A SIMPLE SYNTHESIS OF BORINANE‡

Herbert C. Brown* and Ganesh G. Pai

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907 U.S.A.

Abstract - Hydroboration of 1,4-pentadiene with two molar equivalents of 9-borabicyclo[3.3.1]nonane (9-BBN) in *n*-hexane and subsequent reaction of the trialkylborane so formed with one molar equivalent of the borane-tetrahydrofuran complex (BH_3·THF) or the borane-dimethyl sulfide complex (BMS) forms borinane with regeneration of the 9-BBN. Addition of 100% excess (with respect to borinane) of triethylamine (Et_3N) results in selective complexation of the amine with borinane. Cooling the reaction mixture to -78°C crystallizes out the uncomplexed 9-BBN (∿ 98% recovery). Treatment of the mother liquor with boron trifluoride-etherate (BF_3·OEt_2) removes the amine and liberates free borinane. Alternatively, 1,4-pentadiene can be hydroborated with the borinane-NEt_3 complex and the Et_3N pumped off from the trialkylborane product. BMS now generates pure borinane. The second procedure produces three moles of borinane from two, avoiding the necessity of a separation of products.

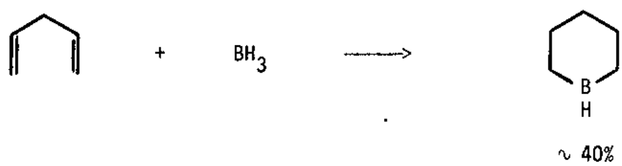
INTRODUCTION

9-BBN (1) is an extremely versatile, valuable reagent which is immensely useful in organic synthesis.[1] Its remarkable thermal and air stability, combined with its exceptionally high regio- and stereoselectivity in hydroboration and its low migratory aptitude, have made it a unique organoborane with wide applicability for syntheses *via* borane chemistry. However, in certain reactions involving free-radical mechanisms, as in the conjugate addition of organoboranes to α,β-unsaturated carbonyl compounds, 9-BBN is unsatisfactory. (Free-radicals rapidly attack the boron atom of the 9-borabicyclononane structure.) For such reactions, the utilization of boracyclanes, such as borinane (2), 3,5-dimethylborinane (3), and 3,6-dimethylborepane (4), solved the problem. All of these compounds had

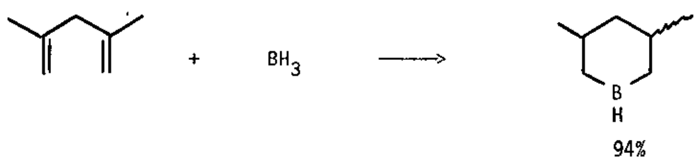
‡ Cordially dedicated to Professor Kyosuke Tsuda on the occasion of his 75th birthday.

(1) (2) (3) (4)

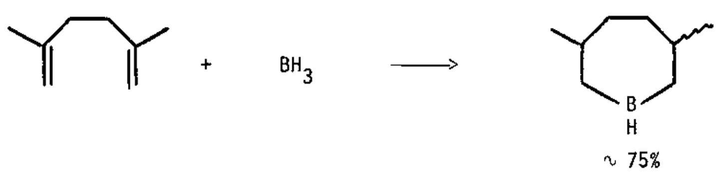
been prepared earlier *via* the cyclic hydroboration of the corresponding dienes[2] (eqs 1, 2, and 3).



