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The Reaction of the Butenyl Grignard Reagent with Trimethylchlorosilane

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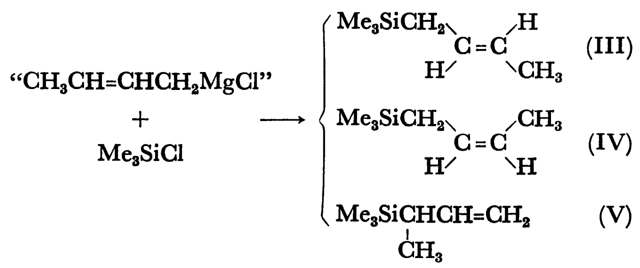
Synopsis. The reaction of trimethylchlorosilane with the butenyl Grignard reagent prepared from either 3-chloro-1-butene or 1-chloro-2-butene yielded *trans*-2-butenyltrimethylsilane, *cis*-2-butenyltrimethylsilane and 1-methyl-2-propenyltrimethylsilane, approximately in the ratio of 30/20/50. Structures of these isomeric butenylsilanes were elucidated by NMR and IR spectra.

During the course of a study on thermolysis of cyclopropylsilanes[1)] and allyltrimethylsilane,[2)] it became desirable to prepare *trans*- and *cis*-2-butenyltrimethylsilanes. Butenyltrimethylsilanes may be prepared by hydrosilylation of butadiene,[3)] but these compounds can also be prepared by direct introduction of a butenyl group into silicon through an organometallic reagent. Accordingly, we prepared three allylic isomers of butenylsilanes by the reaction of trimethylchlorosilane with butenylmagnesium chloride. When the most of the work had been completed, we received reports of Seyferth and coworkers[4,5)] who prepared the compounds in question with butenyllithium in the course of a study on the solution properties of the lithium reagent. Recently, they have published the detail of the experiment.[6)] Slutsky and Kwart also reported the preparation of butenylsilanes recently.[7)] In spite of these circumstances, we would like to publish our results briefly, since results with the Grignard reagent are somewhat different from those with the lithium reagent in product distribution and we have elucidated the structures of butenyltrimethylsilane unequivocally by analyzing the complex NMR spectra.

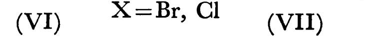
Addition of trimethylchlorosilane at room temperature to the Grignard reagent, which was prepared from either 3-chloro-1-butene (I) or 1-chloro-2-butene (II), resulted in the formation of a mixture of *trans*- and *cis*-2-butenyltrimethylsilanes (III and IV) and 1-methyl-2-propenyltrimethylsilane (V) in 60—90% total yield.



Product distribution was little affected by the structure of the starting chloride, by changing the solvent from ether to THF, and by the order of addition. Thus, relative yields of III/IV/V were, in %: (a) addition of trimethylchlorosilane to the Grignard reagent from I in ether, 27.7/20.4/51.9; (b) addition of trimethylchlorosilane to the Grignard reagent from II in ether, 30.1/21.5/48.4; (c) *in situ* reaction of trimethylchlorosilane, I and magnesium in THF, 26.7/19.8/53.4.

The reaction of the butenyllithium reagent, which was prepared from either *cis*- or *trans*-2-butenyltrimethyltin by *trans*-metallation, with trimethylchlorosilane gave an approximately 3/2 mixture of III/IV.[6)] It was noted that V was not among the products in the reaction of the lithium reagent. This is the most significant difference between two reagents in the reaction with trimethylchlorosilane, although the same *trans*/*cis* ratio of approximately 3/2 is sustained in two experiments.

It is well established that the unsymmetric butenylmagnesium bromide consists mainly of the 2-butenyl isomer in mobile equilibrium with the very minor 1-methyl-2-propenyl isomer.[8)] Therefore, the present finding confirms the rapid equilibration between two isomeric structures of the Grignard reagent.

