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REGIOSELECTIVE HYDROBORATIONS OF METHYLVINYLCHLOROSILANES

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Summary

The regioselectivity of the hydroboration of the methylchlorovinylsilanes, $Cl_{\underline{n}}Me_{3-\underline{n}}SiCH=CH_2$ ($\underline{n}$ = 0 - 3), has been investigated using BH_3←THF, 9-BBN, disiamyl- and dicyclohexylborane. Methylation of the adducts with methylmagnesium bromide is complicated by formation of tetraalkylboronates. Alkaline hydrogen peroxide oxidation of the boronates gives reasonable yields of the corresponding α- and β-trimethylsilylethanols for $\underline{n}$ = 0 and 1. For $\underline{n}$ = 2 and 3, conversion of the adducts to the corresponding α- and β-deuteroethylsilanes by treatment with excess sodium methoxide in methanol-$\underline{O\text{-}d}$ provides a more effective means of derivatization. Addition of the alkenes, $\underline{n}$ = 2 or 3, to excess BH_3←THF gives ca. 90% of the α-boro-organochlorosilanes. For all of the alkenes, the dialkylboranes give ca. 80% of the β-boron adducts.

The use of the hydroboration reaction in synthetic organosilicon chemistry has become increasingly important in recent years [1]. Chlorosilylorganoboranes, I, may be readily prepared by the hydroboration of vinylchlorosilanes without reduction of the silicon-chlorine bonds [2].

$$Cl_{\underline{n}}Me_{3-\underline{n}}SiCH=CH_2 \xrightarrow{H-B=} Cl_{\underline{n}}Me_{3-\underline{n}}Si-(C_2H_4)B= \quad \text{I}$$

In light of the great synthetic utility of the hydroboration reaction [3], and the potential applications to vinylsilanes bearing functionality on silicon, it was desirable to determine the regioselectivity of the hydroboration of vinylchlorosilanes.

The typical derivatization procedure used to determine regioselectivity in the hydroboration of alkenes involves oxidation of the borane adducts to the corresponding alcohols with alkaline hydrogen peroxide [3]. Unfortunately chlorosilylorganoboranes, I, undergo facile polymerization under these conditions. It has therefore been necessary to "defunctionalize" the chlorosilyl groups, usually by conversion to the trimethylsilyl derivatives with methylmagnesium bromide, prior to oxidation [2].

$$\text{I} \xrightarrow{\text{MeMgBr}} \text{Me}_3\text{Si}(\text{C}_2\text{H}_4)\text{B=} \xrightarrow[\text{OH}^-]{\text{H}_2\text{O}_2} \text{Me}_3\text{Si}(\text{C}_2\text{H}_4)\text{OH}$$

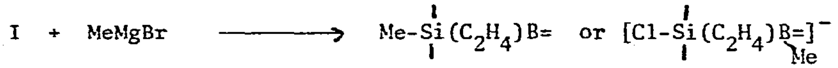
Although this derivatization procedure gives reasonable yields of the α- and β-trimethylsilylethanols for the borane adducts to vinyldimethylchlorosilane and vinylmethyldichlorosilane (I, $\underline{n}$ = 1 and 2, respectively) [2], the results with the adducts to vinyltrichlorosilane are variable and unreproducible, and frequently only polymeric materials are obtained after oxidation.

We recently reported that the methoxide promoted protonolysis of organosilylboranes gives significant yields of products resulting from protonolysis of the C-B bond [4]. Both the α- and β-boro adducts undergo the reaction, and methoxy substituents on silicon favor the reaction. Thus, yields of up to 80% of ethyltrimethoxysilane may be obtained by treatment of the borane adduct to vinyltrichlorosilane with sodium methoxide in methanol, followed by destructive distillation. It was further shown that quantitative incorporation of deuterium in the saturated products occurs when methanol-$\underline{O}$-$\underline{d}$ was used as the solvent for the reaction, and that no rearrangement of alkyl groups attached to silicon occurs [4]. Thus, the methoxide promoted deuteration has the potential of complimenting the Grignard/oxidation procedure for determining the regioselectivity of the hydroboration of vinylchlorosilanes.

