Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The hydroboration of methylchlorosilylalkenes

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(Received November 4th, 1971)

While there are several reports in the literature of the hydroboration of unsaturated organosilicon compounds[1,2], there have been no reports of reactions between silico-functional olefins and diborane. Because of the synthetic versatility of organoboranes we have investigated the hydroboration of a series of allylchloromethylsilanes and vinylchloromethylsilanes.

In spite of the ease of reduction of the silicon—chlorine bond[3] and Wartik's observation that the reaction of vinyltrichlorosilane with sodium borohydride gives cleavage of the Si—H bond to produce silane as the only isolated product[4], the reaction of diborane with chlorosilyl-olefins proceeds smoothly to give adducts. During the addition IR spectra of the reaction mixtures show a decrease in intensity of the bands in the 2600—2500 cm^{-1} (terminal B—H) and in the 1600—1500 cm^{-1} (B—H—B bridge) regions. However, no band appears in the Si—H stretching region of the spectra (2250—2100 cm^{-1}), indicating that no reduction of the Si—Cl groups occurs.

The chlorosilylorganoboranes produced may be methylated using methylmagnesium bromide with no complicating reactions[★]; and alkaline hydrogen peroxide oxidation of the methylated adducts proceeds smoothly to the alcohols.

In a typical experiment 12 ml of a solution of diborane in tetrahydrofuran[5] (1.0*M* in BH_3)[★★] was added slowly to a solution of 20 mmol of olefin in about 10 ml of tetrahydrofuran and stirred at 0° under an atmosphere of dry argon. Although the IR spectra of the reaction mixture indicated that addition was complete in 4—5 h the clear solution was allowed to warm to room temperature and was generally stirred overnight. After treatment with excess methylmagnesium bromide the mixture was stirred for an additional 4 h, and hydrolyzed with dil. hydrochloric acid. The organic layer was separated, combined with ether washings of the aqueous layer and the ether removed using a rotary evaporator. The solution of the methylated adducts was oxidized with alkaline hydrogen peroxide[1], and the product alcohol mixtures analyzed by GLC[★★★].

[★] Treatment of the chlorosilylorganoboranes with other nucleophilic reagents such as methyllithium or hydrides results in coupling and/or cyclization reactions.

[★★] It is extremely important that the excess boron trifluoride etherate be excluded from the diborane solution. Boron trifluoride appears to catalyze elimination reactions of the β-boro-organochlorosilanes.

[★★★] The alcoholic products were characterized by IR and NMR spectra and analyses of samples purified by preparative GLC.

The results for the vinylchloromethylsilanes, summarized in Table 1, indicate that increasing chlorine substitution on silicon leads to increased amounts of the α-adducts, and are consistent with the increased electron withdrawing ability of the chlorosilyl groups. The leveling off of the relative amounts of α and β adducts for the dichloromethyl and trichloro substituents may reflect the point at which steric effects begin to predominate over electronic effects.

TABLE 1

ALCOHOL DISTRIBUTION AND YIELD FOR THE HYDROBORATION OF VINYLCHLOROMETHYLSILANES

R–CH=CH$_2$	Alcohol distribution (mole %)		Yield (%)
	α^a	β^b	
R = Me$_3$Si	47	53	62[c]
ClMe$_2$Si	70	30	69
Cl$_2$MeSi	90	10	59
Cl$_3$Si	88	12	51

[a] 1-Trimethylsilylethanol. [b] 2-Trimethylsilylethanol. [c] Seyferth[1] obtained an approximately 50/50 mixture of the α and β isomers for the reaction of vinyltrimethylsilane with excess $NaBH_4$–$AlCl_3$ reagent in diglyme.

In the allyl series the only silicon containing alcohol obtained was 3-trimethylsilyl-1-propanol. An authentic sample of 1-trimethylsilyl-2-propanol was prepared[6]. It was demonstrated that this alcohol, the expected oxidation product of the internal boron adduct, was not present in the reaction mixtures. The product mixtures did contain 1-propanol which can conceivably arise from an elimination of the internal adduct[7]. The results, summarized in Table 2, reflect a lack of any large inductive effect of the Cl_3SiCH_2 group and are consonant with the steric requirements of the system.

TABLE 2

ALCOHOLIC PRODUCTS AND YIELDS FOR THE HYDROBORATION OF ALLYLCHLOROMETHYLSILANES

R–CH$_2$CH=CH$_2$	Alcohol distribution (mole %)		Yield (%)
	1-propanol	$Me_3Si(CH_2)_3OH$	
R = Me$_3$Si	none[a]	100	73[b]
ClMe$_2$Si	22	78	68
Cl$_2$MeSi	4	96	99
Cl$_3$Si	4	96	93

[a] Within the detectable limits of GLC analysis. [b] An overall yield of 64% of 3-trimethylsilyl-1-propanol may be calculated from Seyferth's report of the reaction of allyltrimethylsilane with the $NaBH_4$–BF_3 reagent in tetrahydrofuran[1].

The facile synthesis of silylorganoboranes with functional groups on silicon opens the door to a wide number of reactions of potential synthetic utility in organosilicon chemistry. The chemistry of the chlorosilylorganoboranes, including elimination, coupling and cyclization reactions are presently under investigation in our laboratories.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and to the Faculty Research Fund of North Texas State University for support of this work.

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