Journal of Organometallic Chemistry, 120 (1976) 27—33

THE METHOXIDE PROMOTED PROTONOLYSIS OF ORGANOSILYLBORANES

PAUL RONALD JONES and THOMAS FAY OY LIM
Department of Chemistry, North Texas State University, Denton, Texas 76203 (U.S.A.)
(Received March 19th, 1976)

Summary

The destructive distillation or pyrolysis of borane 9-borabicyclo[3.3.1]nonane, or dicyclohexylborane adducts to vinylsilanes which have been treated with sodium methoxide in methanol gives significant yields of products resulting from protonolysis of the C—B bond. Both α- and β-boro adducts undergo the reaction, which is favored when silicon has methoxy substituents. Quantitative incorporation of deuterium in the saturated products when methanol-*O-d* is used as the solvent shows that the hydroxyl group of methanol is the proton source. The absence of isomerization of the alkyl groups attached to silicon in the protonolysis of the adducts to propenyltrichlorosilane or isopropenyltrichlorosilane indicates that cyclic intermediates or free carbanions are not involved in the reaction.

While organoboranes are remarkably stable to water, aqueous bases and mineral acids, it is well known that they are susceptible to protonolysis by carboxylic acids [1]. Reports of protonolysis of organoboranes promoted by strong base are extremely rare. Weinheimer and Marsico observed that benzylic organoboranes are susceptible to protonolysis under the influence of aqueous sodium hydroxide [2]. Brown and Sharp noted small yields of ethylbenzene derivatives produced during the alkaline hydrogen peroxide oxidation of borane adducts to substituted styrenes. The yields increased markedly with substitution of electron-withdrawing groups on the aromatic ring, and the saturated products were assumed to arise from the alkaline hydrolysis of the α-boron derivative [3]. Base-catalyzed protonolyses have been observed or postulated in a number of instances where heteroatoms are bonded to carbons bearing boron [1,4,5]. Recently, Hopper and Fine reported that treatment of tris(trimethylsiloxydimethylsilylmethyl)borane with sodium ethoxide in refluxing ethanol for two days gave a 66% yield of ethoxytrimethylsilane along with a 53% yield of hexamethyldisiloxane. Evidence was presented consistent with the suggestion that the ethoxytrimethylsilane

$$(Me_3SiOSiMe_2CH_2)_3B + NaOEt \xrightarrow[2\ days]{EtOH,\ reflux} \underset{(66\%)}{Me_3SiOEt} + \underset{(53\%)}{(Me_3Si)_2O}$$

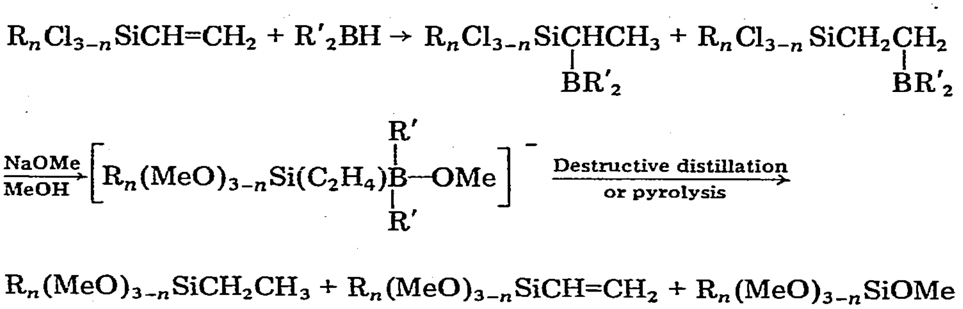
resulted from reaction of ethanol with an intermediate 1,1-dimethylsilaethylene [5].

In the course of our studies of the hydroboration of alkenylchlorosilanes and the reactions of the adducts [6], we have found that alkoxide promoted protonolysis of both α- and β-boro-organosilanes is apparently a general reaction for these compounds. We report herein the results of that investigation.

Results and discussion

When borane adducts to vinylsilanes are treated with sodium methoxide in methanol and then subjected to destructive distillation, there is obtained, in addition to dehydroboration products (II), products resulting from cleavage of the C—Si bonds (III); and products arising from protonolysis of the B—C bond (I) (Scheme 1). Results from typical reactions are presented in Table 1. Under similar conditions 1-octene gave no octane, and styrene gave no detectable ethylbenzene.

