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SIGMATROPIC REARRANGEMENTS OF 2-(TRIMETHYLSILYL)ALLYL ALCOHOL DERIVATIVES: FACILE AND GENERAL ENTRIES TO FUNCTIONALIZED VINYLSILANES

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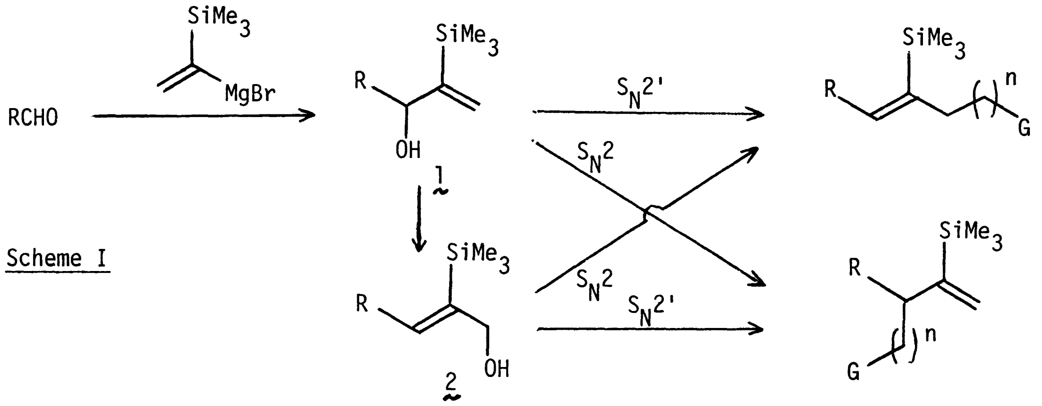
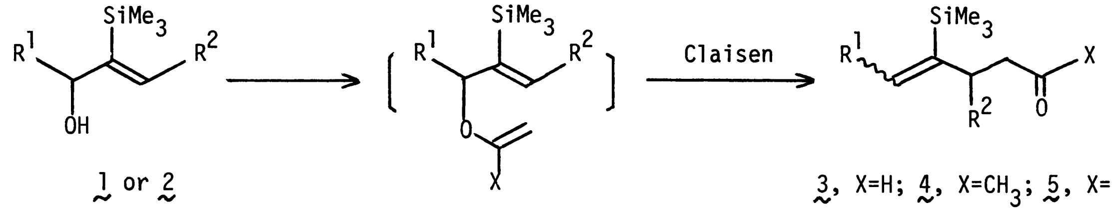
Facile preparations of a variety of vinylsilanes with different functional groups are described which rely upon the utility of the three sigmatropic processes of 2-(trimethylsilyl)allyl alcohol derivatives, *i.e.*, the Claisen and [2,3]-Wittig rearrangement and the tandem [2,3]-Wittig—oxy-Cope rearrangement.

While vinylsilanes have been well secured as versatile intermediates in organic synthesis,$^{1)}$ there exists only a limited number of synthetic methodologies for *functionalized* vinylsilanes.$^{1,2)}$ Herein we report new, general entries to vinylsilanes with different functionalities via sigmatropic rearrangements of 2-(trimethylsilyl)allyl alcohol derivatives. By taking full advantage of the fertile chemistry of sigmatropic rearrangement,$^{3)}$ our basic strategy$^{4)}$ involves the regioselective (S_N2' or S_N2) substitution of the hydroxy group of the allylic alcohol **1** or **2** by a functionalized carbon moiety (Scheme I) which permits ready access to a wide variety of vinylsilanes in terms of the kind of functionality (G), the substitution pattern, and the chain length of the carbon moiety through the choice of the sigmatropic process and the starting alcohol employed.



Scheme I

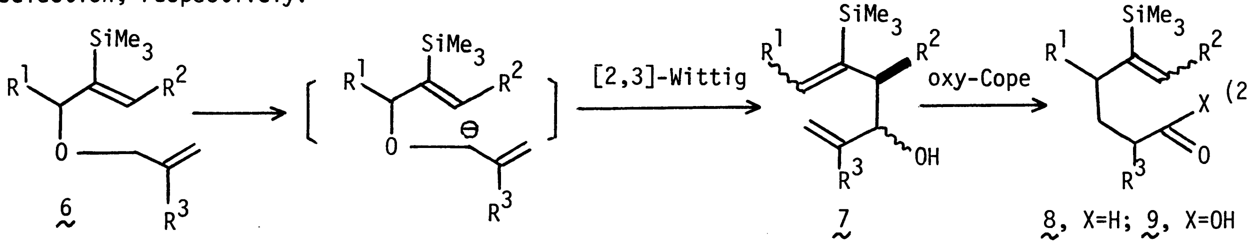
Both the starting alcohols **1** and **2** are easily available; the former is prepared from 1-(trimethylsilyl)vinyl Grignard reagent$^{5)}$ and an aldehyde and the latter is easily derived from **1**.$^{6)}$ First, alcohol **1** or **2** was subjected to the three modifications of the Claisen rearrangement (eq 1). The enol ether Claisen process$^{7)}$ using ethyl vinyl ether and isopropenyl methyl ether (150°C,