Results and Discussion

As we have reported, the reaction of borane tetrahydrofuran solutions with vinylchlorosilanes proceeds smoothly to give adducts. In reactions monitored by IR, the bands attributed to the borane decrease in intensity as the reaction proceeds, and no bands in the Si-H stretching region of the spectrum are observed [2]. The spectra indicate that, for the chlorosilanes, the additions are usually complete in 4-5 h. The reaction is significantly slower than the hydroboration of the great majority of simple olefins for which the reaction is complete in a few minutes [3]. The lack of reduction of the Si-Cl bonds, and the slowness of the addition are both consistent with the fact that borane is an electrophilic reagent. Reduction of chlorosilanes is accomplished with nucleophilic reagents [5]. One would also anticipate that the electron withdrawing effect of the chlorines on silicon decreases the electron density in the vinyl substituent, resulting in a diminished reactivity towards electrophilic reagents.

The Grignard methylation of the adducts is complicated by the fact that there are at least two competing reactions, substitution at silicon to give II, or complexation with boron to produce the boronate, III.



$$\text{I} + \text{MeMgBr} \longrightarrow \underset{\text{II}}{\text{Me-}\overset{|}{\underset{|}{\text{Si}}}(C_2H_4)\text{B=}} \quad \text{or} \quad \underset{\text{III}}{[\text{Cl-}\overset{|}{\underset{|}{\text{Si}}}(C_2H_4)\underset{\text{Me}}{\text{B}}\text{=}]^-}$$

Even when very bulky hydroborating reagents are used this competition is observed. The dicyclohexylborane adduct to vinyldimethylchlorosilane was treated with one equivalent of methylmagnesium bromide in ether. The ^1H NMR spectrum of the reaction mixture showed a decrease in the intensity of the peak at δ 0.33, due to the dimethylchlorosilyl protons, and the appearance of two new peaks in the spectrum, a singlet at δ 0.05 due to the trimethylsilyl protons in the methylated adduct, II; and a broadened quartet at δ -0.82 due to the methyl attached to boron in the boronate, III. Integration of the peaks using added benzene as a standard shows that 77% substitution at silicon and 23% addition to boron has occurred. Because of the addition to boron, it is necessary in the Grignard derivatization to add at least one equivalent of Grignard reagent in excess of the amount required to derivatize all the chlorines on silicon.

The formation of the boronate, III, in the methylation of the borane adducts of the vinylchlorosilanes also leads to complications in the alkaline hydrogen peroxide oxidation. Because the initial step in the oxidation involves attack at boron by the hydroperoxide anion [6], the oxidation of boronates is especially prone to anomalous results [7]. Table 1 gives the yields and isomer distributions of the α- and β-trimethylsilylethanols obtained using a variety of hydroborating reagents followed by the Grignard/oxidation procedure. It shows clearly how the yield of trimethylsilylethanols varies, and in general, decreases as the number of chlorine substituents on silicon increases. The results for the hydroboration of vinyltrimethylsilane using borane in THF are in agreement with those obtained by Seyferth and coworkers [8].

The thermal isomerization of organoboranes to sterically favored isomers is well known [3]. Recently Musker and Larson noted a more facile isomerization of the intermediate organoboranes obtained from the hydroboration of 1-trimethylsilylcyclohexene with thexylborane [9]. In order to test whether such isomerization was occurring in our systems, the effects of the hydroboration time and temperature were investigated for vinylmethyldichlorosilane. The results, for which aliquots of the hydroboration reaction mixtures, held at 0° or room temperature (RT) were derivatized at various times using the Grignard/oxidation procedure, are given in Table 2. Unfortunately, the analytical method did not permit the determination of yields of the trimethylsilylethanols obtained. Nevertheless, certain trends are evident. At low temperature, an apparently "kinetic" product distribution, favoring the α-adduct is obtained. At room temperature the amount of β-adduct relative to α appears to increase with increased reaction time, consistent with isomerization to the thermodynamically more stable β-adducts. However, the change in isomer distribution is small compared to the possible errors in the analytical procedure. We assume that, in hydroborations with reaction times of 12 h or greater, thermodynamic distributions of adducts are obtained for our systems.