SCHEME 1



$$R_nCl_{3-n}SiCH{=}CH_2 + R'_2BH \rightarrow R_nCl_{3-n}Si\underset{\displaystyle BR'_2}{\underset{|}{C}}HCH_3 + R_nCl_{3-n}SiCH_2\underset{\displaystyle BR'_2}{\underset{|}{C}}H_2$$

$$\xrightarrow[MeOH]{NaOMe} \left[R_n(MeO)_{3-n}Si(C_2H_4)\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle R'}{\underset{|}{B}}}}{-}OMe\right]^- \xrightarrow[\text{or pyrolysis}]{\text{Destructive distillation}}$$

$$R_n(MeO)_{3-n}SiCH_2CH_3 + R_n(MeO)_{3-n}SiCH{=}CH_2 + R_n(MeO)_{3-n}SiOMe$$

(I) (II) (III)

R = alkyl or aryl, n = 0—3, R′ = H, 9-BBN, or cyclohexyl

For the 1 : 3 borane adducts to vinyltriethylsilane or vinyldimethylphenylsilane and for the 9-borabicyclo[3.3.1]nonane (9-BBN) adduct to vinyldimethylphenylsilane the saturated products, tetraethylsilane or ethyldimethylphenylsilane, are minor components of the product mixture, and a great deal of polymeric materials remains in the reaction pot after destructive distillation. However, for methoxysilyl adducts, protonolysis to give the saturated product I becomes the major reaction (Table 1).

In typical experiments, the borane adducts were prepared by addition of a tetrahydrofuran solution of the hydroborating reagent (1 equivalent of hydride per mole of alkene) to a tetrahydrofuran solution of the alkene. The resulting mixtures were added to solutions of excess sodium methoxide in anhydrous methanol and refluxed for a minimum of 9 h. Control experiments demonstrated that similar results were obtained when the chlorosilanes were derivatized with methanol in the presence of pyridine in a separate step, and the resulting methoxysilylorganoboranes subjected to the sodium methoxide in methanol

TABLE 1

METHOXIDE PROMOTED PROTONOLYSIS OF SILYLORGANOBORANES

Alkene	Borane [a]	Yield [b]		
		Saturated I	Alkene II	Si—C cleavage III
$Et_3SiCH{=}CH_2$	A	10	30	17
$PhMe_2SiCH{=}CH_2$	A	13	11	26
	B	8.4	34	0
$Cl_3SiCH{=}CH_2$	A	79	20	trace
	B	58	17	10
	C	42 [c]	0	0
$Cl_3SiCH{=}CHCH_3$	A	62 [d]	0	0
	B	52 [d]	0	0
$Cl_3SiC(CH_3){=}CH_2$	A	69 [e]	0	0
	B	40 [e]	0	0

[a] A = 1/3 equiv. $BH_3 \leftarrow THF$; B = 1 equiv. 9-BBN; C = 1 equiv. dicyclohexyl borane. [b] For the chlorosilanes the products are the methoxy derivatives. Yield based on alkene and determined by GLC analysis of distillates using internal standards. Roman numerals refer to compounds indicated in Scheme 1. [c] Yield based on (dicyclohexylboroethyl)trimethoxysilane. [d] n-Propyltrimethoxysilane only. [e] Isopropyltrimethoxysilane only.

treatment. Thus, when the dicyclohexylborane adduct to vinyltrichlorosilane is converted to the trimethoxy derivative, and then refluxed with 1/3 equivalent of sodium methoxide in methanol; destructive distillation of the resulting mixture gave a 42% yield of ethyltrimethoxysilane. The dicyclohexylborane adduct was greater than 85% of the β-boro-organosilane [7].

$$(C_6H_{11})_2B(C_2H_4)Si(OMe)_3 \rightarrow EtSi(OMe)_3$$

$$(42\%)$$

Base-promoted elimination—rehydroboration reactions of organoboranes containing heteroatoms β to boron which are good leaving groups have been observed [8]. However, to our knowledge, our reactions represent the first examples of base-promoted protonolysis of organoboranes containing a heteroatom β to boron.

