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THE PREPARATION OF PROPARGYLTRIMETHYLSILANES

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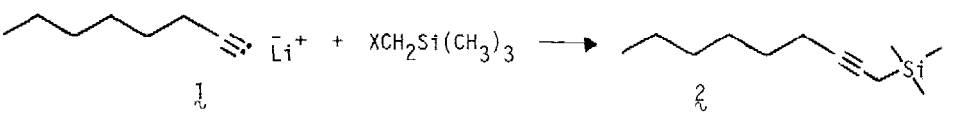
ABSTRACT: The preparation of propargyltrimethylsilanes from trimethylsilylmethyl halides or triflate is reported.

Allyltrialkylsilanes have recently received intensive study[1] because of their ability to undergo reactions with electrophiles to form carbon-carbon or other bonds with a concomitant double bond shift and cleavage of silicon. However, the corresponding 1-trimethylsilyl-2-alkynes (propargyltrimethylsilanes), $RC{\equiv}CCH_2Si(CH_3)_3$, are relatively obscure compounds. One failure[2] and one success[3] (involving CCl_3CHO) have been recorded when propargylsilanes are allowed to react with cationic carbon species. More recently we reported an intramolecular example which involved the formation of a five membered ring having an exocyclic allene group.[4] Importantly, ring D of a steroid precursor has now been formed by a comparable reaction.[5]

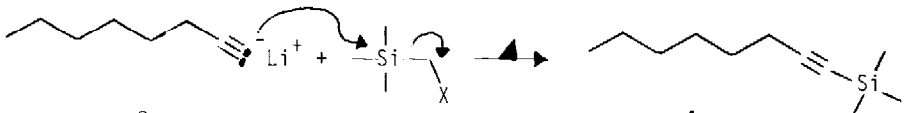
Propargyltrimethylsilanes have been reported to result from the reaction of lithiated 2-alkynes with trimethylsilyl chloride,[6] but extensive triple bond migration to give isomeric trimethylsilylated 1-alkynes tended to occur. Experimental details for obtaining a propargylsilane in a specified yield were not given. The parent propargylsilane, 1-trimethylsilyl-2-propyne[7] and a few other compounds,[8] have been prepared from the propargyl bromide via the Grignard reagent.

We now report several procedures for the formation of propargylsilanes from the lithium salts of 1-alkynes, exemplified by 1-octyne, and trimethylsilylmethyl halides or sulfonates (eq. 1). One such procedure, involving the relatively expensive but now accessible[9] triflate,



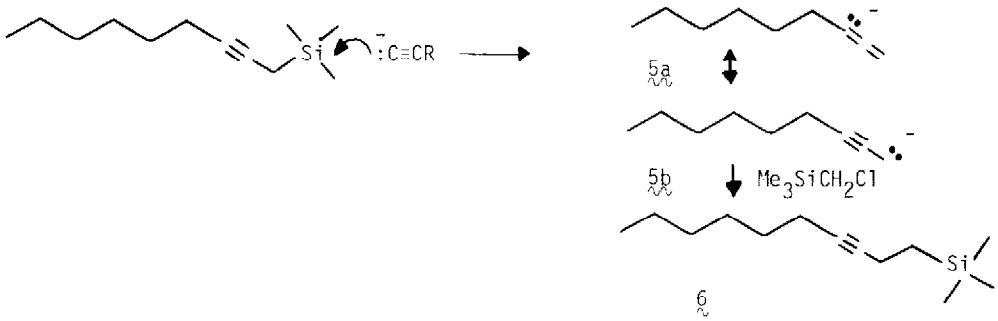
1 2 (1)

(X = O_3SCF_3 = OTf) has been included in our communication in which ring formation is reported.[4] However, we find that the more direct (one step) formation from commercially available trimethylsilylmethyl chloride (X = Cl) is the procedure of choice for obtaining the larger amounts of simple propargylsilanes needed for a study of their reactions. In the case of less readily available alkyne precursors the one step method has the disadvantage that the yield is only approximately 60% and the products of side reactions must be separated. The principal side reaction was trimethylsilylation, ascribed to attack on silicon of $(CH_3)_3SiCH_2X$ (eq. 2).[10] The propargylsilane 2 has one more CH_2 group than the side product 4 making the compounds separable by careful distillation. Fortunately, the terminally silylated alkyne isomeric with 2, anticipated to arise by triple bond migration in the basic medium,[6] was absent.



3 4 (2)

Surprisingly, a silane, 6, which incorporated an additional CH_2 group (compared to 2) was a minor side product under "forcing" conditions. The formation of 6 may occur as follows:



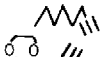
6

A small amount of allene, the product of protonation of resonance form 5a, also was observed in some reactions of Me_3SiCH_2Cl.

