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STEREOSELECTIVE SYNTHESIS OF ALLYLSILANES FROM CHLOROMETHYLSILYLALKYNES

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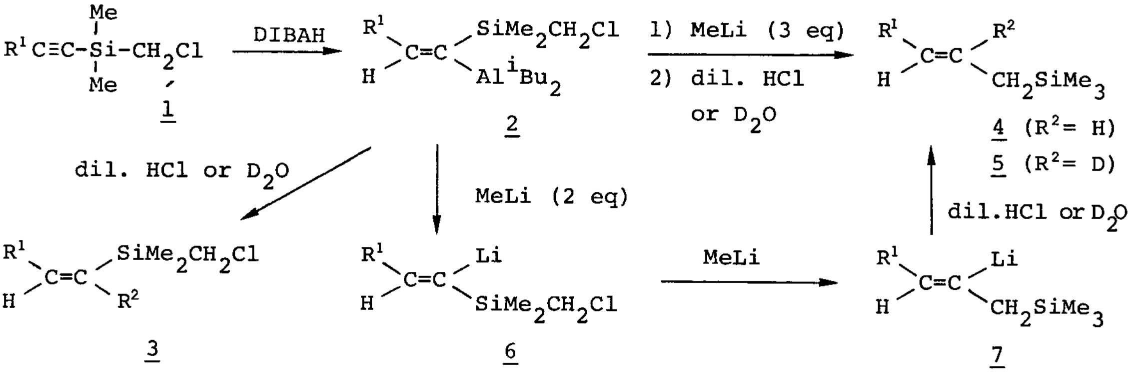
Abstract - Regio- and stereoselective hydralumination of 1-chloromethyldimethylsilyl-1-alkyne with DIBAH affords (Z)-1-chloromethyldimethylsilyl-1-diisobutylalumino-1-alkene which gives (E)-1-trimethylsilyl-2-alkene as a sole product by successive treatment with 3 equiv of methyllithium and water. Reaction of the organoaluminium intermediate with trimethylaluminium in refluxing heptane produces a mixture of (Z)- and (E)-1-trimethylsilyl-2-alkene.

Allylsilanes have attracted considerable attention as versatile synthetic reagents.[1,2,3] In connection with the stereocontrolled preparation of 1-alkenylsilanes from 1-alkynes,[4,5,6] stereoselective synthesis of allylsilanes bearing metallic substituent on β-carbon has been examined.[7] Preparation of the target molecule could be conceivable from 1-chloromethyldimethylsilyl-1-alkyne by hydralumination followed by the action of organometallic reagent. Hydrolytic work up of the product would give (E)- and (Z)-allylsilanes. This paper describes selective formation of (E)-1-trimethylsilyl-2-alkenes from 1-chloromethyldimethylsilyl-1-alkynes by successive treatment with DIBAH, methyllithium, and dil. hydrochloric acid. A mixture of (Z)- and (E)-allylsilanes is produced by the action of trimethylaluminium, in place of methyllithium.



Hydralumination of 1-trimethylsilyl-1-alkyne with DIBAH has been reported to give pure cis-adduct in hydrocarbon-ether and a mixture of cis- and trans-adducts in hydrocarbon.[4,8] When trimethylsilyl group is substituted with chloromethyldimethylsilyl, stereoselective formation of cis-adduct could be expected even in hydrocarbon by intramolecular interaction of chlorine to aluminium.

The starting material 1 was easily obtained from 1-alkyne by the action of chloromethyldimethylsilyl chloride. A heptane solution of 1 (R^1 = n-C_6H_{13}) was treated with DIBAH at room temperature. Hydrolytic work up of the reaction mixture gave pure (Z)-1-chloromethyldimethylsilyl-1-octene (3, R^1 = n-C_6H_{13}, R^2 = H) almost quantitatively. Hydralumination in heptane-ether also afforded (Z)-isomer after hydrolytic work up. Treatment of the hydraluminated product with D_2O gave 1-deuterated alkenylsilane 3 (R^1 = n-C_6H_{13}, R^2 = D). These results indicated that the addition of DIBAH to 1 was regio- and stereoselective to produce 2 and that the stereochemistry of the adduct 2 was not disturbed during the reaction at room temperature.

The reaction mixture containing 2 (R^1 = n-C_6H_{13}) was treated with methyllithium (3 equiv, ether solution) at room temperature for 2 h.[9] Hydrolytic work up of the reaction mixture afforded (E)-1-trimethylsilyl-2-nonene (4, R = n-C_6H_{13}, purity >99%) selectively. Work up with D_2O gave the deuterated product 5 (R^1 = n-C_6H_{13}). Results are summarized in Table 1 (entry 1 - 6).

Selective formation of (E)-allylsilane 4 from 2 by the action of methyllithium can be explained by the assumption of selective formation of (E)-1-chloromethyldimethylsilyl-1-lithio-1-octene (6, R^1 = n-C_6H_{13}) from 2 (R^1 = n-C_6H_{13}) by the action of 2 equiv of MeLi.[10] Reaction of methyllithium to the above lithiated alkenylsilane 6 (R^1 = n-C_6H_{13}) produced lithiated allylsilane 7 (R^1 = n-C_6H_{13}) by stereospecific migration of methylene.

