Journal of Organometallic Chemistry, 156 (1978)C12—C16

Preliminary communication

VINYLMETALLOIDS*

II**. THE HIGH REGIOSELECTIVITY OF DIALKYLBORANES IN THE HYDROBORATION OF VINYLTRIMETHYLSILANE

JOHN A. SODERQUIST and ALFRED HASSNER

Richard B. Wetherill Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907 and Department of Chemistry, State University of New York, Binghamton, New York 13901 (U.S.A.)

(Received February 14th, 1978)

Summary

Dialkylboranes such as disiamylborane, dicyclohexylborane and 9-borabicyclo[3.3.1]nonane add cleanly to vinyltrimethylsilane (I) with high regiospecificity (⩾ 95%) to give the corresponding β-silylethylboranes, valuable intermediates in the synthesis of functionalized organosilanes. Oxidation of these adducts provides a convenient, high-yield route to 2-trimethylsilylethanol (IIβ). Reduction of acetyltrimethylsilane (IX) with borane-tetrahydrofuran provides a simple route to the isomeric 1-trimethylsilylethanol (IIα). These new developments illustrate the utility of borane reagents in the regiospecific syntheses of trimethylsilylethanols (II).

The hydroboration of vinyltrimethylsilane (I) with representative dialkylboranes such as disiamylborane, dicyclohexylborane, and 9-borabicyclo[3.3.1]nonane proceeds cleanly with high regiospecificity placing the boron in ⩾ 95% on the β carbon of the double bond. Consequently, the hydroboration of I with such dialkylboranes provides a simple route to β-silylethylboranes, useful intermediates in the syntheses of functionalized organosilanes. Oxidation of these adducts provides a convenient method for the preparation of 2-trimethylsilylethanol (IIβ).

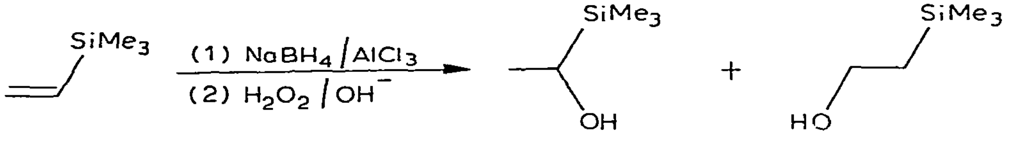
The hydroboration/oxidation of vinyltrimethylsilane (I) was first studied by Seyferth [1] using the sodium borohydride/aluminum chloride reagent of Brown and Subba Rao [2].

The relative amounts of the isomeric trimethylsilylethanols were found to depend on the ratio of borohydride to vinylsilane used. A large excess of hydride gave essentially equal amounts of these alcohols and reducing this excess gave IIβ

---

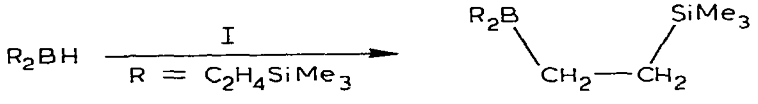
*This work is dedicated to Professor H.C. Brown for his outstanding contributions to chemistry.

**For part I see ref. 9.



(I) (II α) (II β)

predominantly (IIα/IIβ ~ 37/63). Treatment of the hydroboration mixture with ethanol gave isolable dialkylborinate esters as well as trialkylborane products. Oxidation of these two borane types revealed that the trialkylborane gave proportionately more IIβ than the dialkylborane derivatives. These results were explained in terms of steric factors which would be expected to favor placement of the boron atom β to the trimethylsilyl group in the more alkylated borane intermediates.



(III) (IV)

Since Seyferth's report, a number of studies have confirmed the lack of selectivity of borane-THF in the hydroboration/oxidation of I [3].

Terminal alkenes such as 1-hexene or 3,3-dimethyl-1-butene give only 6—7% of the internal alcohol using diborane (or borane-THF) [4a]. This internal product is essentially eliminated using a dialkylborane for the hydroborating reagent [1b]. Hence such borane derivatives provide a convenient route to terminal alcohols of high isomeric purity. These factors led us to investigate the selectivities of several dialkylboranes in the hydroboration/oxidation of I and these results are given in Table 1*.