Table 1

Adduct Distributions for the Hydroboration of Vinylchlorosilanes

R-CH=CH$_2$,R	Run	Borane[a] (h)	Analysis[b]	α	β	Yield[c]
Me$_3$Si	1	BH$_3$,2:1 (24)	Ox	47	53	62
	2	BH$_3$,1:1	NMR	32	68	
	3	Dicyclohexyl (20)	Ox	12	88	76
	4	Disiamyl (4)	Ox	24	76	64
Me$_2$ClSi	5	BH$_3$,3:1 (46)	Deut	56	44	45
	6	BH$_3$,2:1 (3)	Ox	70	30	69
	7	BH$_3$,1:1 (46)	Deut	36	64	35
	8	BH$_3$,1:1	NMR	42	58	
	9	Dicyclohexyl (20)	Ox	16	84	31
	10	9-BBN (12)	Deut	20	80	64
	11	Disiamyl (8)[d]	Ox	78	22	77
MeCl$_2$Si	12	BH$_3$,3:1 (17)	Deut	86	14	60
	13	BH$_3$,2:1 (3)	Ox	90	10	59
	14	BH$_3$,1:1 (17)	Deut	68	32	57
	15	BH$_3$,1:1	NMR	66	34	
	16	Dicyclohexyl (20)	Ox	22	78	50
	17	9-BBN (12)	Deut	23	77	47
	18	Disiamyl (4)	Ox	16	84	70
Cl$_3$Si	19	BH$_3$,3:1 (18)	Deut	88	12	80
	20	BH$_3$,2:1 (4)	Ox	88	12	51
	21	BH$_3$,1:1 (18)	Deut	73	27	71
	22	Dicyclohexyl (20)	Ox	16	84	30
	23	9-BBN (12)	Deut	24	76	61
	24	Disiamyl (4)	Ox	11	89	30

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[a] BH_3 = Borane THF solution, ratio of hydride to olefin. For dicyclohexyl borane, and disiamyl borane, and 9-BBN a 1:1 ratio of hydride to olefin was used.

[b] Ox = Grignard/oxidation, Deut = methoxide promoted deuteration, NMR = analysis of the NMR spectra of the borane adducts.

[c] Determined by GLC using an internal standard.

[d] Disiamylborane contaminated with excess borane.

Because the methoxide promoted protonolysis of organosilylboranes gives increased yields of saturated products with increasing alkoxide substituents on silicon [4], we investigated this derivatization procedure as a means of determining the regiospecificity of the hydroboration reaction using methanol-$\underline{O}$-$\underline{d}$ as the solvent.

$$\mathrm{I} \xrightarrow[\mathrm{MeOD}]{\mathrm{NaOMe}} \underset{\mathrm{IV}}{(MeO)_{\underline{n}}Me_{3-\underline{n}}SiCHDCH_3} + \underset{\mathrm{V}}{(MeO)_{\underline{n}}Me_{3-\underline{m}}SiCH_2CH_2D}$$

This derivatization method has the advantage that, by the use of excess sodium methoxide, the chlorosilyl groups are converted to methoxysilyl groups

Table 2

Effect of Time and Temperature on the Hydroboration of Vinylmethyldichlorosilane[a]

Conditions[b]	Alcohol Distribution[c]	
	α	β
3 h, 0° (1.65)	100	0
2 h, 0°; 1.5 h, RT. (1.65)	73	27
2 h, 0°; 10 h, RT. (1.65)	69	31
3 h, RT. (1.5)	64	36
7 h, RT. (1.5)	62	38
12 h, RT. (1.5)	60	40

[a] Olefin added to a $BH_3 \cdot THF$ solution (ratio of hydride to olefin), aliquots derivatized by methylation with excess methylmagnesium bromide and alkaline hydrogen peroxide oxidation.

[b] Time and temperature for hydroboration step.

[c] α- and β-trimethylsilylethanol.

in the initial step of the analysis procedure. The relative amounts of α-deuteroethylsilane, IV, and β-deuteroethylsilane, V, can be readily determined by analysis of the ^{1}H NMR spectra of the products. Table 1 gives the results of these analyses.