In contrast to the above case, treatment of a heptane solution of 2 (R^1 = n-C_6H_{13}) with trimethylaluminium (1.1 equiv) at 98°C afforded a mixture of (E)- and (Z)-1-trimethylsilyl-2-nonene (4, E/Z = 30/70). Ratio of E/Z depended upon the reaction conditions. Hydralumination of 1 (R^1 = n-C_6H_{13}) in heptane at room temperature for 30 min followed by the action of trimethylaluminium at 70°C for 3 h gave (E)-isomer as the major product (4, E/Z = 70/30). Use of triethylaluminium, in place of trimethylaluminium, afforded (Z)-isomer predominantly (Table 1, entry 11). Work up with D_2O gave deuterated product whose formation indicated that the aluminium moiety was still alive on olefin carbon after migration of methylene.

Rearrangement induced by trialkylaluminium could be explained: (1) geometry of 2 gradually changed to (E)-isomer at elevated temperature in heptane; (2) rearrangement of chloromethylsilylalkene into allylsilane occurs stereospecifically, (3) geometry of the rearranged product does not change under the applied reaction conditions.

Table 1. Allylsilanes from 1-Chloromethyldimethylsilyl-1-alkynes (1)

Entry	R^1	Alkylmetal	Reaction Conditions			Work up	Product
		(equiv)	solvent	temp.	time		(yield %, E/Z)
1	n-C_6H_{13}	MeLi (3)	Et_2O	r.t.	2 h	H_2O	4 (82, E only)^a
2	"	"	"	"	"	D_2O	5 (80, E only)
3	"	"	"	0°C	"	H_2O	3 (90, Z only)
4	"	BuLi (3)	hexane	r.t.	"	--	1 (94)^b
5	n-C_4H_9	MeLi (3)	Et_2O	"	"	H_2O	4 (80, E only)
6	Ph	"	"	"	1 day	"	4 (73, 21/79)^c
7	n-C_6H_{13}	Me_3Al (1.1)	heptane	98°C	3 h	H_2O	4 (70, 30/70)
8	"	"	"	"	"	D_2O	5 (74, 30/70)
9	"	"	"	"	"	H_2O	4 (75, 85/15)^d
10	"	"	"	70°C	"	"	4 (80, 70/30)
11	"	Et_3Al (1.1)	"	98°C	"	"	10 (83, 10/90, R^3=Et)
12	n-C_4H_9	Me_3Al (1.1)	"	"	"	"	4 (75, 30/70)
13	Ph	"	"	"	8 h	"	4 (85, 68/32)^e
14	n-C_6H_{13}	{^{i}Bu$_3$Al (2.0), heptane, 98°C, 3 h to 2}^{f}					10 (74, 5/95, R^3=^{i}Bu)

[a] Typical procedure: To a heptane solution of DIBAH (2.3 mmol, 1.8 mL of 1.28 M solution), 1 (2.3 mmol) was added and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was treated with methyllithium (7.0 mmol, 3.2 mL of 2.2 M ethereal solution) at 0°C. The whole was stirred for 2 h at room temperature, poured onto dil. HCl and crushed ice, and extracted with ether. Washing (brine), drying (Na_2SO_4), and concentration of the ethereal extract afforded 4, which was analyzed by glc cnd 200 MHz ^{1}H-nmr.

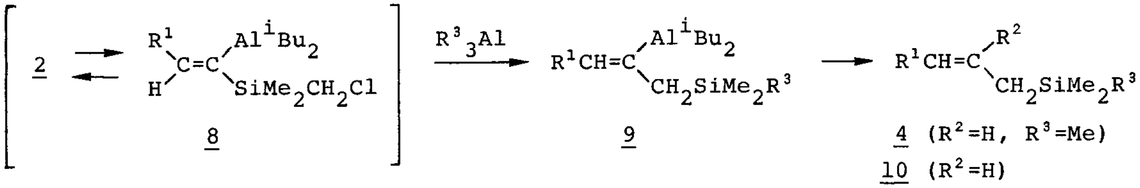
[b] Hydralumination product 2 was treated with BuLi in hexane affording retrohydraluminated product, namely, the starting material 1.

[c] In the case of R^1 = Ph, transmetallation giving 6 from 2 seems slow. Treatment of 2 with MeLi at room temperature for 2 h afforded vinylsilane 3 (R^1 = Ph, R^2 = H, containing 23% of E-isomer) as the major product after hydrolytic work up. Allylsilane 7 and 9 (or the corresponding aluminium ate complex) are seemed to be produced by the attack of MeLi to chloromethylsilyl group on both 6 and 2 (or the corresponding ate complex).

[d] Hydralumination at 50°C for 5 h and successive treatment with Me_3Al.

[e] Predominant formation of E-isomer is responsible for the fast isomerization of 2 into 8 when R^1 = Ph (ref. 8).

[f] Direct treatment of chloromethylsilylalkyne 1 with ^{i}Bu$_3$Al (2.0 equiv) gave 10 (R^3 = ^{i}Bu), whose formation could be explained that hydralumination proceeded with ^{i}Bu$_3$Al.



When (Z)-1-chloromethyldimethylsilyl-1-octene (3, R^1 = n-C_6H_{13}, R^2 = H) was treated with methyllithium under the above described reaction conditions, 3 was recovered.[11,12,13] Synthetic utilities of the metallic functionality are under investigation.

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