excellent yield to the disilanes **4** (*Table*). Whereas metallation and silylation of (*Z*)-sulfide **3c** was not complete under the above standard conditions, only configurational pure (*Z*)-disilane **4c** was isolated besides some starting material.

When the disilanes **4** were stirred at RT. with 2.5 to 3 equiv. of trimethyl-oxonium tetrafluoroborate [13] in  $\text{CH}_2\text{Cl}_2$  rearranged 1-(dimethylfluorosilyl)-1-(trimethylsilyl)-2-alkenes **5** were isolated in good yields (*Table*). The rearrangement occurs with high configurational stability of the allylic double bond. When rearranged under the above standard conditions, (*Z*)-disilane **4c** gave rise to the isolation of (*Z*)-**5c** contaminated by 7% of the (*E*)-isomer **5b**. Fluorine coupling constants in  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. of **5a-d** are shown in *Scheme 3*. They are smaller than the coupling constants in fluoroalkanes.

Table

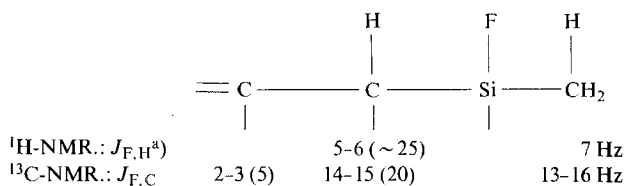
Sulfides resp. Selenide <sup>a)</sup>	Disilanes	Yield <sup>b)</sup>	Disilylalkenes	Yield <sup>b)</sup>
<b>3a</b>	<b>4a</b>	93%	<b>5a</b>	73%
<b>3b</b>	<b>4b</b>	96%	<b>5b</b>	74%
<b>3c</b>	<b>4c</b>	70%	<b>5c</b> <sup>c)</sup>	86%
<b>3d</b>	<b>4d</b>	90%	<b>5d</b>	70%
<b>3e</b>	<b>4e</b>	91%		93%
<b>3f</b>	<b>4f</b>	87%		58%

<sup>a)</sup> Prepared from the corresponding bromides and sodium benzenethiolate [10], sodium methanethiolate or sodium benzeneselenolate [11]; the bromides were prepared from allylic alcohols [12].

<sup>b)</sup> Yield of chromatographed pure material; analytical samples were prepared by short path distillation only.

<sup>c)</sup> Mixture of **5c**:**5b** 93:7 by capillary GC.

Scheme 3

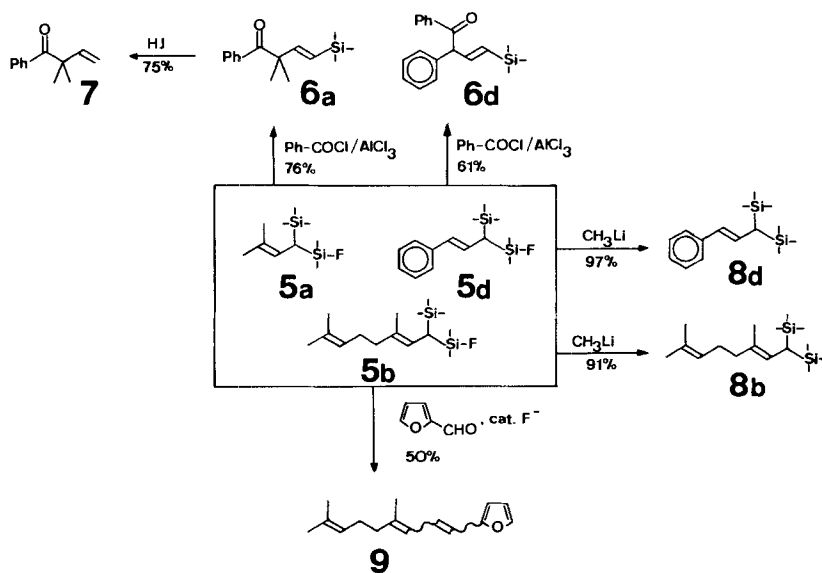


<sup>a</sup>) In parenthesis are the corresponding coupling constants in the all-carbon skeleton [14].

The synthetic potential of disilylalkenes **5** is indicated in *Scheme 4*. Acylation of **5a** or **5d** with benzoyl chloride/aluminium trichloride [4] [15] at  $-70^\circ$  in  $\text{CH}_2\text{Cl}_2$  yields the corresponding (*E*)-vinylsilanes **6a** and **6d** (76% and 61% respectively). Vinylsilane **6a** was desilylated by hydrogen iodide in benzene [16] yielding **7** (75%). Treatment of **5b** and **5d** with 1.2 equiv. of methyllithium at  $-60^\circ$  cleanly gave the bis(trimethylsilyl)alkenes **8b** and **8d** (91% and 97% respectively). Alternatively, when disilylalkene **5b** was heated under reflux in THF. with 1.2 equiv. of furfural and a catalytic amount of tetrabutylammonium fluoride [17] the triene **9** was obtained in 50% yield as a mixture of (*E*)- and (*Z*)-isomers.