(1)



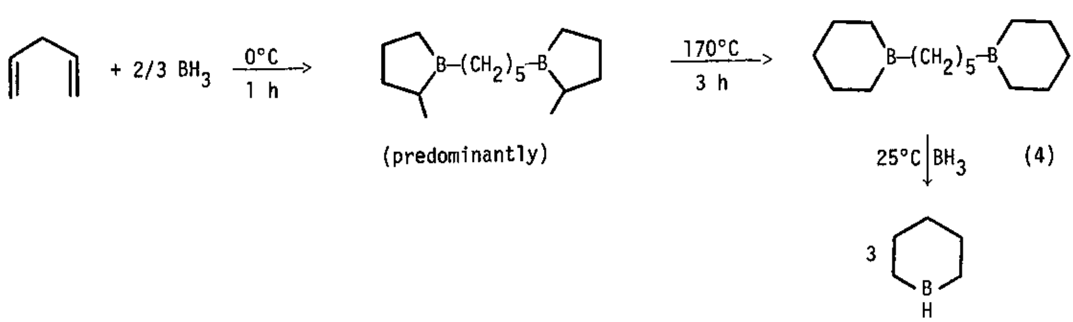
(2)



(3)

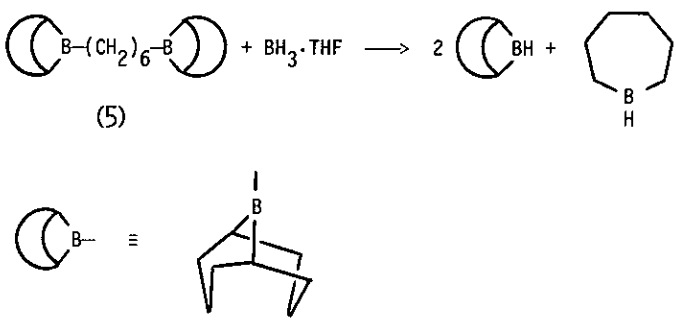
It is unfortunate that the yield is poorest with borinane, which has the most favorable characteristics for this and related applications.

Later on, Köster's method was improved by incorporating an isomerization step[3] (eq 4).



(4)

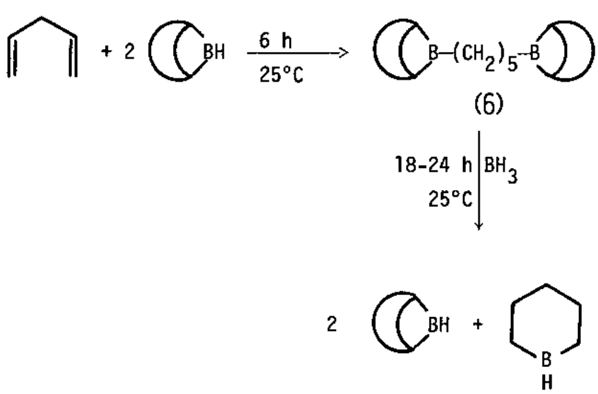
During the elucidation of the course of the hydroboration of 1,5-hexadiene with $BH_3 \cdot THF$, it was discovered in our laboratory that dumbbell-shaped compounds, such as 5, are cleanly converted to boracyclanes on treatment with $BH_3 \cdot THF$[4] (eq 5). We decided to examine the applicability of this method



(5)

to the synthesis of borinane.

The exceptionally high regioselectivity of 9-BBN cleanly forms the dumbbell-shaped compound (6) without any regio-isomers. Treatment of (6) with either BH_3·THF or BMS gave a mixture of 9-BBN and borinane (eq 6). The reaction is best followed by ^{11}B NMR. During hydroboration, one can see both

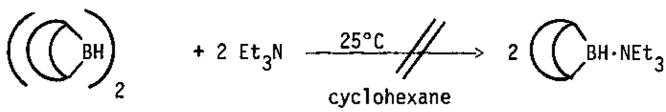


(6)

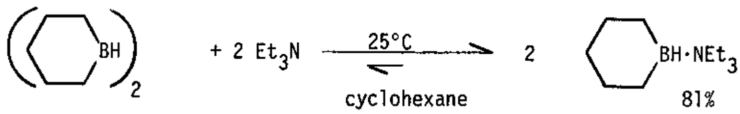
R_2BH and R_3B peaks (δ 27 and 84 respectively). Following completion of the hydroboration, only the R_3B peak is seen. During the cyclization stage, initially both the R_3B and the BH_3 peaks (δ -20 when BMS is used) are apparent. At the end of the redistribution, both of these peaks vanish and only the R_2BH peak is observed.

