

REACTION OF TRIMETHYLSILYLPROPARGYL PHENYL ETHER WITH ORGANOBORANES
IN THE PRESENCE OF SODIUM METHOXIDE

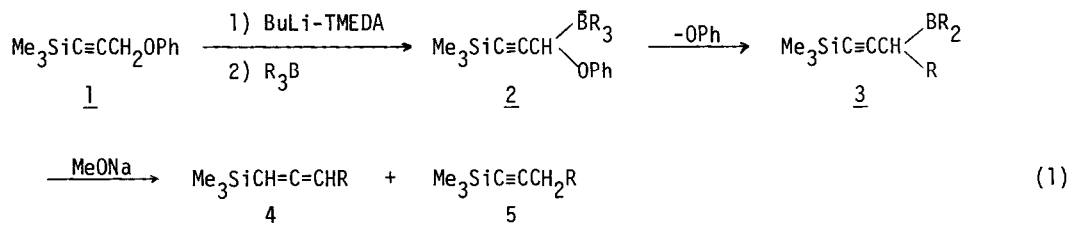
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Summary: Silylallenes (4) are selectively prepared from trimethylsilylpropargyl phenyl ether and trialkylboranes by treatment with sodium methoxide.

Organic syntheses of acetylenic or allenic derivatives via propargylic or allenic boranes have been reported by Zweifel et al.¹ and Midland.² Recently, we have reported that the reaction of ate-complexes (2) obtainable from trialkylboranes and trimethylsilylpropargyl phenyl ether (1), with a mixture of acetic acid and hexamethylphosphoric triamide (HMPT) gives trimethylsilylacetylenes (5) selectively.³ We wish to report here that trimethylsilylallenes (4) are selectively formed by the reaction of 2 with sodium methoxide instead of acetic acid and HMPT.

To a mixture of trialkylborane and the carbanion generated from 1, an excess of sodium methoxide was added at -70°C followed by stirring at room temperature (eq. 1). The migration of an alkyl group with elimination of a phenoxy group gave mainly 3 as reported previously.³



At the beginning of the reaction with sodium methoxide, both trimethylsilylallene (4) and trimethylsilylacetylene (5) are formed. However, an excess of sodium methoxide desilylated 5. Consequently, the reaction carried out for longer time gave only allenic derivative (4), as indicated in Table 1. The representative results are also summarized in the same table.

The following procedure for the preparation of 1,2-heptadienyltrimethylsilane is representative. To a mixture of butyllithium in ether (16.0 ml; 22.0 mmol) and 1.0 ml of tetramethylethylenediamine was added a solution of trimethylsilylpropargyl phenyl ether⁴ (4.08 g; 20.0 mmol) in 20 ml of THF at -78°C with stirring under argon. Tributylborane (6.5 ml of 3.1 M solution in THF; 20.0 mmol) was added to the resultant carbanion solution at -78°C. The mixture was stirred for 1 h and then allowed to warm to room temperature. After 1 h, the mixture was cooled to -60°~ -70°C, and sodium methoxide in methanol (15.5 ml; 80.0 mmol) was added to the yellow

suspension. The mixture was brought to room temperature and stirred over night. The reaction mixture was treated with water, and the organic layer thus separated was then successively washed with saturated sodium chloride solution and 3N hydrochloric acid followed by drying over magnesium sulfate. The solvent was evaporated and the residue was purified by chromatography (silica gel; hexane) affording 1.95 g (58%) of 1,2-heptadienyltrimethylsilane: ^1H NMR (CCl_4); δ , 0.04 (9H, s, CH_3Si) and 4.76 ppm (2H, m, $\text{CH}=\text{C}=\text{CH}$). ^{13}C NMR (CDCl_3); δ , 82.2, 83.2 and 210.1 ppm ($\text{C}=\text{C}=\text{C}$).⁵ IR (neat); ν , ($\text{C}=\text{C}=\text{C}$), 1940 cm^{-1} . Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{Si}$: C, 71.34; H, 11.98. Found. C, 71.35; H, 12.14.

In general, the syntheses of trimethylsilylallenes are reported to accompany the concurrent formation of isomeric acetylenic derivatives.⁶ Although a selective method for the formation of triethylsilylallenes via the insertion of alkyl vinylidene carbene into Si-H bond has been recently reported,⁷ this procedure is synthetically inconvenient, because such alkyl vinylidene carbenes are generated only from corresponding 1-bromo-1,2-dienes which are rather inaccessible. On the other hand, the present synthesis gives silylallenes (4) by the homologation reaction with trialkylboranes readily available from various olefins by hydroboration.

Silylallenes (4) thus readily prepared seems to be versatile intermediates for organic syntheses and such conversions are now actively under investigation.

Table 1. Selective Synthesis of Silylallenes by the Reaction of Trimethylsilylpropargyl Phenyl Ether (1) with Trialkylboranes

Organoborane, R_3B , R =	Total yield of <u>4</u> and <u>5</u> , % ^a (ratio of <u>4</u> : <u>5</u>) ^b	Yield of <u>4</u> , % ^c	n_D^{20} of <u>4</u>
Propyl	71 (96 : 4)	68	1.4500
Butyl	68 (97 : 3)	66	1.4581
Isobutyl	71 (79 : 21)	56	1.4503
sec-Butyl	62 (22 : 78)	14	1.4512
Pentyl	67 (94 : 6)	63	1.4537
Cyclopentyl	70 (60 : 40)	42	1.4760

^aGlpc yield based on 1. ^bCarried out at r. t. for 2 h. ^cAt r. t. for 14 h.

References and Notes

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