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(TRIMETHYLSILYL)VINYLLITHIUM

I. THE REACTION OF (1- AND *trans*-2-BROMOVINYL)TRIMETHYLSILANE WITH LITHIUM METAL

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SUMMARY

(1- and *trans*-2-bromovinyl)trimethylsilane react rapidly with lithium in ether, however, dehydrohalogenation and coupling reactions preclude good yields of the lithium reagent. *In situ* trapping with excess trimethylchlorosilane yields *trans*-bis(trimethylsilyl)ethylene and demonstrates $>80\%$ conversion to lithium reagents. In this latter case, prolonged reaction with lithium leads to reductive silylation of the derivative product and formation of 2,2,4,4,7,7,-hexamethyl-6-(trimethylsilyl)-2,4,7-trisilaoctane.

Studies have been undertaken to compare derivatives of trimethylvinylsilane with analogous derivatives of styrenes and α-olefins. In the study of the reactions of (1-and *trans*-2-bromovinyl)trimethylsilane with lithium metal, we have found that serious complicating side reactions (dehydrohalogenation, coupling, and polymerization) preclude good, isolable yields of the vinyllithium reagent. Thus, the reactions appear to resemble those of analogous styrene derivatives[1-5] to a much greater extent than similar derivatives of α-olefins[1,5-9].

When (*trans*-2-bromovinyl)trimethylsilane is reacted with excess lithium dispersion in anhydrous ether at room temperature, the initial reaction is complete within five minutes, and product ratios remain nearly constant for at least thirty minutes. The course of this reaction was monitored by GLC by determining ratios of derivatives from both hydrolysis and reaction with trimethylchlorosilane. These derivative products and their ratios are shown in Table 1, Section A. Comparison of the two sets of derivative products and their ratios leads us to conclude that the compounds shown in Table 1, Section B, were present in the stated ratios at the end of reaction 1, prior to derivatization.

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TABLE 1

PRODUCTS AND PRODUCT RATIOS[a] RELATED TO REACTION 1

Section A: Products and product ratios from derivatization
1. With water:
$Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CH$/"Coupling Products"[b] 5/1/3
2. With trimethylchlorosilane:
$Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CSiMe_3/$*trans*-$Me_3SiCH{=}CHSiMe_3$/"Coupling products" 2/1/3/3

Section B: Products present before derivatization
$Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CLi/Me_3SiCH{=}CHLi$/"Coupling products" 2/1/3/3

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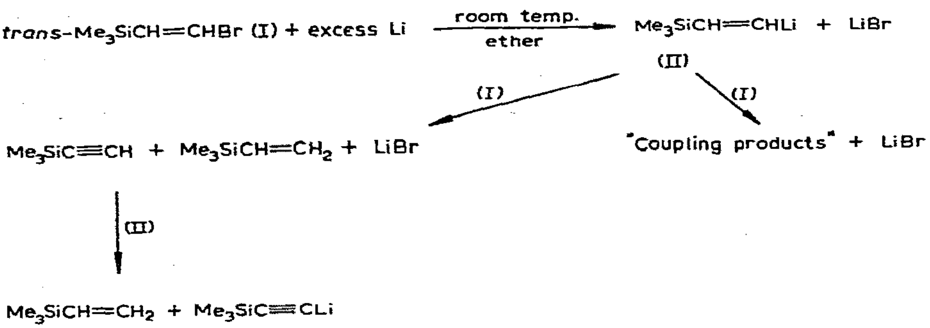
[a] Product identity ascertained by isolation and comparison with authentic samples. Reported yields are in mole proportions, relative to total GLC detectable products. Isolation and monitoring carried out on a Hewlett Packard F & M Model 700 GC utilizing 10% SE-30 on acid-washed, silanized Chromosorb W.
[b] Designation of (IV), a mixture of at least three components, as "coupling products" is based upon identical retention times in sections A1 and A2, and observed PMR absorption ratios of vinyl/silyl-methyl = 1.9/9.