TABLE 1

THE DISTRIBUTION OF ISOMERIC TRIMETHYLSILYLETHANOLS (II) USING DIFFERENT HYDROBORATING REAGENTS IN TETRAHYDROFURAN [a]

Run	Borane	Hydride equivalents	Reaction temperature (°C) (time (h))	IIα/IIβ	Yield [b,c]
1	$BH_3 \cdot THF$	1	25(9)	49/51	86
2	$BH_3 \cdot THF$	3	0(0.25)	61/39	99
3	$BH_3 \cdot THF$	6	0(0.25)	60/40	98
4	$BH_2(t\text{-}C_6H_{13})$	1	0(6)	28/72	86
5	$BH(Sia)_2$	1	0(1)	5/95	96
6	$BH(CyC_6H_{11})_2$	1	0(1)	1/99	97
7	9-BBN	1	25(1)	0/100	100

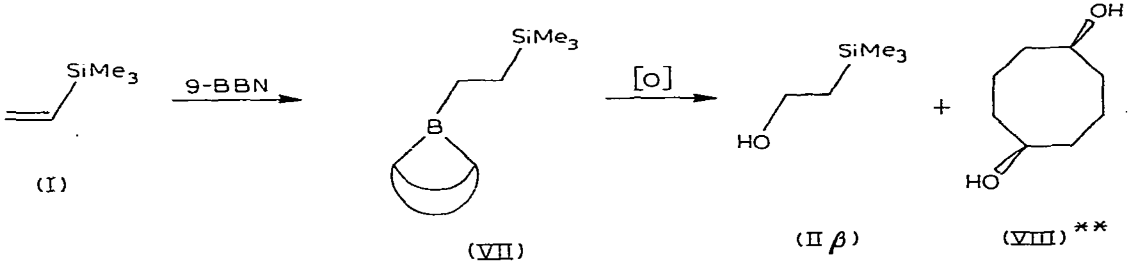
[a] The molarity of the borane was 1.00 *M* in all cases except run 1 (0.94 *M*). In runs 4 and 5, the solid borane was allowed to dissolve as it reacted to make the 1.00 *M* solution. [b] These values were determined by GC (5′ × 1/4″; 10% Carbowax on silylated Chromosorb W) using either decane or tetradecane as an internal standard. [c] For runs 4—7, the alkyl groups on boron were analyzed as the corresponding alcohols and were obtained in > 95% yields in all cases.

---

*It was recently reported [3e] that hydroboration/oxidation of I with disiamyl- and dicyclohexylborane gave predominantly IIβ (76% and 88% respectively). However, in our hands, these reagents gave selectivities (Table 1) approaching the exceptional regioselectivity exhibited by 9-BBN.

Our findings confirm the lack of selectivity using borane-THF in the hydroboration of I. Using excess hydride slightly favors formation of the α product (60/40) and completely consumes I. By contrast, the reaction of I with a stoichiometric amount of borane-THF or thexylborane does not consume the active hydride and I (ca. 14%) remains unreacted. While the latter borane does give more of the β alcohol than borane itself, only the dialkylboranes give this alcohol in high isomeric purity.

In particular, 9-BBN adds to I to give the β-trimethylsilylethylborane (VII) exclusively*. This derivative is oxidized with alkaline hydrogen peroxide to give IIβ and *cis*-1,5-cyclooctanediol (VIII) quantitatively. Alternatively, this sequence can be carried out without isolation of VII.



It is important to point out that particular care must be exercised in the preparation of these borane reagents to obtain this high selectivity. For example, in one trial run a 5% deficiency of cyclohexene was used to prepare dicyclohexylborane. The conversion of I to II was quantitative but the ratio of IIα to IIβ increased to 3/97. In several runs with disiamylborane, the 5/95 selectivity was reproducible. However, we cannot rule out the possibility that incomplete formation of the R_2BH species is responsible for part of the α product.

One further difficulty was encountered in the oxidation of the organoborane reaction mixtures. Incomplete oxidation of these boranes in the reaction of I with borane-THF always gave a lower IIα/IIβ ratio. For example, in run 3, oxidation of a sample of the reaction mixture with 60% of the theoretical amount of hydrogen peroxide gave IIα and IIβ in 5% yield in a 1/2 ratio. This is quite different from the 60/40 mixture obtained in the completely oxidized mixture. While it is possible that the β trimethylsilylethyl group is oxidized in preference to its α counterpart, this would not be expected based on findings which indicate that secondary groups are more easily oxidized than primary ones [5]. At present, a more attractive explanation lies in the assumption that the more alkylated boranes (i.e., R_3B) contain an excess of the β substitution. Since such trialkylboranes are known to be oxidized in preference to partially alkylated boranes (i.e., R_2BOR' or $RB(OR')_2$ [5], formation of IIβ would be favored over IIα.

From our results, the high regioselectivity of the dialkylboranes in the hydroboration of I is apparent. The increase in the amount of IIβ formed using a stoichiometric amount of hydride as compared to cases where excess hydride is used seems likely to be due to the conversion of dialkylboranes (III) to trialkyl derivatives such as IV.

---

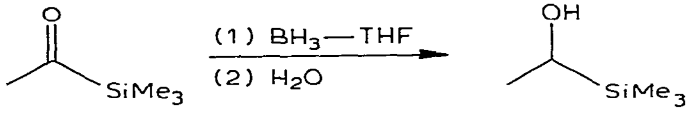
*This borane (b.p. 80°C/0.1 Torr) was isolated in 97% yield.

