Switching of the Reaction Pathway for [1,2]/[1,4]- and [2,3]-Wittig Rearrangements of 3-Aryl-2-propenyl Propargyl Ethers

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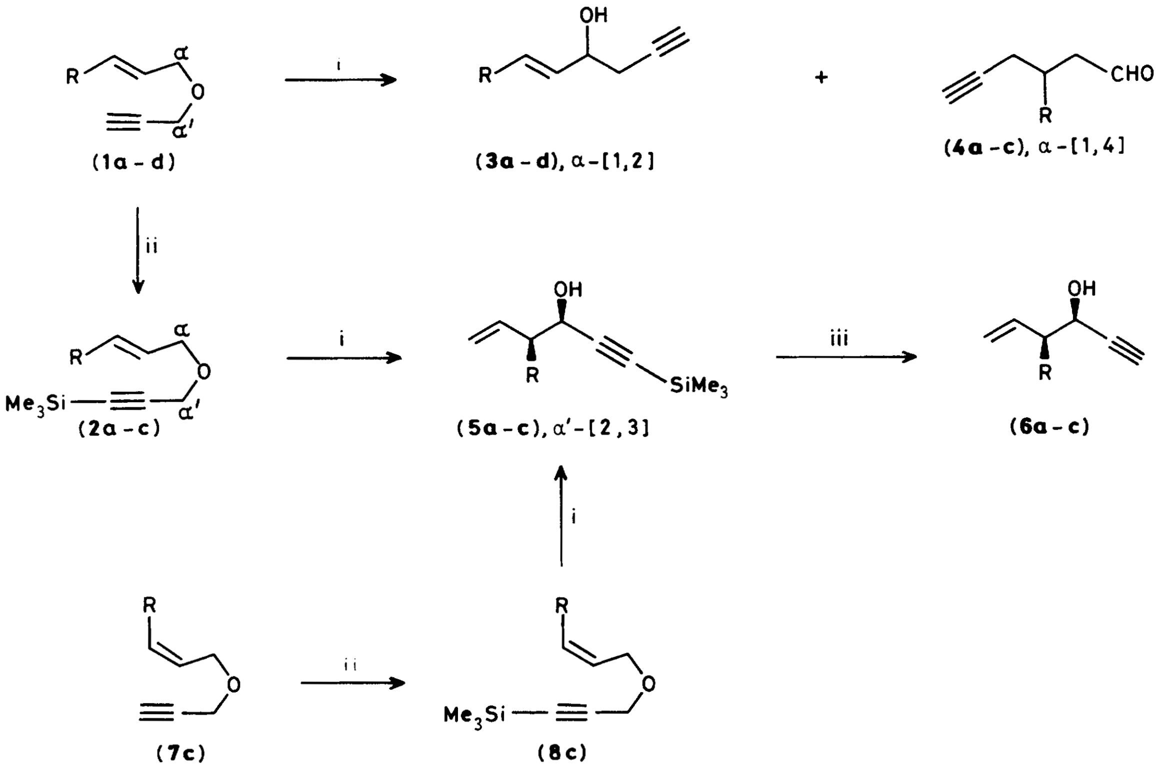
3-Aryl-2-propenyl propargyl ethers (**1**) undergo the [1,2] (and [1,4]) sigmatropic rearrangement periselectively on treatment with Bu^nLi at −78 °C, whereas the silylated derivatives (**2**) perform exclusively the [2,3]-Wittig rearrangement.

The sigmatropic rearrangements of α-metallated allyl ethers (the Wittig rearrangements)[1] are of current interest for their versatile applications to organic synthesis.[2—5] However, in contrast to the well-documented synthetic utility of the [2,3]-Wittig rearrangement,[2—4] the [1,2]-Wittig rearrangement has gained less attention due to the general lower yields of this reaction.[5] The control elements of the periselectivity of these anionic rearrangements also need to be investigated. Herein, we report on a highly periselective anionic [1,2]/[1,4]-sigmatropic rearrangement of 3-aryl-2-propenyl propargyl ethers (**1**) as well as a remarkable effect of the silyl-substituent for switching of reaction pathway.

During the course of our studies on the base-catalysed pericyclic reactions of various propargyl ethers,[6] we found an efficient sigmatropic rearrangement of the dianions of 3-aryl-2-propenyl propargyl ethers (**1**; R = aromatic) with unusual periselectivity, *i.e.* it only underwent the [1,2] (and [1,4]) sigmatropic rearrangement, although the [2,3] sigmatropic rearrangement is much more common to this class of compound, *e.g.* (**1**; R = H or alkyl).[3,7] Thus, treatment of

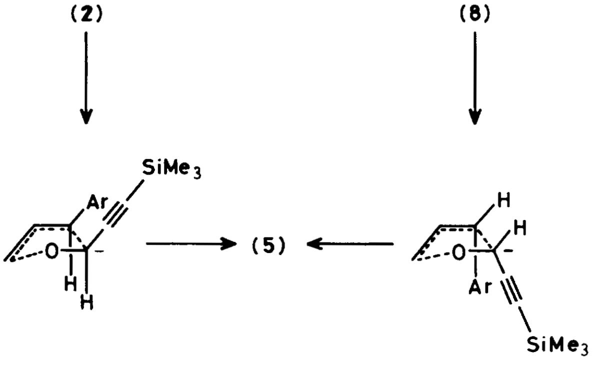


a; R = Ph
b; R = 2-furyl
c; R = 5-methyl-2-furyl
d; R = 2-thienyl

Scheme 1. *Reagents and conditions*: i, Bu^{n}Li (2.3 equiv.), THF, −78 °C; ii, Bu^{n}Li (1.0 equiv.), THF, −78 °C, then chlorotrimethylsilane (3.0 equiv.); iii, CsF, MeOH–H_2O (9 : 1), room temp.

