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Preliminary communication

ADDITION OF ORGANOLITHIUM REAGENTS TO α-CHLOROVINYLTRIMETHYLSILANE

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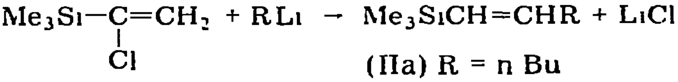
Summary

α Chlorovinyltrimethylsilane adds n and t-butyllithium to form 1-trimethylsilyl-1-hexene and 3,3 dimethyl 1-trimethylsilyl-1 butene, whereas its reaction with phenyllithium affords mainly phenyltrimethylsilane and ethynyltrimethylsilane

Traditionally, access to vinylsilanes of the type represented by II has largely been accomplished via substitution at silicon by vinylmetallic reagents or by eliminative introduction of the π bond using an α or β functionalized saturated organosilane precursor [2, 3] We now report that the reaction of certain organolithium reagents with α chlorovinyltrimethylsilane (I) affords II in a process which formally represents a direct introduction of the R moiety at the β-vinyl position.



$$\underset{\displaystyle (\mathrm{I})}{\mathrm{Me_3Si{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH_2}} + \mathrm{RLi} \rightarrow \mathrm{Me_3SiCH{=}CHR} + \mathrm{LiCl}$$

(IIa) R = n Bu
(IIb) R = t Bu
(IIc) R = Ph

Results are summarized in Table 1. Moderate to good yields of adducts IIa and IIb are realized by the use of n-butyllithium and t-butyllithium in hydrocarbon media***. However, the synthetic utility of the reaction does not extend to the use of phenyllithium in ether, as only a trace of adduct corresponding to IIc was detected. Instead, the principal products were found to be phenyltrimethylsilane and ethynyltrimethylsilane The observation that small amounts of

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**Organolithium reagents add to perfluorovinylsilanes by what is probably an addition—elimination mechanism to form fluoroolefinic silane adducts of type $R_3SiCF{=}CFR'$ [1]

***Preliminary results indicate that ethereal solvents are also effective with n-butyllithium in this regard

TABLE I

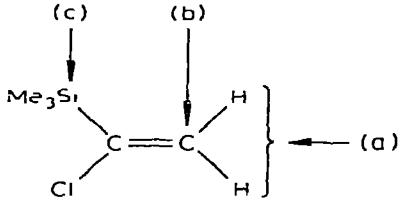
REACTION OF α-CHLOROVINYLTRIMETHYLSILANE (I) WITH RLi [a,b]

R	Solvent	Time (h) at 25°C	I (%) consumed	Yield (%) [c]		
				$RSiMe_3$	$Me_3SiC{\equiv}CH$	II
n Bu	hexane	48	98	3	3	51*trans*, 10*cis*
t-Bu	pentane	1	98	1	6	84*trans*, [e]
n-Bu	hexane—TMEDA	24	83	[f]	35	21*trans*, 4*cis*
t-Bu	pentane—TMEDA	24	93	[f]	30	21*trans*, [e]
Ph	ether	36	73	39	20	1 (*trans* + *cis*)

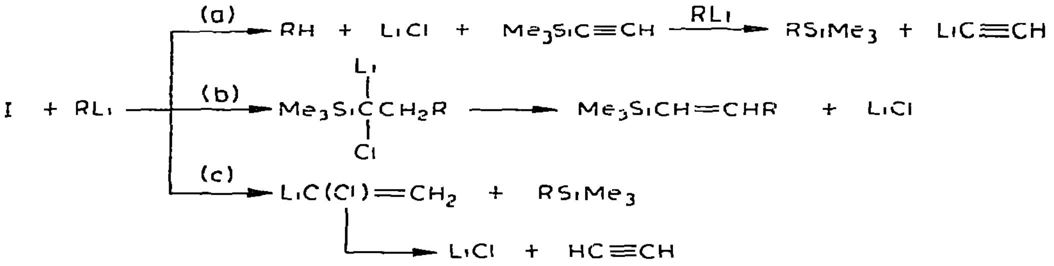
[a] Equimolar amounts of I and RLi [b] I added to RLi at −30° and then allowed to warm to 25° [c] Yields are based on consumed I and were determined by GLC except as noted [d] Yield of distilled material [e] A trace of material which may be *cis*-IIb was also indicated by GLC [f] Not determined

n- and t-butyltrimethylsilane, together with ethynyltrimethylsilane, were also produced along with adducts IIa and IIb when n and t butyllithium were employed suggests a commonality of behavior among organolithium reagents towards I, but one in which the predominant mode of reaction may be determined by the nature of the carbanion in solution. A working hypothesis which would account for the formation of observed products is shown below, where sites of initial carbanionic attack on I are lettered.

The adducts II are viewed as arising* from carbanionic attack at the methylene terminus of the π system (path b) to form a transient α chlorolithium species which undergoes rapid loss of lithium chloride concerted with hydrogen migration [4]. The ability of silicon to stabilize an adjacent carbanionic center [5] would be expected to facilitate the initial step of this sequence. Ethynyltrimethylsilane could be produced by vicinal dehydrochlorination of I initiated by nucleophilic attack at a β hydrogen (path a). In fact, the addition of a molar equivalent of tetramethylethylenediamine (TMEDA) to the alkyllithium in such experiments resulted in a large increase in elimination relative to addition, an



(I)



Control experiments show that II does not arise from the addition of organolithium reagents to ethynyltrimethylsilane observation which is in accord with the known base-enhancing effect of TMEDA on organolithium reagents [6]. The species $RSiMe_3$ may in principle be formed via several pathways as shown (paths a, c); precedents are known for the displacement of electronegatively-substituted alkynes [7] and alkenes [1, 8] from silicon under similar conditions. Work is in progress to explore the scope and mechanistic details of this method.

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[*] In addition, we have preliminary evidence that n-butyllithium reacts with ethynyltrimethylsilane to, in part, afford n-butyltrimethylsilane