SOME NEW ASPECTS OF CONJUGATE ADDITION OF GRIGNARD AND ALKYLLITHIUM REAGENTS TO VINYLSILANES[1]

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Summary: A structure and reactivity relationship has been determined on the reaction of iso-propyl and *n*-butyl Grignard reagents and *n*-butyllithium with vinyl-(alkoxy)silanes and (amino)silanes. The addition to the vinyl group has been analyzed in terms of the nucleophile HOMO-vinyl group LUMO interaction.

α-Silyl carbanions play an important role in, for example, Peterson olefination of carbonyl compounds[2] or asymmetric Grignard cross-coupling reactions.[3] Among several methods for the generation of α-silyl carbanions,[4] addition of organolithium[4,5] or Grignard reagents[4,6] to vinylsilanes seems to be extremely useful in synthetic organic chemistry.[7] In the course of our recent work on the transformations of silafunctional compounds, we were interested in the formation of a carbanion α to an (alkoxy)silyl or (amino)silyl group. Buell et al. reported in 1970 that *sec*-alkyl Grignard reagents add to vinyl(alkoxy)silanes.[6] There has been a report on the polymerization of vinyl(amino)silanes initiated by alkyllithium reagents.[8] Quite recently, addition of alkyllithiums to vinyl(siloxy)silanes has also been studied.[5a,9]

In order to get a wider scope and limitation, we have treated a variety of alkoxy- and amino-vinylsilanes with isopropyl and *n*-butyl Grignard reagents and *n*-butyllithium, and discussed the reactivity of the vinylsilanes by the structural analysis of the LUMO of the vinyl group.

Results are listed in Table 1, in which some literature data are also included for comparison. Vinyl(alkoxy)silanes are regarded as ambient electrophiles in the reaction with Grignard or organolithium reagents. Therefore, addition to the double bond [Addn] and substitution at silicon [Substn] are the competing processes, as shown by eq. 1.

$$R-m \; + \; \underset{}{\overset{\backslash/}{Si}-X} \longrightarrow R\underset{m}{\diagdown}\overset{\backslash/}{Si}-X \; + \; \overset{\backslash/}{Si}-R \tag{1}$$

[Addn]   [Substn]

With the isopropyl Grignard reagent, only addition reaction was observed with mono-alkoxy- and dialkoxy-vinylsilanes 2-6, regardless of the nature of the alkoxy group. An interesting feature has been observed with 2-dimethylaminoethoxy-silanes 8 and 9: while addition occurs exclusively with the monoalkoxy derivative 8 even at room temperature, only substitution takes place with the dialkoxyvinylsilane 9. This result indicates that the
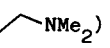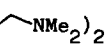
Table 1. Reaction of Grignard reagents or n-butyllithium with vinylsilanes.

silyl group in vinylsilane	i-PrMgBr Et$_2$O/rfx/15-20 h[a]	n-BuMgBr Et$_2$O/rfx/15 h[a]	n-BuLi THF/hexane/0°C/1 h[a]
-SiMe$_3$ 1	No RXN	No RXN	[Addn][b]
-SiMe$_2$(OEt) 2	[Addn][c]	[Addn] and Substn[c,d,e]	Substn
-SiMe$_2$(O—│—) 3	[Addn][f]	No RXN[e]	[Addn][g]
-SiPh$_2$(OEt) 4	[Addn][h]	No RXN	----
-SiMe(OEt)$_2$ 5	[Addn][c,h]	Substn[i]	----
-SiMe(OPr-i)$_2$ 6	[Addn][i]	No RXN	Substn[k]
-Si(OEt)$_3$ 7	[Addn] and Substn[c]	Substn	Substn
-SiMe$_2$(O⌒NMe$_2$) 8	[Addn][l,m]	Substn[l]	----
-SiMe(O⌒NMe$_2$)$_2$ 9	Substn[i,l]	----	----
-SiMe(NEt$_2$)$_2$ 10	No RXN	No RXN	[Addn][n]
-SiMe(NMe⌒NMe$_2$)$_2$ 11	[Addn][o]	----	[Addn][o]

[a] R-m : vinylsilane = 2 : 1. Yields were determined by GLC after hydrolysis (NH$_4$Cl solution, unless otherwise noted). [b] See ref. 4. [c] See ref. 6. [d] We have observed no reaction, as opposed to the result reported by Buell et al. (ref. 6). [e] Substitution was observed in THF. [f] Refluxed for 4 days, 40%. [g] 52% yield. [h] Quantitative yield. [i] Only mono-substitution product was formed. [j] Refluxed for 40 h, 72% yield. [k] Mono-substitution product was formed in 57% yield. [l] At room temperature for 15 h. [m] White precipitates were formed, 77% yield. [n] 80% yield. [o] Yields were 27 and 54% respectively, after coupling with allyl bromide followed by oxidation (see the subsequent paper).

2-dimethylaminoethoxy group not only activates the addition of the Grignard reagent to the vinyl group (8 vs. 2), but also facilitates the substitution at silicon (9 vs. 5), possibly due to the chelation effect. A similar effect may be noted in the aminosilane series 10 and 11: no reaction occurred with diethylaminosilane, while the addition takes place with 2-(dimethylamino)ethyamino-silane.