(*E*)-cinnamyl propargyl ether (**1a**) with 2.3 equiv. of Bu^{n}Li in tetrahydrofuran (THF) at −78 °C resulted in a rapid reaction to give the [1,2] rearrangement product (**3a**) (67%)† and the [1,4] rearrangement product (**4a**) (13%)† (Scheme 1). Both sigmatropic rearrangements were considered to arise from the α-lithiated (**1a**) (α-[1,2] and α-[1,4]) presumably due to the increased stabilization of the α-carbanion through conjugation with the aromatic ring. Similarly, (*E*)-ethers (**1b—d**) and the (*Z*)-ether (**7c**), prepared from (*E*)-3-(5-methyl-2-furyl)acrylate by photochemical *trans*/*cis* isomerization, followed by $LiAlH_4$ reduction and propargylation, only underwent the α-[1,2] (and α-[1,4]) sigmatropic rearrangements (Table 1).

In sharp contrast, the similar base-treatment of the silylated (*E*)-ethers (**2a—c**), prepared from (**1a—c**) [Bu^{n}Li (1 equiv.), Me_3SiCl, −78 °C], resulted in exclusively the α′-[2,3] sigmatropic rearrangement in a high degree of *erythro* selectivity (>95%, 270 MHz ^{1}H n.m.r.)[8]‡ to give (**5a—c**)† in good yields (Table 1). Interestingly, the (*Z*)-ether (**8c**), prepared from (**7c**), also underwent the *erythro*-selective α′-[2,3] sigmatropic rearrangement to give the same product as (*E*)-(**2c**) [(**5c**)] (Scheme 1), suggesting a preference for the *cis*-relationship of the aromatic ring and propargyl group in the α′-[2,3] transition



Scheme 2

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† All new compounds gave satisfactory analytical and spectral data. For example, (**3a**): i.r. ν_{max} 3380, 3280, 2160 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$) 6.64 (d, *J* 16.0 Hz, 1H), 6.20 (dd, *J* 16.0, 6.0 Hz, 1H), 4.40 (m, 1H), 2.49 (dd, *J* 6.0, 3.0 Hz, 2H), 2.05 (t, *J* 3.0 Hz, 1H).

(**4a**): i.r. ν_{max} 3280, 2360, and 1730 cm^{-1}; ^{1}H n.m.r. δ 9.71 (t, *J* 1.5 Hz, 1H), 3.47 (m, 1H), 2.91 (m, 2H), 2.53 (dd, *J* 6.5, 3.0 Hz, 2H), 2.00 (t, *J* 3.0 Hz, 1H).

(**6a**): i.r. ν_{max} 3400, 3280, and 2100 cm^{-1}; ^{1}H n.m.r. δ 6.18 (ddd, *J* 17.9, 10.4, 8.2 Hz, 1H), 5.27 (dm, *J* 10.4 Hz, 1H), 5.23 (dm, *J* 17.9 Hz, 1H), 4.59 (dd, *J* 6.5, 2.1 Hz, 1H), 3.60 (dd, *J* 8.2, 6.5 Hz, 1H), 2.44 (d, *J* 2.1 Hz, 1H), 2.09 (br s, D_2O-exchange, 1H); high resolution mass spectrum for $C_{12}H_{12}O$ calc. *m*/*z* 172.0888, found 172.0914.

‡ It is well established that the proton of *erythro* isomers attached to the C–OH group in 2-alkyl-3-hydroxycarbonyl compounds resonates at lower fields than those in *threo* isomers. In addition, the coupling constants (*J ca.* 3.0—6.5 Hz) of the *erythro* isomers appear smaller than those in the *threo* isomers (*J ca.* 7.0—9.0 Hz).

Table 1. Bu^nLi catalysed rearrangement of (**1**), (**2**), (**7**), and (**8**).[a]

Compound	Product, % Yield[b] (**3**), [1,2]	(**4**), [1,4]	(**5**),[c] [2,3]
(**1a**)	67	13	
(**1b**)	64	16	
(**1c**)	54	22	
(**1d**)[d]	19	—	
(**2a**)			85
(**2b**)			53
(**2c**)			62
(**7c**)	67[e]	12	
(**8c**)			73

[a] All reactions were carried out in THF at −78 °C using 2.3 equiv. of Bu^nLi (30 min—1 h). [b] Isolated yields. [c] 95% *Erythro* by the 270 MHz ^1H n.m.r. analysis. [d] A large amount of the starting material (~70%) was recovered unchanged, even with 3 equiv. of Bu^nLi. [e] *E*/*Z* = 2 : 1.

states regardless of the alkene geometry of the starting materials (Scheme 2). The clean-cut change of persiselectivity between (**1**) [or (**7**)] and (**2**) [or (**8**)] may be mainly attributed to the α′-carbanion stabilizing effect (vinylagous α-effect) of silicon in (**2**) and (**8**), since the similar reaction of 2-butynyl (*E*)-3-(5-methyl-2-furyl)-propenyl ether gave a 1 : 2 mixture of α-[1,2] and α′-[2,3] rearrangement products.

Desilylation (CsF, MeOH–H_2O, r.t.) of (**5a**—**c**) afforded almost quantitative yields of (**6a**—**c**),† a formal α′-[2,3] sigmatropic rearrangement product of (**1**) (Scheme 1).

The above results provide a new method to control periselectivity in the base-catalysed sigmatropic rearrangements of (**1**). Indeed, the [1,2] products thus obtained may serve as the useful synthetic intermediates for the synthesis of the natural product secofuranoeremophilane.[9]

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