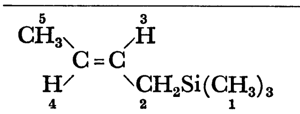
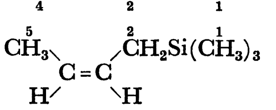
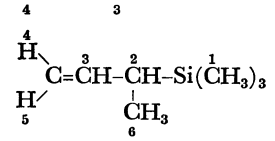


$$\underset{\text{(VI)}}{\underset{\text{MgX}}{CH_3\underset{|}{C}HCH{=}CH_2}} \rightleftarrows \underset{\text{(VII)}}{\underset{\text{MgX}}{CH_3CH{=}CH\underset{|}{C}H_2}} \qquad X=Br,\ Cl$$

A path for the dominant formation of V, which must occur only in the reaction of the Grignard reagent, may be provided by the S_E2' type reaction of VII,[9)] since the direct displacement reaction of VI (S_E2 reaction) with trimethylchlorosilane is unlikely because of both steric reason and unfavorable equilibrium concentration. The reaction of a secondary Grignard reagent with trimethylchlorosilane usually resulted in the reduction of the chlorosilane.[10)]

The NMR spectra of III and IV are very complicated and have not been analyzed completely yet. We have

TABLE 1. NMR DATA OF $C_4H_7Si(CH_3)_3$ IN CCl_4

Compound	Chemical Shifts (δ) and Coupling Constants (Hz)
	−0.03 (s, H_1), 1.46 (m, H_2), 5.23 (m, H_3 and H_4), 1.63 (m, H_5); $J_{H_3-H_4}=15.5$[a)]
	−0.01 (s, H_1), 1.45 (m, H_2), 5.28 (m, H_3 and H_4), 1.52 (m, H_5); $J_{H_3-H_4}=12.0$[a)]
	0.04 (s, H_1), 1.56 (m, H_2), 5.77 (d, d, d, H_3), 4.83 (m, H_4 and H_5), 1.04 (d, H_6); $J_{H_4-H_5}=1.5$[b)], $J_{H_3-H_4}=11.0$, $J_{H_3-H_5}=16.5$, $J_{H_2-H_6}=6.0$, $J_{H_2-H_3}=7.5$

a) The coupling constants were obtained by irradiation at both H_2 and H_5. b) The coupling constant was obtained by irradiation at H_2.

Table 2. IR data of $C_4H_7Si(CH_3)_3$ (cm^{-1})

Mode of Vibration	Compound		
	(III)	(IV)	(V)
$=CH_2$ stretching			3080 (m)
$=CH-$ stretching	3020 (m)	3020 (m)	
C=C stretching	1660 (w)	1645 (m)	1625 (m)
CH in-plane deformation		1400 (m)	1415 (m)
CH out-of-plane deformation	965 (s)		900 (s)

determined all chemical shifts and coupling constants. by using triple resonance technique on pure samples The results are listed in Table 1. The data of IR spectra are listed in Table 2.

Experimental

NMR spectra were obtained at 100 MHz using a Varian HA-100 spectrometer. IR spectra were measured with a Nippon Bunko DS-402G Grating Infrared Spectrophotometer. 2-Chloro-1-butene and 1-chloro-2-butene were prepared from 1,3-butadiene and hydrogen chloride according to the literature.[11]

The Grignard reactions were carried out by the standard procedure. A typical example is shown below.

A solution of 1-chloro-2-butene (9.05 g, 0.1 mol) dissolved in ether (14 ml) was added to magnesium (3.16 g, 0.13 g-atom) in ether (14 ml) very slowly with stirring. After 6 h, a solution of trimethylchlorosilane (10.8 g, 0.1 mol) in ether (14 ml) was added to the mixture. After an exothermic reaction had ceased, the mixture was heated at reflux for 1 h and hydrolyzed with water. The dried organic layer was distilled using a short Vigreux column to give 9.5 g (74%) of a mixture of butenylsilanes, bp 110—118 °C.

The mixture was analyzed by GLC with a phenylacetonitrile-$AgNO_3$ column. Relative retention times were critically influenced by the silver content, and finally a column packed with *ca.* 30% by weight of an approximately 1 : 1 complex of $PhCH_2CN$-$AgNO_3$ on Celite 545 was used at 45 °C with 0.9 atom helium. Under these conditions the retention times were 2.0 min for III, 6.6 min for IV and 10.5 min for V. A portion of the mixture was also separated by GLC and identified by spectroscopic studies.

Mass spectra (25 eV) *m/e* (rel. intensity), (III): 128 (10.6), 113(5.5), 85(6.9), 73(100), 59(10.1), 55(11.1); (IV): 128(9.3), 113(4.8), 85(6.2), 73(100), 59(9.7), 55(14.5); (V): 128 (5.9), 113(4.3), 85(6.3), 73(100), 59(8.7), 55(6.7).

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