In contrast to Hopper's results [5], after refluxing the reaction mixtures with alcoholic alkoxide, examination by GLC indicated the presence of only trace amounts of alkyltrimethoxysilanes or products resulting from Si—C bond cleavage. The difference between Hopper's findings and ours might be related to the lability of the leaving group on silicon. In his systems, the loss of a trimethylsiloxy group from silicon to produce "silaethylene" type intermediates could resonably be expected to require a lower activation energy than the loss of methoxide from silicon, which would be required for analogous reactions in our systems. In one experiment, the 9-BBN adduct to vinyltrichlorosilane was treated with excess sodium methoxide in refluxing methanol for over 9 hours. High vacuum was then applied to the reaction mixture, and all volatile components were collected in a liquid nitrogen trap. In addition to tetrahydrofuran and methanol, there were only traces of ethyltrimethoxysilane and vinyltrimethoxysilane in the trap. When the remaining pot residue was heated to 200—300°C, a 57% yield of

TABLE 2

PYROLYSIS OF $MeOSiMe_2(C_2H_4)B(OMe)_2$ [a]

	Yields (%)	
Equiv. NaOMe	$MeOSiMe_2CH_2CH_3$	$(MeO)_2SiMe_2$
0	none	none
trace	trace	
1	58	23
1.67	52	41
1.67 [b]	63	36
9	39	44

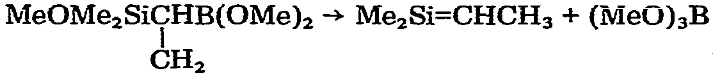
[a] 56% α, 44% β based on deuteration experiments. [b] The pyrolysis sample from the preceding experiment was diluted with an equal volume of dry methanol.

ethyltrimethoxysilane was obtained. It appears that, in our system, the protonolysis occurs during the destructive distillation of the residue from the sodium methoxide/methanol treatment. Further support for this conclusion was obtained from pyrolysis studies of the methoxy derivative of the 1 : 1 borane adduct to vinyldimethylchlorosilane (Table 2).

$$MeOSiMe_2(C_2H_4)B(OMe)_2 \xrightarrow[MeOH]{NaOMe} \xrightarrow{ca.\ 350^\circ C} MeOSiMe_2CH_2CH_3 + (MeO)_2SiMe_2$$

Examination of the pyrolysis mixtures by GLC prior to pyrolysis showed only traces of protonated and cleaved products which might be produced in the injection port of the gas chromatograph. The results given in Table 2 show that no protonolysis or Si—C bond cleavage occurs in the absence of methoxide. In the presence of one or more equivalents of methoxide more than 80% of the borane adduct is accounted for as either protonated or cleaved product. Increased amounts of methoxide in the pyrolysis mixture favor Si—C bond cleavage, while increased amounts of methanol favor the protonolysis reaction.

It might be suggested that the protonolysis product arises from addition of methanol to a dimethylsilaethylene intermediate produced by pyrolysis of the α-boron adduct. However, in separate experiments employing methanol-*O-d*,



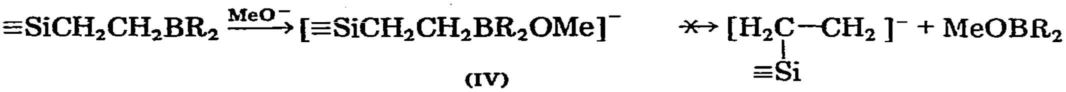
$$MeOMe_2Si\underset{\displaystyle CH_2}{\underset{|}{C}}HB(OMe)_2 \rightarrow Me_2Si{=}CHCH_3 + (MeO)_3B$$

$$Me_2Si{=}CHCH_3 + MeOH \rightarrow MeOMe_2SiCH_2CH_3$$

the saturated product is 56% $MeOMe_2SiCHDCH_3$ and 44% $MeOMe_2SiCH_2CH_2D$. Furthermore, all of the saturated product is monodeuterated [7]. These deuteration experiments, used as a means to determine the direction of addition in the hydroboration of alkenylsilanes will be the subject of a future publication. For the present, they mitigate against a silaethylene intermediate as the sole precursor of the saturated product and demonstrate that the hydroxy group of the methanol is the proton source.

The last four entries in Table 1 give our results with propenyl- and isopropenyltrichlorosilane in the protonolysis reaction. When either borane or 9-BBN was used as the hydroborating reagent, propenyltrichlorosilane gave n-propyltrimethoxysilane as the only saturated product. Similarly isopropenyltrichlorosilane gave only isopropyltrimethoxysilane. These results rule out a silacyclopropane as the precursor of the β-protonated product. Both the propenyl and isopropenyl silanes would give the same silacyclopropane if cyclization occurred. Methanolysis of this intermediate should give the same mixture of n-propyl- and isopropyl-silanes regardless of which alkene was the starting material.

