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SYNTHESIS OF 4-{(BENZYLOXYMETHYL)(*TERT.*-BUTYL)METHYLSILYLOXY}-1,2,3-PENTATRIENE VIA BROOK REARRANGEMENT

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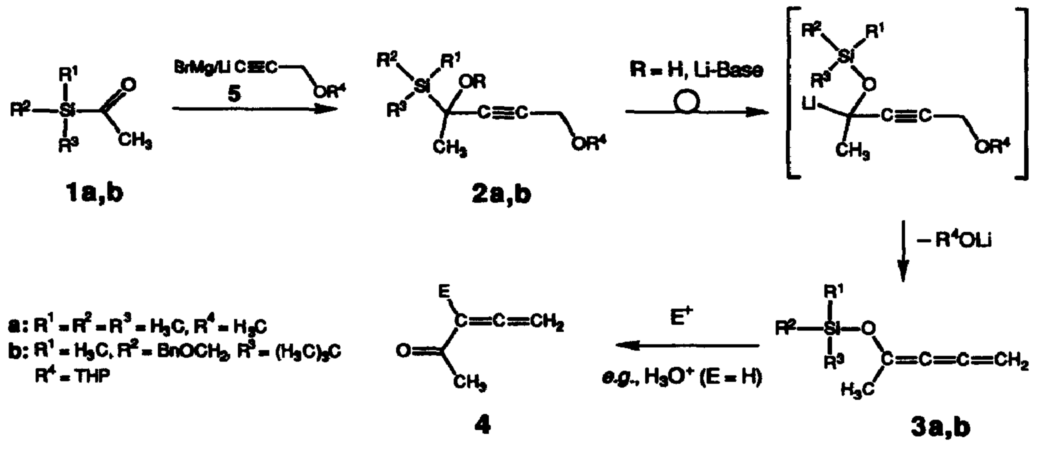
Abstract: The reaction of 1-lithium-3-tetrahydropyranyloxy-1-propyne with {(benzyloxymethyl)-(*tert.*-butyl)methylsilyl} methyl ketone gave rise to the corresponding α-silylated propargylic alcoholate anion, which led in a succession of Brook rearrangement and 1,4-elimination to the title compound in good yield.

Substituted cumulenes like 1,2,3-butatrienyl ethers are highly reactive compounds used in organic chemistry as components in cycloaddition reactions[2-4] and as starting materials in the synthesis of α-allenic aldehydes or ketones[5,6], of 1-alkoxy-1,3-butadienes[7,8], 3-alkene-1-ynes[8], 1-alkoxy-1-butene-3-ynes[9], and 1-alkene-3-ynes[10]. They are prepared on different routes[5,11-14], the most important being the1,4-elimination of alcohols or silanols from suitably substituted 2-butynyl ethers under the influence of a strong base[5,11,14]. The entry to cumulenic silyl ethers using this methodology, however, was rather limited as a consequence of the Brook rearrangement undergone by the α-lithiated intermediates generally involved in the reaction sequence[5]. The formation of 4-(trimethylsilyloxy)-1,2,3-pentatriene **3a**, a close relative of the title compound **3b**, was proposed by Kuwajima *et al.*[6] as an intermediate in the preparation of the α-allenic ketone **4** (E = H), obtained from propargylic alcohol **2a** in a succession of a base-induced Brook rearrangement, a 1,4-elimination, and a hydrolysis step.



In the course of our continuing investigations of diastereoselective 1,2-additions to chiral alkoxymethyl substituted acylsilanes[15] we treated acetylsilane **1b** with several lithium and bromomagnesium acetylides. The treatment of silane **1b** with the lithium acetylide **5** (R = THP) at –78° in ether afforded in good yields the desired propargyl alcohols **2b**. When the reaction temperature was raised to –20°, however, the cumulenic silyl ether **3b**[16], which was already detected by TLC in samples taken from the reaction mixture at low temperature, was formed instead in 74% yield. In contrast to **3a**, as observed by Kuwajima *et al.*, the corresponding silyl ether **3b**, probably due to the sterically more hindered silyl group, is stable towards pH-neutral aqueous work-up conditions, surviving even flash chromatography on silica gel. Yet, like other 1,2,3-butatrienyl ethers, the silyl derivative **3b** rapidly polymerizes in presence of oxygen even at low temperature.

Our preparation of **3b** not only proves that compound **3a** is indeed the intermediate in the synthesis of ketone **4** (E = H) but it offers as well the opportunity to use this silyl enol ether for further transformations, like, *e.g.*, Lewis acid catalyzed reactions with different electrophiles (E^+) under formation of various compounds of the type **4**. The influence of the silicon centered chirality on the stereochemical direction of new chiral elements (chiral axis and/or chiral center) will be interesting to study.

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16. **3b**: colorless liquid, air sensitive (polymerization): IR (film, $\tilde{\nu}$ in cm^{-1}): 2070*s* and 1625*m* (C=C=C=C), 1235*s* (C-O-Si). ^{1}H-NMR ($CDCl_3$, δ in ppm, J in Hz): 7.12-6.89 (*m*, 5 arom. H); 4.31, 4.29 (*AB* of ABX_3, $J_{AB} = 9.4$, $J_{AX} = 0.96$, $J_{BX} = 0.77$, $H_2C{=}$); 4.15 (*s*, $PhCH_2O$); 3.243, 3.240 (*AB*, $J = 13.5$, CH_2Si); 1.72 (*dd*, $J = 0.96, 0.77$, H_3C-C); 0.91 (*s*, *t*-Bu); 0.20 (*s*, H_3CSi). CI-MS (NH_3, *m/z* (rel%)): 303 (67, $[M + 1]^+$), 256 (86), 238 (24), 196 (100).

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