1 or 2 3, X=H; 4, X=CH_3; 5, X=OH

$Hg(OAc)_2$) afforded aldehyde 3 (entries 1 and 2, Table I) and ketone 4 (entry 3), respectively. The ester enolate Claisen process[8] of the acetate of 2 (LiN(*i*-Pr)$_2$/Me_3SiCl, -78°C→ room temp.) gave acid 5 (entry 4). Notable are the stereochemical outcomes; the high stereoselectivity of the Claisen rearrangement in general is completely missing in the present variants leading to aldehyde 3, while ketone 4b was >90% *Z*.[9] The functionalized vinylsilanes available via this technology are valuable synthetic intermediates. In particular, vinylsilanes 3 and 4 serve as useful precursors of 1,4-dicarbonyl compounds and 2-cyclopentenones including jasmonoids.[10]

Second, we have examined the [2,3]-Wittig rearrangement[11] of the bis-allylic ethers (6)[12] easily derived from 1 or 2 (eq 2). Treatment of 6 with lithium dicyclohexylamide[13] (THF, -30°C) gave dienol 7 (entries 5-8). The regiochemical outcomes are consistent with the general rule[11] that the [2,3]-Wittig process of unsymmetrical bis-allylic ether system gives rise to the *single* regioisomer arising from the exclusive lithiation on the *less substituted* allylic moiety. Also notable are the stereochemical outcomes in comparison with the respective counterpart in the cases without the silyl group;[11] 6a and 6b show much lower levels of stereoselection with regard to the newly formed olefinic bonds, while 6c and 6d exhibit a comparable or higher degree of diastereoselection, respectively.[9]

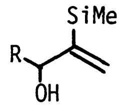
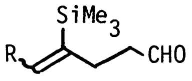
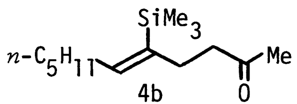
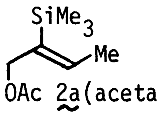
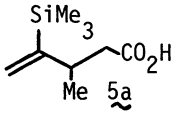
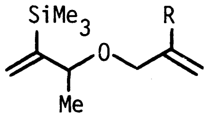
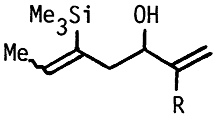
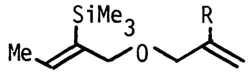
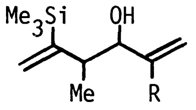
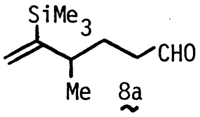
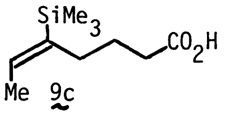


6 7 8, X=H; 9, X=OH

Finally, the oxy-Cope rearrangement of dienol 7 thus obtained was examined to complete the tandem [2,3]-Wittig–oxy-Cope rearrangement[14] (eq 2), which eventually achieves the otherwise difficult S_N2-type substitution. Thermolysis of 7a in *N*-methylpyrrolidone[15] (202°C, N_2) afforded aldehyde 8a (entry 9).[16] The rearrangement of 7c, however, was best performed via the siloxy-Cope modification.[17,18] Thus 7c was converted with hexamethyldisilazane (imidazole (cat.), 150°C) to the siloxy derivative (93% yield) which was then thermolyzed (neat, 210°C, N_2) followed by oxidation (Ag_2O, aq. NaOH) giving acid 9c (entry 10). Of special interest is that the double sigmatropic sequence eventually affords homologs of the Claisen products described above.

The *functionalized* vinylsilanes available via the present strategy obviously afford yet unexplored potentials for further elaborations. Work along this line is now in progress.

Table 1

Entry	Substrate	Product[a]	%Yield (Bp,°C/mmHg)	Stereochemistry[b] E:Z[c](threo:erythro)[d]
				
1	1a,R=Me	3a,R=Me	82 (84-88/12)	34 : 66
2	1b,R=n-C_5H_{11}	3b,R=n-C_5H_{11}	88 (86-90/0.4)	46 : 54
3	1b	 4b	95 (79-84/0.2)	9 : 91
4	 2a(acetate)[e]	 5a	67 (112-125/4)	
				
5	6a,R=H	7a,R=H	62 (77-79/5)	36 : 64
6	6b,R=Me	7b,R=Me	89 (f)	41 : 59
				
7	6c,R=H[e]	7c,R=H	80 (87.5-91.5/12)	(82 : 18)
8	6d,R=Me[e]	7d,R=Me	73 (f)	(91 : 9)
9	7a	 8a	62 (72-74/4)	
10	7c	 9c	59 (110-116/0.8)	80 : 20