SCHEME 1.

REACTION OF (*trans*-2-BROMOVINYL)TRIMETHYLSILANE WITH LITHIUM

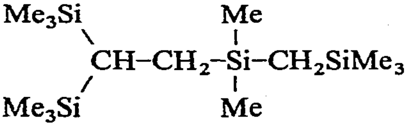


Reaction 1 is represented by Scheme 1.

While any rigorous definition of reaction rates is presently impossible, it is obvious from product ratios (Table 1) that about 66% of the vinyl bromide was converted to vinyllithium reagent. This is clearly the fastest reaction. The derived ratio of "coupling products" to lithium (trimethylsilyl)acetylide indicates that coupling reactions probably proceed about three times as fast as the dehydrohalogenation under these conditions. Further, the derived 2/1 ratio of vinyltrimethylsilane to lithium (trimethylsilyl)acetylide indicates that the lithium acetylide participates neither in the coupling nor in the dehydrohalogenation reaction.

When the products of reaction (1) (Scheme 1) are permitted to stir for an additional lengthy period of time in the presence of excess lithium, a gradual decrease of (2-lithiovinyl)trimethylsilane, vinyltrimethylsilane, and "coupling products" is observed concurrent with the appearance of compounds with high GLC retention times. This may be reasonably attributed to polymerization.

When (*trans*-2-bromovinyl)trimethylsilane reacts with excess lithium in ether in the presence of a large excess of trimethylchlorosilane, a brief induction period occurs. At the end of thirty minutes, reaction is complete with an 82% yield of *trans*-bis(trimethylsilyl)ethylene. Thus, under these conditions, both coupling and dehydrohalogenation is diminished due to the fast reaction of the vinyllithium reagent with trimethylchlorosilane. Continued reaction of the mixture in the presence of excess lithium and excess trimethylchlorosilane, however, leads to polymerization of vinyltrimethylsilane, very slow reaction of bis(trimethylsilyl)acetylene probably via reductive silylation[10], and rapid reductive silylation of *trans*-bis(trimethylsilyl)ethylene to form 2,2,4,4,7,7-hexamethyl-6-trimethylsilyl-2,4,7-trisilaoctane in $>80\%$ yield:



Molecular weight determinations and elemental analysis* are in excellent agreement for $C_{14}H_{38}Si_4$. The infrared spectrum** contains a significant sharp spike at 1050 cm^{-1} indicative of the disilyl–methylene linkage[10]. A variable temperature PMR study*** was necessary for final structure assignment. The methylene and methine protons were well resolved at ambient temperatures. A very sharp doublet at 0.60 ppm (δ) (J 10 Hz) is attributed to the monosilyl–methylene group and a sharp triplet at -0.22 ppm (J 10 Hz) to the coupled bis-silylmethine proton. The isolated bis-silyl–methylene protons occur as a sharp singlet at -0.24 ppm. In contrast, the silyl–methyl absorptions presented a very complex pattern. At 175°, however, the silyl–methyl protons were resolved into three sharp resonances at about 0.06 ppm, 0.01 ppm, and -0.06 ppm with relative ratio of 2/6/3, respectively.

Attempts to carry out the reaction of (*trans*-2-bromovinyl)trimethylsilane with lithium in solvents other than diethyl ether in such a fashion as to detect the presence of appreciable amounts of vinyllithium reagent were unsuccessful. Reactions in THF led only to dehydrohalogenation and "coupling". No reaction was observed in hydrocarbon solvents. Attempts to effect reaction in ether at lower than room temperature resulted in no appreciable reaction, an unexpected result when one considers the facility with which it occurs at room temperature. Clearly, more investigation is warranted at lower temperature.