Based on our results and Brown's observations [9], it is reasonable to assume that the borane adducts in this study are attacked rapidly by sodium methoxide to form "ate" complexes (IV) which are the direct precursors of all products. The dissociation of these "ate" complexes to give carbanions prior to the protonation step seems highly unlikely. Anionic rearrangements of organosilicon compounds are well known reactions [10]. The lack of rearrangement for the propenyl and isopropenyl adducts is thus evidence that a carbanionic pathway is not involved in the protonolysis reaction.



$$\equiv SiCH_2CH_2BR_2 \xrightarrow{MeO^-} \underset{(IV)}{[\equiv SiCH_2CH_2BR_2OMe]^-} \not\leftrightarrow [H_2\underset{\equiv Si}{\underset{|}{C}}-CH_2]^- + MeOBR_2$$

The protonolysis of tetraalkylborate anions has been explained in terms of an electrophilic attack at the carbon α to boron because of the high electron density at that carbon [11]. A similar pathway, involving electrophilic attack by the hydroxyl proton of methanol on the methoxyborate complexes would be consistent with our results. The high temperatures required for the reaction are suggestive of a rather high activation energy for this attack. The methanol involved in the protonation is presumably complexed with the "ate" complex in some way. Kramer and Brown have noted that methoxytrialkylborate complexes are stabilized by ether or tetrahydrofuran [12], and sodium methoxide is known to complex with methanol [13]. It is clear from our results that the trimethoxysilyl group α or β to boron facilitates the protonolysis reaction of the methoxyborate complexes. The reasons for this are not clear at the present time.

Experimental

Materials

Reagent grade olefins were used. Styrene and vinyltrichlorosilane were distilled prior to use. Anhydrous methanol was distilled from magnesium metal under an atmosphere of dry nitrogen immediately prior to use. Borane, tetrahydrofuran, dicyclohexylborane, and 9-BBN were prepared using procedures given by Brown [14]. 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.

For the GLC analyses a 5′ by 1/4″ stainless steel column containing 10% SE-30 on 60—80 mesh acid washed Chromosorb W was used for products other than chlorosilanes. For the chlorosilanes a 5′ by 1/4″ stainless steel 10% QF-1 column pretreated with silicon tetrachloride was used. Larger columns of the same types were used for the preparative work. Yields were determined in most cases by GLC analysis of the distillates using n-hexane or n-octane as an internal standard.

All of the products reported are known compounds, which were identified by ^{1}H NMR and mass spectra of GLC purified samples, or by comparison of retention time with authentic samples.

Propenyl- and isopropenyl-trichlorosilane

In a dry stainless steel lecture bottle were placed 25 ml (250 mmol) of trichlorosilane and 0.4 ml of chloroplatinic acid catalyst solution (1.0 g of $H_2PtCl_6 \cdot 6H_2O$ in 20 ml of isopropanol). The valve of the lecture bottle was replaced. By means of a high vacuum system, 250 mmol of propyne were condensed into the lecture bottle, using standard vacuum transfer techniques. The valve on the lecture bottle was closed, the lecture bottle removed from the vacuum line, and a stainless steel pressure gauge attached to the valve. The bottle was warmed to room temperature, and then heated in an oil bath to ca. 60° C for a period of about 7 h, at which time the pressure was no longer decreasing. The bottle was cooled to room temperature, opened, and the contents distilled to give a 74% yield of the mixed propenyltrichlorosilanes, b.p. 108° C. GLC analysis of the distillate showed that it was 87% *trans*-propenyltrichlorosilane; ^{1}H NMR (CCl_4) δ (ppm) 1.98 (3H) β-Me, δ 5.86 (1H) α-H, δ 6.76 (1H) β—H, $J(\alpha\text{-H—}\beta\text{-H})$ 18 Hz, $J(\alpha\text{-H—}\beta\text{-Me})$ 7 Hz, $J(\beta\text{-H—}\beta\text{-Me})$ 2 Hz; lit. b.p. 117° C [15]; and 13% isopropenyltrichlorosilane; ^{1}H NMR (CCl_4) δ (ppm) 2.05 multiplet (3H) α-Me, 5.95 multiplet (2H) β-H's; lit. b.p. 113.5° C/731 torr [16]. Samples of these compounds for the hydroboration experiments were purified by preparative GLC prior to use.