These few examples demonstrate the synthetic possibilities of the disilylalkenes **5**, especially the easy accessibility to (*E*)-vinylsilanes **6**, useful intermediates in organic synthesis [1].

Scheme 4



## REFERENCES

- [1] *E.W. Colvin*, Chem. Soc. Rev. 7, 15 (1978); *I. Fleming*, Chemistry & Industry 1975, 449; *P.F. Hudrlik*, J. organometal. Chemistry Library 1, 127 (1976); *T.-H. Chan*, Accounts chem. Res. 10, 442 (1977).
- [2] a) *W.E. Fristad, T.R. Bailey & L.A. Paquette*, J. org. Chemistry 43, 1620 (1978); *R.T. Taylor, C.R. Degenhardt, W.P. Melega & L.A. Paquette*, Tetrahedron Letters 1977, 159; *T.H. Chan, A. Baldassarre & D. Massuda*, Synthesis 1976, 801; *K. Sachdev*, Tetrahedron Letters 1976, 4041; b) *J. J. Eisch & G.A. Damasevitz*, J. org. Chemistry 41, 2214 (1976); *K. Uchida, K. Utimoto & H. Nozaki*, J. org. Chemistry 41, 2215, 2941 (1976); *R. Köster & L.A. Hagelee*, Synthesis 1976, 118; *K. Yamamoto, O. Nunokawa & J. Tsuji*, Synthesis 1977, 721; *H. Westmijze, J. Meijer & P. Vermeer*, Tetrahedron Letters 1977, 1823; *M. Obayashi, K. Utimoto & H. Nozaki*, Tetrahedron Letters 1977, 1805.
- [3] *D. Seyferth, K.R. Wursthorn & R.E. Mammarella*, J. org. Chemistry 42, 3104 (1977).
- [4] *I. Ojima, M. Kumagai & Y. Miyazawa*, Tetrahedron Letters 1977, 1385.
- [5] *J. Slutsky & H. Kwart*, J. Amer. chem. Soc. 95, 8678 (1973); *J.-P. Pillot, J. Dunoguès & R. Calas*, Tetrahedron Letters 1976, 1871.
- [6] *M.J. Carter & I. Fleming*, Chem. Commun. 1976, 679; *I. Fleming & A. Percival*, Chem. Commun. 1976, 681; *B.-W. Au-Yeung & I. Fleming*, Chem. Commun. 1977, 79, 81.
- [7] *K. Tamao & M. Kumada*, J. organometal. Chemistry 30, 329 (1971).
- [8] *J.F. Biellmann & J.B. Ducep*, Tetrahedron Letters 1968, 5629; *J.F. Biellmann & D. Schirlin*, Synth. Commun. 8, 409 (1978).
- [9] *M. Kumada, M. Yamaguchi, Y. Yamamoto, J.-I. Nakajima & K. Shiina*, J. org. Chemistry 21, 1264 (1956); *H. Sakurai, K. Tominaga, T. Watanabe & M. Kumada*, Tetrahedron Letters 1966, 5493; *M. Ishikawa, M. Kumada & H. Sakurai*, J. organometal. Chemistry 23, 63 (1970).
- [10] *C.D. Hurd & H. Greengard*, J. Amer. chem. Soc. 52, 3356 (1930).
- [11] *K.B. Sharpless & R.F. Lauer*, J. Amer. chem. Soc. 95, 2697 (1973).
- [12] *H.L. Simon, A. Kaufmann & H. Schinz*, Helv. 29, 1133 (1946).
- [13] *T.J. Curphey*, Org. Syntheses 51, 142 (1971).
- [14] *S.L. Stafford & J.D. Baldeschwieler*, J. Amer. chem. Soc. 83, 4473 (1961); *F.J. Weigert & J.D. Roberts*, J. Amer. chem. Soc. 91, 4940 (1969).
- [15] *I. Fleming & A. Pearce*, Chem. Commun. 1975, 633.
- [16] *K. Utimoto, M. Kitai & H. Nozaki*, Tetrahedron Letters 1975, 2825.
- [17] *A. Hosomi, A. Shirahata & H. Sakurai*, Tetrahedron Letters 1978, 3043.

---

## 292. A New Method for the Construction of Macrolides. Stereoselective Synthesis of ( $\pm$ )-Phoracantholide J

Preliminary communication

by **Martin Petrzilka**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

(6.XI.78)

---

### Summary

Starting from 5-chloro-2-pentanone (**1**) the naturally occurring 10-membered lactone phoracantholide J (**8a**) has been synthesized as its racemate in a sequence of six steps (*Scheme 2*). Salient features of the synthesis include an internal selenium assisted acetal formation (**4** $\rightarrow$ **5**) and a stereoselective *Claisen* rearrangement (**6** $\rightarrow$ **7** $\rightarrow$ **8**). This general synthetic strategy offers an alternative approach towards the construction of macrocyclic lactones.

---