While our previous work did not demonstrate that deuterium incorporation occurred at the specific site of boron substitution in the hydroboration adducts [4], the consistency of the results obtained in the Grignard/oxidation method, and in the methoxide promoted deuteration, Table 1, strongly indicate that this is the case. Thus, the same adduct distribution is obtained by either method for the hydroboration of vinyltrichlorosilane with excess $BH_3 \leftarrow$ THF, Runs 19 & 20. In runs of comparable reaction times, 5 & 7, 12 & 14, 19 & 21, there is a decrease in the relative amount of α-adduct with decreasing hydride to olefin ratio, consistent with the increased steric requirements of a tri-organoborane vs. a mono-organoborane.

Further support of this conclusion arises from the detailed analysis of the ^{1}H NMR spectra which can be obtained for some of the adducts [10]. For hydroborations under comparable conditions, Runs 7 & 8 or 14 & 15, reasonable agreement is obtained between the results for the deuteration and NMR analytical methods.

Taken together, the results indicate that the hydroboration of methylchlorovinylsilanes can be highly regiospecific. When excess $BH_3 \leftarrow$ THF is used as the hydroborating reagent (Table 1, Runs 1, 5, 12, 19) there is a clear trend favoring the α-adduct. Increasing chlorine substitution on silicon leads to increased amounts of the α-adducts so that, for vinylmethyldichlorosilane and vinyltrichlorosilane, the reaction has sufficient regiospecificity to be of synthetic utility. This effect of electron withdrawing substitutents has been previously observed to a lesser extent in the hydroboration of various substituted styrenes [11].

As the steric requirements of the hydroborating reagent increase, increasing substitution at the β-position is observed. Thus, with 1:1 $BH_3 \leftarrow$ THF (Runs 2, 7, 8, 14, 15, 21) increased amounts of the β-adduct are produced. When very bulky hydroborating reagents are used such as 9-BBN (Runs 10, 17, 23) disiamylborane (Runs 4, 18, 24) or dicyclohexylborane (Runs 3, 9, 16, 22) the adducts are 80 to 90% β-isomer. For these boranes with high steric requirements the reaction is again of sufficient regiospecificity to be synthetically useful in the preparation of β-boro-organochlorosilanes. Based on the relative amounts of α- and β- adducts obtained, the steric requirements of the hydroborating reagents appear to increase in the order:

3:1 BH_3 + THF << 1:1 BH_3 + THF < 9-BBN < dicyclohexylborane < disiamylborane

This order is roughly consistent with the structures of the several hydroborating reagents.

Overall, the electronic and steric effects observed are consistent with the mechanisms for the hydroboration reaction which we have proposed [12]. The synthetic applications of these regiospecific preparations of silicofunctional organoboranes are presently under investigation in our laboratories.

Experimental

Materials

Reagent grade olefins were used, and were distilled prior to use. Borane-tetrahydrofuran, dicyclohexylborane, disiamylborane, and 9-BBN were prepared using procedures given by Brown [3]. All glassware was oven-dried prior to use, assembled hot, and cooled while flushing with prepurified nitrogen. Reactions were carried out under a static pressure of nitrogen or argon.

The method of Bunnet and co-workers for the preparation of ethanol-O-d [13] was adapted for the preparation of methanol-O-d which was distilled from magnesium metal under an atmosphere of dry prepurified nitrogen prior to use.

Hydroborations were carried out by addition of the alkene to a standardized solution of the appropriate borane in THF at 0°. The mixture was allowed to warm to room temperature and stirred for the times indicated in Table 1 prior to derivatization. The procedure for methoxide promoted deuteration has been described previously [4].

For the GLC analyses of the deuterated products, a 5' by 1/4" stainless steel column containing 10% SE-30 on 60-80 mesh acid washed Chromosorb W was used at 85° with a helium flow of 50 ml/min. Yields were determined using diglyme as an internal standard.

Oxidation and analysis of the alcohol mixtures

The methylated adducts were oxidized with alkaline hydrogen peroxide using the method of Seyferth [8]. Authentic samples of α and β-trimethylsilyl ethanol were prepared by the oxidation with alkaline hydrogen peroxide of the diborane adducts to vinyltrimethylsilane and characterized by their mass spectra, vpc retention time, and infrared spectra.