The main purpose of the present study was to attain the addition of n-alkyl Grignard reagents to silafunctional vinylsilanes, but, unfortunately, substitution predominated with ethoxysilanes 5 and 7 and dimethylaminoethoxysilane 8 or no reaction occurred with sterically hindered vinylsilanes 3, 4, and 6 and with aminosilane 10. Instead, n-butyllithium gave adducts with (t-butoxy)vinylsilane 3 and (diamino)vinylsilanes 10 and 11. Of particular interest is the last result obtained with diethylaminosilanes, since Speier et al.[8] observed only polymerization upon treatment of (dimethylamino)vinylsilanes with n-butyllithium. The
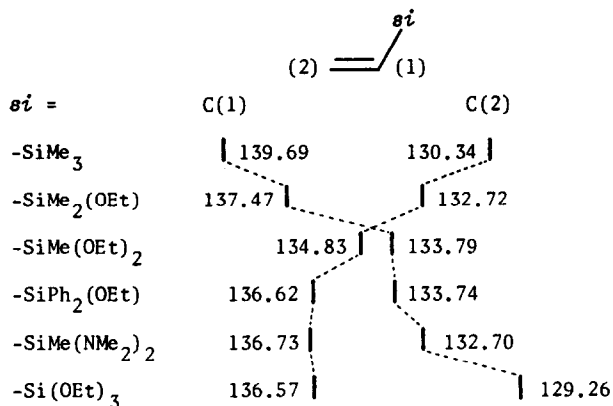
$$si = \qquad C(1) \qquad\qquad C(2)$$

si =	C(1)	C(2)
-SiMe$_3$	139.69	130.34
-SiMe$_2$(OEt)	137.47	132.72
-SiMe(OEt)$_2$	134.83	133.79
-SiPh$_2$(OEt)	136.62	133.74
-SiMe(NMe$_2$)$_2$	136.73	132.70
-Si(OEt)$_3$	136.57	129.26

Figure 1. ^{13}C NMR chemical shifts (down-field from TMS) of some pertinent vinylsilanes (ref. 11a).
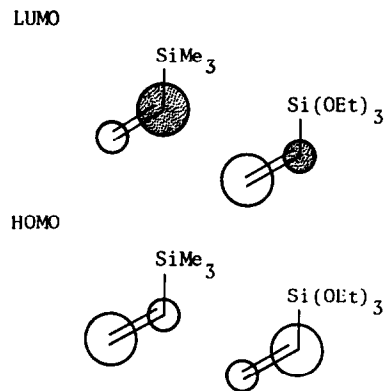
Figure 2. A schematic representation of p coefficients of π-HOMO and π*-LUMO of vinyl-SiMe$_3$ and vinyl-Si(OEt)$_3$.

present result, therefore, provides the first successful case for the formation of the 1 : 1 adduct of vinyl(amino)silane with n-butyllithium. In connection with this we have also observed a similar addition reaction with sec- and $tert$-butyllithium.[10]

While reactions and further transformations of these adducts, α-silyl carbanion species, will be reported in the subsequent paper,[10] the mechanism of the addition reaction will be discussed in this paper.

The addition reaction may proceed through the interaction of the nucleophile HOMO with the electrophilic vinyl group LUMO. The ^{13}C NMR data of a variety of vinylsilanes which have been recently reported[11] clearly demonstrate that the successive displacement of the methyl group on silicon by an alkoxy group results in the steady upfield shift of the C(1) chemical shift, and conversely in the down-field shift of the C(2), as shown by the schematic representation in Fig. 1. The differences between ^{13}C chemical shifts of the sp^2 carbon atoms in ethylenic compounds can be used as an approximation of the differences between the relative magnitudes of the two sp^2 carbon atom p coefficients of the π-HOMO and π*-LUMO.[12] As shown in Fig. 2, in vinyltrimethylsilane the largest coefficient is on the C(2) in the π-HOMO and on the C(1) in the π*-LUMO. Conversely, in dialkoxy- and trialkoxy-vinylsilanes, the largest coefficient is on the C(2) in the π*-LUMO and on the C(1) in the π-HOMO. The interaction between the carbanion HOMO with the π*-LUMO on the C(2) becomes much more favorable in (alkoxy)vinylsilanes in comparison with trimethylvinylsilane, resulting in the facilitation of the addition reaction. It can be also expected that a possible complexation of the electrophilic part, e.g., Mg^{2+}, with the alkoxy oxygen atom[13] should make the π*-LUMO lobe on the C(2) larger and consequently make the addition more favorable. It should be noted here that the argument is similar to that devoted to the Diels-Alder dienophile[14] for which the Lewis acid exhibits an activation and selectivity-improvement effect. The reactivities of vinyl(alkoxy)silanes are thus parallel with those of α,β-enones.[15]

An energy-matching is another important factor. Since the energy levels of both of the π-HOMO and π*-LUMO are expected to be lower in (alkoxy)vinylsilane than in trimethylvinyl-

silane,[11b] the energy factor is also more favorable to the former. The n-butyl Grignard reagent cannot add to those vinylsilanes which react with the isopropyl Grignard reagent, because the former is more stable than the latter.

n-Butyllithium may attack inherently the silicon center and therefore its addition is restricted to vinyl-silanes which contain a trimethylsilyl, sterically hindered alkoxysilyl, or aminosilyl group.[16]

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(15) It should be noted that an alkoxysilyl group may be regarded as a "ketal" of an imaginary "silacarbonyl" group $>Si=0$.

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