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[a] All products were fully characterized by IR and NMR spectra. [b] The stereoisomeric ratio was determined by a combination of GLC (PEG 20M or SE 30) and NMR analyses prior to and/or after protodesilylation via the reported procedure: K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, 1975, 2825. [c] The geometrical assignment was made according to the literature method: T. H. Chan, W. Mychajlowskij, and A. Amouroux, *Tetrahedron Lett.*, 1977, 1605. In certain cases, the assignments were confirmed through GLC comparisons of the protodesilylated products with authentic samples. [d] The threo/erythro nomenclature is based on Heathcock's convention [C. H. Heathcock, *et al.*, *J. Org. Chem.*, 45, 1066 (1980)]. The stereochemical assignment was made similarly to that described in the literature: H. Felkin, Y. Gault, and G. Roussi, *Tetrahedron*, 26, 3761 (1970). [e] *E*:*Z* = 8 : 92 (see ref 6). [f] Isolated via column chromatograghy (SiO_2).

Acknowledgment. Support of this research by Grants from the Kurata Foundation and from the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), Chap. 7.

2) For leading more recent examples, see R. J. P. Corriu, C. Guerin, and J. M'boula, *Tetrahedron Lett.,* **22**, 2985 (1981).

3) Recent reviews include: G. B. Bennett, *Synthesis,* **1977**, 589; F. E. Ziegler, *Acc. Chem. Res.,* **10**, 227 (1977); R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.,* **18**, 563 (1979).

4) Only one example has been recorded of such a vinylsilane synthesis via sigmatropic rearrangement: T. Nakai and K. Mikami, *Chem. Lett.,* **1979**, 1081. For allylsilane synthesis by strategies related to ours, see S. R. Wilson and M. F. Price, *J. Am. Chem. Soc.,* **104**, 1124 (1982); I. Kuwajima, T. Tanaka, and K. Atsumi, *Chem. Lett.,* **1979**, 779; P. R. Jenkins, R. Gut, H. Wetter, and A. Eschenmoser, *Helv. Chim. Acta,* **62**, 1922 (1979).

5) R. K. Boeckman, Jr., D. M. Blum, B. Ganem, and N. Halvey, *Org. Synth.,* **58**, 152 (1978). The distilled yields were 87% (**1a**, R=Me) and 65% (**1b**, R=n-C_5H_{11}).

6) Conversion of **1** to **2** was performed via the three operations: chlorination ($SOCl_2$, Et_2O, 20°C), acetoxylation (AcONa, DMF, 70°C), and hydrolysis (aq. NaOH, MeOH, 40°C); **2a**, 92% distilled yield; *E/Z* = 8 : 92 (by GLC assay after protodesilylation). For the procedure of chlorination and its stereochemistry, see T. H. Chan, W. Mychajlowskij, B. S. Ong, and R. N. Harpp, *J. Org. Chem.,* **43**, 1526 (1978).

7) G. Saucy and R. Marbet, *Helv. Chim. Acta,* **50**, 1158, 2091 (1967).

8) R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Am. Chem. Soc.,* **98**, 2868 (1976).

9) The intriguing stereochemical results will be discussed on mechanistic grounds in a full paper.

10) Quite recently F. Sato, *et al.* have successfully synthesized dihydrojasmone from **4b** prepared via an entirely different route: F. Sato, Y. Tanaka, Y. Yamaji, and M. Sato, 45th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1982, Abstr. No. 2C43.

11) For similar rearrangements of non-silylated substrates, see T. Nakai, K. Mikami, S. Taya, and Y. Fujita, *J. Am. Chem. Soc.,* **103**, 6492 (1981).

12) Obtained in 79 - 91% distilled yields via the reaction of **1** or **2** with an appropriate allylic chloride (aq. NaOH, n-Bu_4NHSO_4 (cat.), 55°C). The alternative etherification between the allylic chloride⁽⁶⁾ derived from **1** with an allylic alcohol failed.

13) The use of this specific base is essential since the use of n-BuLi produced a complicated mixture arising in part from addition of the base to the vinylsilane moiety.

14) For similar tandem sequences of non-silylated substrates, see K. Mikami, S. Taya, T. Nakai, and Y. Fujita, *J. Org. Chem.,* **46**, 5447; K. Mikami and T. Nakai, *Chem. Lett.,* **1982**, 1349.

15) For the specific role of this solvent, see Y. Fujita, S. Amiya, T. Onishi, and T. Nishida, *Bull. Chem. Soc. Jpn.,* **52**, 1983 (1979).

16) The attempted anionic oxy-Cope modification of **7a** according to Evans' procedure produced a complicated mixture: D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.,* **102**, 774 (1980).

17) R. W. Thies, M. T. Wills, A. W. Chin, L. E. Schick, and E. S. Walton, *J. Am. Chem. Soc.,* **95**, 5281 (1977).

18) The attempted thermolysis of **7c** in *N*-methylpyrrolidone led to a mixture of aldehyde **8c** and 2-trimethylsilyl-2-vinyl-1-cyclopentanol, an intramolecular ene product of **8c**.

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