Destructive distillation experiments

In typical experiments the borane adducts were prepared by the addition of a solution containing one equivalent of the alkene in dry tetrahydrofuran to a standarized solution of the borane [14] at 0°C. The resulting solutions were warmed to room temperature and stirred for a minimum of 9 h to insure completion of the hydroboration reaction. The resulting solution was then added to a methanolic solution of sodium methoxide containing at least one equivalent of sodium methoxide in excess of the amount required to derivatize the chlorosilane. All mixtures were refluxed for a minimum of 9 h before products were distilled. The solutions or volatile portions of the reaction mixtures, examined by GLC, showed only traces of protonated or cleavage products. The saturated products were obtained when the pot residues were subjected to destructive distillation after the removal of solvents. The results are summarized in Table 1.

Pyrolysis experiments

To a solution of 20 mmol of $BH_3 \cdot THF$ in tetrahydrofuran at 0° C was added 20 mmol of vinyldimethylchlorosilane. After stirring the resulting solution at room temperature for 45 min, a mixture of 20 mmol of pyridine in approximately 2.5 ml of dry methanol was added, resulting in immediate gas evolution and formation of a white precipitate. The mixture was stirred for 3 h and then filtered to remove the pyridine hydrochloride. The volatile components were removed by applying vacuum. The residue was indicated to be about 97% $MeOMe_2Si(C_2H_4)B(OMe)_2$, along with traces of pyridine and methanol, by its

^{1}H NMR spectrum. The residue was dissolved in a measured volume of dry tetrahydrofuran. Measured volumes of this solution were mixed with methanol or with measured volumes of an 0.2 *M* solution of sodium methoxide in methanol to give the desired pyrolysis samples.

Pyrolyses were performed using a pyrolysis apparatus similar to that described by Sommer and coworkers [17]. A flow of dry nitrogen at approximately 27 ml/min was maintained through the tube, and the pyrolysate condensed in a U trap cooled to —78° C. The pyrolysis temperature, measured with an iron-constantan thermocouple, was 330—360° C. Pyrolysis samples were introduced at the rate of 1 ml in 5—10 min, through a rubber septum at the upper end of the pyrolysis tube using a syringe. The pyrolysate was analyzed by GLC and yields calculated using n-hexane as an internal standard to give the results reported in Table 2.

Acknowledgment

The authors gratefully acknowledge the support of this work by the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund.

References

1 H.C. Brown and K. Murray, J. Amer. Chem. Soc., 81 (1959) 4108; H.C. Brown and G. Zweifel, ibid., 83 (1961) 3834.
2 A.J. Weinheimer and W. Marsico, J. Org. Chem., 27 (1962) 1926.
3 H.C. Brown and R.L. Sharp, J. Amer. Chem. Soc., 88 (1966) 5851.
4 D.J. Pasto and J.L. Miesel, J. Amer. Chem. Soc., 85 (1963) 2118; D. J. Pasto and C.C. Cumbo, 86 (1964) 4343.
5 S.P. Hopper and J.S. Fine, J. Organometal. Chem., 80 (1974) C21.
6 P.R. Jones and J.K. Myers, J. Organometal. Chem., 34 (1972) C9.
7 P.R. Jones and T.F.O. Lim, unpublished results.
8 D.J. Pasto and R. Snyder, J. Org. Chem., 31 (1966) 2773, 2777.
9 G.W. Kramer and H.C. Brown, J. Organometal. Chem., 90 (1975) C1.
10 R. West, Pure Appl. Chem., 19 (1969) 291; A.G. Brook, Accounts Chem. Res., 7 (1974) 77; A. Wright and R. West, J. Amer. Chem. Soc., 96 (1974) 3214, 3222, and 3227; and references therein.
11 R. Damico, J. Org. Chem., 29 (1964) 1971.
12 G.W. Kramer and H.C. Brown, J. Organometal. Chem., 73 (1974) 1.
13 P.J. Wheatley, J. Chem. Soc., (1960) 4270.
14 H.C. Brown, Organic Synthesis via Boranes, Wiley-Interscience, New York, 1975.
15 D.T. Hurd, J. Amer. Chem. Soc., 67 (1945) 1813.
16 A.D. Petrov, V.F. Miranov and V.G. Glukhovtsev, Dokl. Akad. Nauk SSSR, 110 (1956) 93.
17 C.M. Golino, R.D. Bush, D.N. Roark and L.H. Sommer, J. Organometal. Chem., 66 (1974) 29.