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Silicon-Directed Regiocontrol in Wittig Rearrangements of Bis-Allyl Ethers and Allyl Propargyl Ethers

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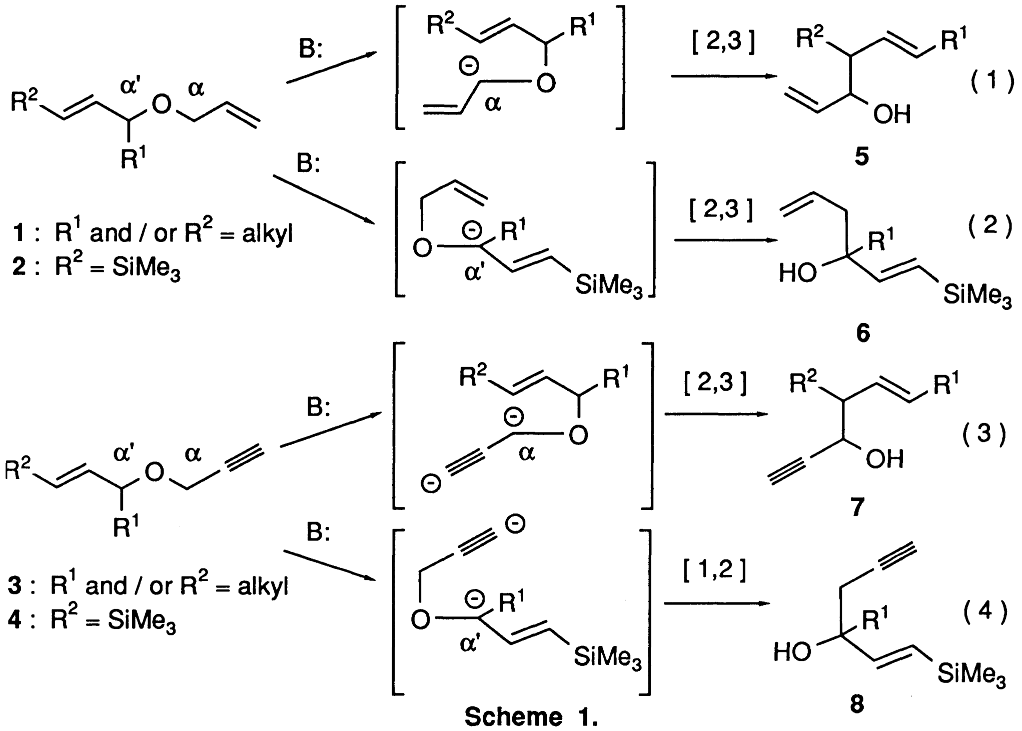
The carbanion rearrangements of (γ'-silyl)allyl ethers are shown to afford the single regioisomers arising from the exclusive lithiation on the silylated allyl parts followed by either the [2,3]-sigmatropic shift of the other allyl group or the [1,2]-shift of the propargyl group.

In previous papers, we have reported the empirical regioselection rule for the carbanion rearrangements of the unsymmetrical bis-allyl ether system (**1**) and the allyl propargyl ether system (**3**).1) Namely, the rearrangement of **1** proceeds via the site-selective lithiation on the less substituted allyl part (α) followed by the periselective [2,3]-shift to afford the single regioisomer **5** (Eq. 1),1b) and the rearrangement of **3** also provides the single regioisomer **7** via the exclusive dilithiation at the propargyl site (α) followed by the [2,3]-shift (Eq. 3).1c) In view of the well-known ability of a silyl group to stabilize



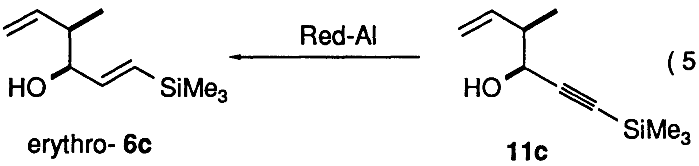
Scheme 1.