The NMR spectra of samples collected by vpc were recorded in carbon tetrachloride solution using a Jeolco MH-60 spectrometer. The chemical shifts were (ppm downfield from TMS):

$Me_3SiCH(OH)CH_3$: singlet (9H), δ0.16 [$(CH_3)_3Si$]; doublet (3H) δ 1.24 [CH_3]; quartet (1H), δ 3.30 [CH], and a broad singlet (1H), δ 1.99 [OH].

$Me_3SiCH_2CH_2OH$: singlet (9H), δ 0.16 [$(CH_3)_3Si$]; triplet (2H) δ 0.94 [CH_2 adjacent to Si], triplet (2H), δ 3.57 [CH_2adjacent to OH] and a broad singlet (1H), δ 3.06 [OH].

The retention times of the alcohols (5', 10% Carbowax-20M on Chromosorb W, 80°, 90 ml He/min) were: $Me_3SiCH(OH)CH_3$, 2.1 min; $Me_3SiCH_2CH_2OH$, 4.8 min. Results of the analyses are given in Table 1.

Analysis of the deuterium labeled products

The labeled ethyl silanes, $Me_2MeOSiC_2H_4D$, $Me(MeO)_2SiC_2H_4D$, and $(MeO)_3SiC_2H_4D$, produced in this work have two groups of peaks for their ethyl protons in the ^1H NMR. The methylene protons occur in the region of δ 0.40-0.66, and the methyl protons of the ethyl group occur in the region of δ 0.76-1.00. In addition, the methyl protons on silicon occur at δ0.04, and the methoxy protons at ca. δ3.48. Comparison of the integration of the ethyl protons with that for methoxy protons showed that, in each case, one deuterium was incorporated per ethyl group. Mass spectra of GLC purified samples verified this observation.

Using the relative integrations of the methylene protons, A, and the methyl protons, B, in the ^1H NMR, the following simultaneous equations were solved to calculate the ratio of α and β deuterioisomers.

$\underline{A} = \alpha + 2\beta$ $\underline{B} = 3\alpha + 2\beta$

The results are given in Table 1.

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References

1. K. Uchida, K. Utimoto, and H. Nozaki, J. Org. Chem., 41 (1976) 2940; G. Manuel, P. Mazerolles, and J. Gril, J. Organometal. Chem., 122 (1976) 335; B. Miller and T. Reichenbach, Tetrahedron Lett. (1974) 543; T. Araki, D. Terunuma, F. Kato, H. Kaneda, and A. Iino, Bull. Chem. Soc., Japan, 46 (1973) 644.
2. P. R. Jones and J. K. Myers, J. Organometal. Chem., 34 (1972) C9.
3. H. C. Brown, "Organic Syntheses via Boranes," Wiley Interscience, New York (1975).
4. P. R. Jones and T. F. O. Lim, J. Organometal. Chem., 120 (1976) 27.
5. C. Eaborn, "Organosilicon Compounds," Butterworths, London (1960), p. 194 ff.
6. H. Minato, J. C. Ware, and T. G. Traylor, J. Amer. Chem. Soc., 85 (1963) 3024. .
7. G. W. Kramer and H. C. Brown, J. Organometal. Chem., 90 (1975) C1.
8. D. Seyferth, J. Inorg. Nucl. Chem., 7 (1958) 152; J. Amer. Chem. Soc., 81 (1959) 1844; D. Seyferth, H. Yamazaki and Y. Sato, Inorg. Chem, 2 (1963) 734.
9. W. K. Musker and G. L. Larson, Tetrahedron Letters, (1968) 3481.
10. P. R. Jones, and T. F. O. Lim, 169th Meeting of the American Chemical Society, Philadelphia Pa. April, 1975, Abstract No. INOR 124; T. F. O. Lim, Ph.D. Dissertation, North Texas State University, 1977.
11. H. C. Brown and R. L. Sharp, J. Amer. Chem. Soc., 88 (1966) 5851.

12. P. R. Jones, J. Org. Chem., 37 (1972) 1886.

13. J. F. Bunnett, M. M. Rauhut, D. Knutson, and G. E. Bussell, J. Amer. Chem. Soc., 76 (1954) 5755.