**The diol was analyzed by GC (Apiezon L) as the silylated derivative.

The failure of I to completely consume all of the active hydride indicates that certain boranes formed in these mixtures may be too hindered to react with this compound.

Using 9-BBN, the hydroboration/oxidation sequence effected the clean anti-Markovnikov hydration of I giving IIβ in 74% isolated yield.

However, none of the hydroborating reagents studied gave isomerically pure 1-trimethylsilylethanol (IIα). The previously reported route to this compound is long and difficult [6]. Consequently, a more convenient synthesis of this alcohol was desirable. Borane-THF has been found to quantitatively reduce ketones to the corresponding alcohols [8]. Indeed, acetyltrimethylsilane (IX)* undergoes clean reduction with this reagent giving IIα in 82% isolated yield.



(IX) (II α)

The following procedures were used for the preparation of these alcohols. To a cold (0°C) solution of borane-THF (26 ml, 1.62 *M*; 42 mmol) was added IX (4.8 g, 42 mmol) dropwise. After the addition was completed, water (30 ml) was carefully added (2.7 l of H_2 are evolved). Following separation of the aqueous layer (K_2CO_3 treated), the dried organic material was concentrated and distilled to give 4.2 g (82%) of IIα, b.p. 48—49°C/33 Torr (lit. [6] 127.3°C). This material contained no unreacted IX or isomeric IIβ by GC analysis. The isomeric IIβ was prepared by the addition of I (10.0 g, 100 mmol) to a stirred mixture of 9-BBN (12.2 g, 100 mmol) in THF (85 ml). After 1 h at room temperature, complete dissolution of the solid 9-BBN had occurred and no hydride activity could be detected. Ethanol (25 ml), water (10 ml), and 3.0 *N* NaOH (40 ml) were added followed by the slow, dropwise addition of 30% hydrogen peroxide (40 ml) (reaction temperature ~ 30—40°C). After the addition was complete, the mixture was heated at reflux temperature for 1 h. After the normal (K_2CO_3) workup, distillation gave 8.7 g (74%) of IIβ, b.p. 66°C/32 Torr (lit. [7] 95°C/100 Torr). In both of the above preparations, the reactions were carried out in a nitrogen atmosphere using oven-dried glassware.

Acknowledgment

The stimulating conversations and helpful suggestions of Professor H.C. Brown, Dr. J.L. Hubbard, Dr. S. Krishnamurthy, Mr. J. Campbell, Mr. S.U. Kulkarni, Mr. K.L. Thompson and Mr. K.K. Wang regarding this work are gratefully acknowledged. Support for this work from NCI Grant CA-19203 and NSF Grant CHE-76-20846 is appreciated.

---

*This compound was prepared in ca. 60% overall yield from the treatment of α-methoxyvinyllithium with trimethylsilyl chloride and subsequent hydrolysis of the adduct to give IX.

References

1 (a) D. Seyferth, J. Inorg. Nucl. Chem., 7 (1958) 152; (b) J. Amer. Chem. Soc., 81 (1958) 1844.
2 H.C. Brown and B.C. Subba Rao, J. Amer. Chem. Soc., 78 (1956) 2582; 78 (1956) 5694.
3 (a) D. Seyferth, H. Yamazaki and Y. Sato, Inorg. Chem., 2 (1963) 734; (b) M. Kumada, N. Imaki and K. Yamamoto, J. Organometal. Chem., 6 (1966) 490; (c) A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, J. Amer. Chem. Soc., 89 (1967) 431; (d) P.R. Jones and J.K. Myers, J. Organometal. Chem., 34 (1972) C9; (e) T.F.O. Lim, J.K. Myers, G.T. Rogers and P.R. Jones, ibid., 135 (1977) 249.
4 (a) H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Syntheses via Boranes, John Wiley and Sons, N.Y., 1975, p. 5; (b) ibid., p. 37—42.
5 G.W. Kabalka and S.W. Slayden, J. Organometal. Chem., 125 (1977) 273 and ref. cited therein.
6 A.D. Petrov, V.A. Ponomarenko, L.L. Mkhitaryan and A.D. Snegova, Dokl. Akad. Nauk SSSR, 100 (1955) 1107; Chem. Abstr., 49 (1955) 10166.
7 V.L. Speier, J.A. Webster and G.H. Barnes, J. Amer. Chem. Soc., 79 (1957) 974.
8 H.C. Brown, Boranes in Organic Chemistry, Cornell University Press, Ithaca, N.Y., 1972.
9 J.A. Soderquist and A. Hassner, J. Organometal. Chem., 156 (1978) 227.