carbanions,2) one might expect that the strategic introduction of a silyl group would result in an alternation in the regiochemical course concerned (Scheme 1). Reported herein are the highly regioselective Wittig rearrangements of the γ'-(trimethylsilyl)allyl ethers (**2** and **4**), which provide an entirely different regiochemistry from the empirical selection rule1) in terms of the site-selectivity in the lithiation step and/or the peri-selectivity in the rearrangement step (Eqs. 2 and 4).3)

The carbanion rearrangements of the γ'-silylated allyl ethers **2** and **4**4) were carried out under the standard conditions using n-BuLi as a base.1) Usual work-up followed by silica gel column chromatography or distillation afforded the regioisomerically pure alcohols (**6** or **8**). The representative results are summarized in Table 1.

Inspection of Table 1 reveals several characteristic features of the present Wittig variants. (1) The crucial regiochemistry in the lithiation step is dramatically changed from α to α' by the introduction of the γ'-silyl group. Thus the bis-allyl ether **2** affords the [2,3]-rearranged product **6** as the single regioisomer arising from the site-specific lithiation on the silylated allyl part (α') irrespective of the absence or the presence of an α'-alkyl group (R^1) which might depress the α'-lithiation1) (entries 1-4). (2) The propargyl ether (**4**) also provides a single regioisomer (**8**) arising from the α'-lithiation followed by the [1,2]-shift, however (entries 5 and 6). (3) The γ-silylated propargyl ether **9a**, in turn, provides the [2,3]-product (**10a**) via the specific lithiation at the propargyl site (α) in favor of the allylic counterpart (α') (entry 7). (4) Of synthetic importance is the extremely high erythro-selectivity observed for the rearrangements of (Z)-crotyl ether **2c** (entry 4) and (E)-γ'-silylated allyl propargyl ether **9a** (entry 7).

The stereochemical assignments of **6c** and **10a** deserve comments. The stereochemistry of **6c**6) is assigned through ^1H NMR comparison with an authentic erythro-rich sample prepared from the known erythro-alcohol **11c** (Eq. 5).1c) The erythro configuration of **10a**7) is confirmed by the formation of (E)-olefin8) via syn-elimination9) under basic conditions (Eq. 6).10)



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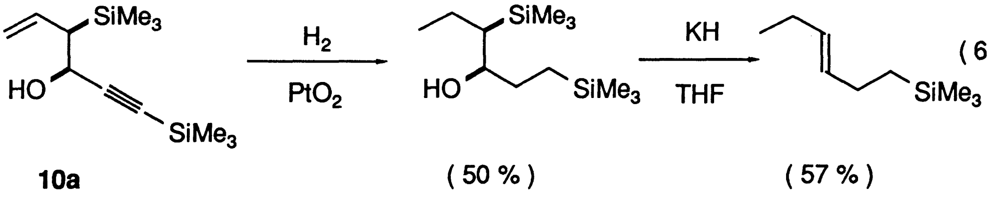
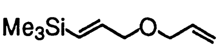
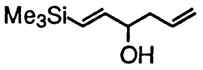
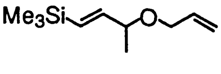
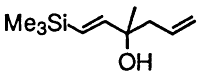
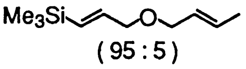
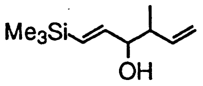
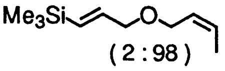
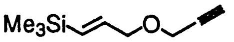
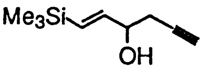
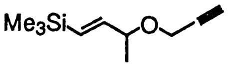
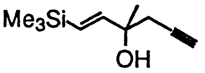
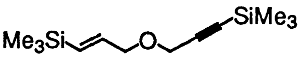
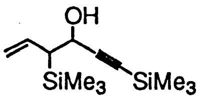


(6)