Our preparative experiments are summarized in Table I, including the previously reported preparation from Me_3SiCH_2OTf. Usually, hexamethylphosphoramide (a carcinogen) was needed to activate the lithiated alkynes, although tetramethylethylenediamine was usable for a triflate reaction (entry 2, Table I). The compatibility of the triflate procedure with the presence of an unprotected (except by lithiation) OH group (last entry, Table I), may have exceptional significance for the preparation of substrates for cyclization (including steroid-

forming cyclizations). In the cyclizations, OH groups may serve as initiator groups or as the source of initiator groups (e.g. sulfonates). The preparative conditions also are compatible with the ketal function, another potential initiator of cyclizations (next to last entry, Table I). The use of $(CH_3)_3SiCH_2I$ offered no advantage over $(CH_3)_3SiCH_2Cl$ (entry 3, Table I).

Table I. Quantitative Data for Preparations of Trimethylsilyl-2-alkynes (Propargyltrimethylsilanes)

1-Alkyne (Amount)		Solvent	X in $(CH_3)_3SiCH_2X$	1-Trimethylsilyl-2-alkyne, %[a]	1-Trimethylsilyl 1-alkyne, %[a]	Yield %[b]
	(2.33g)	ether	SO_3CF_3	90[c]	0	78
	(0.5g)	ether	SO_3CF_3	75[d]	0	-
	(0.5g)	THF	I	70	23	62
	(33.0g)	THF	Cl	65	27[e]	57
	(10.0g)	THE	Cl	-	-	53
	(20.0g)	THF	Cl	-	-	50
	(1.8g)[f]	THF	SO_3CF_3	-	-	67

[a]Yield, determined by gas chromatography of undistilled products by comparison with standard solutions of known concentration. Reactions were usually initiated at -78° and brought to room temperature, using the procedure of reference 4 with variations.

[b]Distlled propargyltrimethylsilane fraction.

[c]Reported in ref. 4. Hexamethylphosphoramide activator was used.

[d]Tetramethylethylenediamine activator was used. The reaction was slower than that using HMPA.

[e]Seven percent of 1-trimethylsilyl-3-decyne, 6, also was isolated, ^1H NMR δ0.02 $[(CH_3)_3Si]$, ^{13}C NMR δ - 1.63 $[(CH_3)_3Si]$, 13.36 and 16.50 $[CH_2CH_2Si]$, 82.15 and 79.58 $[C \equiv C]$.

[f]Two moles of BuLi and two moles of HMPA were used.

An attempt to prepare 1-trimethylsilyl-2-octyne by the reaction of the lithium salt of the parent propargyltrimethylsilane with iodopentane gave the desired coupling product accompanied by the terminally silylated alkyne arising from triple bond migration.

The preparation of the dioxolane of 8-trimethylsilyl-6-octyn-2-one (6th entry, Table I) follows: To a solution of 20.0 g of the dioxolane of 5-hexyn-2-one[11] (0.13 mole) in 200 mL of tetrahydrofuran at -78°C was added 86 mL of n-butyllithium in hexane (1.5 M, 0.13 mole) and 23.3 g hexamethylphosphoramide (0.13 mole). After 2 h stirring at -78°C, trimethylsilylmethyl chloride (16.0 g, 0.13 mole) was added. The resulting mixture was allowed to warm

up to room temperature for 8 h. Gas chromatographic analysis showed the presence of three compounds (see below). Water (300 mL) was added and the mixture was extracted with 5 x 200 mL of ether and dried ($MgSO_4$). Distillation gave 15.6 g of the desired propargylsilane (50%): b.p. 98°C/0.7 mm; H^1NMR ($CDCl_3$) δ 0.09 (s, 9H), 1.23 (s, 3H), 1.41 (t, 2H, J = 3 Hz), 1.68 (m, 4H), 2.18 (m, 2H), and 3.95 ppm (4H); C^{13} NMR ($CDCl_3$) δ -2.09 [$-Si(CH_3)_3$], 6.97 [$-CH_2-Si$], 64.60 [$-O-(CH_2)_2O-$], 77.53 and 78.42 [$-C\equiv C-$], and 110.01 [O-C-O]. Anal. Calcd. for $C_{13}H_{24}O_2Si$: C, 64.94; H, 10.06. Found: C, 64.62; H, 10.17. An early fraction gave 7.3 g of the dioxolane of 7-trimethyl-6-heptyn-2-one analogous to 4 (25%). The chain extended alkyne analogous to 6 (3.0 g, 9%) was obtained as a higher boiling fraction.

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