Initial studies of the reaction of (1-bromovinyl)trimethylsilane with excess lithium in ether, followed by derivatization with trimethylchlorosilane resulted in the following products and ratios:

$$Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CSiMe_3/(Me_3Si)_2C{=}CH_2/\text{“Coupling products”}$$

$$2/1/1/<1$$

In comparison with the reaction of (*trans*-2-bromovinyl)trimethylsilane, one notes that the rate of dehydrohalogenation has increased in relation to formation of the vinyllithium, and decreased in respect to coupling. The increased rate of dehydrohalo-

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* Analytical Determinations by Galbraith Laboratories, Knoxville, Tenn.

** Infrared spectra were obtained on a Perkin Elmer Model 337 Spectrometer.

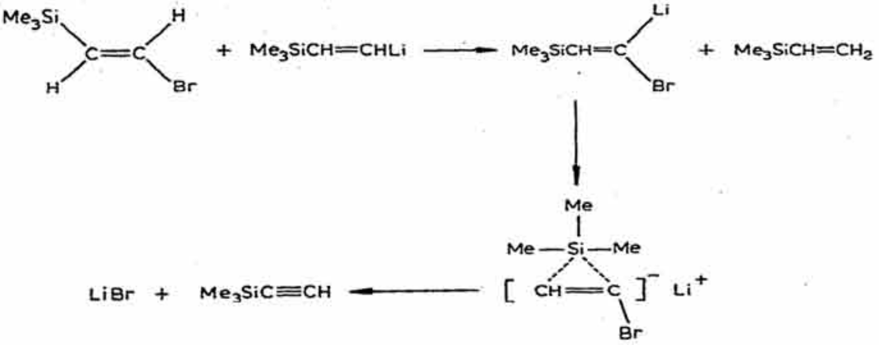
*** PMR spectra were obtained using a Varian Associates Model A-60 spectrometer with a variable temperature probe.

genation may be attributable to an increased facility for *trans*-dehydrohalogenation, possible with (1-bromovinyl)trimethylsilane but not directly so with (*trans*-2-bromovinyl)trimethylsilane.

Three possible dehydrohalogenation mechanisms can be suggested for (*trans*-2-bromovinyl)trimethylsilane. Dehydrohalogenation may occur directly in a *cis*-fashion; as a deprotonation–isomerization–elimination sequence; or even, perhaps, via deprotonation followed by trimethylsilyl migration. The latter would be analogous to the phenyl migrations with 1-methyl-2-bromostyrene[1] and with the 1,1-diarylvinyl halides[11,12]. The silyl analog, involving a bridging trimethylsilyl group, is represented in Reaction Scheme 2. Studies are presently underway to gain more quantitative data and elucidate the mechanism of the elimination reaction.

REACTION SCHEME 2

DEHYDROHALOGENATION VIA DEPROTONATION–SILYL MIGRATION



While the presence of (1- and 2-lithiovinyl)trimethylsilane has been well established, pure solutions of these compounds would not seem readily available from a direct reaction of the (trimethylsilyl)vinyl halides with lithium. A more promising path would seem to be the transmetallation of (trimethylsilyl)vinyl tin compounds. Kraihanzel[13] has shown that at least one of these is readily obtainable, and studies towards utilizing this method are now underway

EXPERIMENTAL

General

(*trans*-2-Bromovinyl)trimethylsilane was prepared according to the procedure of Mironov[14]. (1-Bromovinyl)trimethylsilane was prepared via the method of Agre and Hilling[15]. Lithium dispersion (50% in hexane) was obtained from Foote Mineral Co.

Procedural

An argon atmosphere was maintained throughout all operations either via dry-box or on-line techniques. A typical time-study procedure is described. Lithium dispersion (0.07 mol) was transferred to a pre-dried reaction flask. Hexane was removed under vacuum, and anhydrous ether (50 ml) was distilled directly from lithium aluminum hydride into the flask. [When simultaneous derivatization was desired, freshly distilled trimethylchlorosilane (0.04 mol) was added.] The bromovinyltrimethylsilane (0.006 mol) was added to the flask. The reaction mixture was stirred magnetically at room temperature. Aliquots were taken by syringe at intervals, quenched in water (or trimethylchlorosilane), and the ether layer examined by GLC.

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