Table 1. Wittig Rearrangements of γ'-(Trimethylsilyl)allyl Ethers

Entry	Ethers (*E* : *Z*)[a]	Alcohols (%yield)[b]	Regioselectivity	threo / erythro[c]
1	 **2a**	 **6a** (93)	α'-[2,3]	
2	 **2b**	 **6b** (50)	α'-[2,3]	
3	 (95:5) (*E*)-**2c**	 **6c** (58)	α'-[2,3]	51 : 49
4	 (2:98) (*Z*)-**2c**	**6c** (72)		7 : 93
5	 **4a**	 **8a** (60)	α'-[1,2]	
6	 **4b**	 **8b** (64)	α'-[1,2]	
7	 (98:2)[d] **9a**	 **10a** (65)	α -[2,3]	3 : 97

a) Refers to the geometrical ratio of the crotyl alcohol employed.

b) Isolated yield, not optimized yet. The data (^{1}H NMR, ^{13}C NMR, and IR) of these products are in good agreement with the assigned structures.

c) Determined by a combination of GLC, ^{1}H NMR, and ^{13}C NMR analyses.

d) Refers to the geometrical ratio of the γ'-(trimethylsilyl)allyl alcohol employed.

In summary, we have developed the silicon-directed regiospecific Wittig rearrangements which provide single but entirely different regioisomer from the empirical selection rule. Thus, the results of this work convincingly expands the synthetic potentiality of the Wittig rearrangement of allyl and propargyl ethers.

References

1) a) Review on [2,3]Wittig rearrangement: T. Nakai and K. Mikami, Chem. Rev., 86, 885 (1986); b) T. Nakai, K. Mikami, S. Taya, and Y. Fujita, J. Am. Chem. Soc., 103, 6492 (1981); c) K. Mikami, K. Azuma, and T. Nakai, Tetrahedron, 40, 2303 (1984).
2) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), Chap. 2.
3) For [1,2]-Wittig shift, see: U. Schollkopf, Angew. Chem., Int. Ed. Engl., 9, 763 (1973); D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York (1965), Chap. 4.
4) Allyl and propargyl ethers (**2** and **4**) were prepared in more than 80% isolated yields from γ'-(trimethylsilyl)allyl alcohols (Ref. 5) and allyl bromide or propargyl bromide.
5) S. E. Denmark and T. K. Jones, J. Org. Chem., 47, 4595 (1982). K. Mikami, T. Maeda, and T. Nakai, Tetrahedron Lett., 25, 5151 (1984).
6) ^{1}H NMR ($CDCl_3$) 3.80 (dd, J=6.6 and 4.1 Hz, 0.93H), 3.95 (dd, J=5.0 and 4.1 Hz, 0.07H).
7) GLC (PEG 20M, 130 °C) t_R=15.4 and 18.6 min (3 : 97); ^{13}C NMR ($CDCl_3$) -1.7 and 0.9 (9 : 91), 0.7 and 1.9 (97 : 3), 44.7 and 45.1 (91 : 9), 63.6 and 63.9 (1 : 9), 90.1, 108.0, 116.0, 136.6.
8) IR (neat) 965 cm^{-1}; ^{1}H NMR (CCl_4) -0.08 (s, 9H), 0.78-1.06 (m, 3H), 1.20-1.56 (m, 2H), 1.72-2.16 (m, 4H), 5.36-5.51 (m, 2H); GLC (PEG 20M, 120°C) t_R=2.2 min.
9) Review: D. J. Ager, Synthesis, 1984, 384.
10) Both the Z → erythro (entry 4) and E → erythro (entry 7) selectivities can be reasonably explicable on the basis of our transition state model. However, the mechanistic argument on the diastereoselection would be the subject of a forthcoming full account. For our transition state model, see: K. Mikami, Y. Kimura, N. Kishi, and T. Nakai, J. Org. Chem., 48, 279 (1983); K. Mikami and T. Nakai, "Physical Organic Chemistry 1986" (A Collection of the Invited Lectures Presented at the 8th IUPAC Conference on Physical Organic Chemistry), Elsevier, Amsterdam (1987), pp. 153-160.

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