The reaction product consists of a mixture of two moles of 9-BBN and one mole of borinane. Initially we attempted to separate the borinane from the 9-BBN by fractional crystallization. However, none of the solvents examined, solvents such as THF, ether, dimethoxyethane, dioxolane, *n*-pentane, and *n*-hexane, effected a complete separation of the two. Generally, on cooling the reaction mixture to -78°C, about 70-80% of pure 9-BBN crystallized out. Concentration of the mother liquor and cooling to -78°C or even lower resulted in simultaneous precipitation of both dialkylboranes. Possibly, the two reagents form a mixed hydrogen-bridged dimer.

Next we turned our attention towards chemical methods. The structures of 9-BBN and borinane suggest that there could be a significant difference in their steric requirements which would affect their abilities to coordinate with amines. For example, it is known that 9-BBN does not form an adduct with Et_3N[5,6] in cyclohexane solution. On the contrary, borinane is about 80% associated with Et_3N[7] under comparable conditions (eqs 7 and 8). Consequently, it appeared that selective complexation



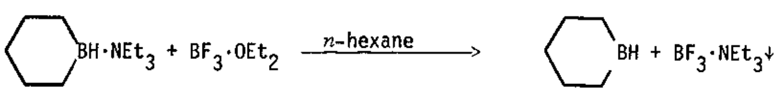
(7)



(8)

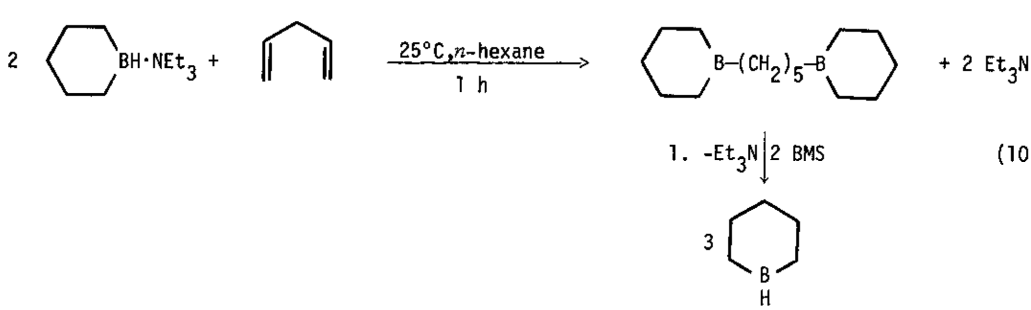
with Et_3N should be possible and thereby facilitate the separation. Accordingly, a reaction mixture with 9-BBN and borinane in the ratio of 2:1 was treated with 100% excess Et_3N with respect to the contained borinane. The ^{11}B NMR of the solution showed in addition to the original R_2BH peak at δ 27 (9-BBN and borinane) a peak at δ -2 (doublet) attributed to $R_2BH\cdot$amine. These two peaks were in a ratio of 2:1,[8] corresponding to a complete conversion of borinane into its adduct with the 9-BBN remaining unchanged. Fortunately, the borinane$\cdot NEt_3$ complex proved to be more soluble than borinane itself in *n*-hexane. Indeed, 98% of the 9-BBN used in the initial reaction could be recovered in fractional crystallization. This material was pure 9-BBN. Oxidation of the mother liquor showed that it contained ∿ 3% of 9-BBN and a nearly quantitative yield of borinane.

Two alternative procedures for obtaining pure borinane from its complex were developed. In the first method, the *n*-hexane mother liquor containing the complex is treated with $BF_3\cdot OEt_2$. The $BF_3\cdot NEt_3$ complex forms and separates, providing a *n*-hexane solution of free borinane (eq 9).



(9)

Alternatively, 1,4-pentadiene is treated directly with the complex. Hydroboration takes place readily at 25°C. The trialkylborane thus formed is only weakly associated with Et_3N and the latter can readily be removed under reduced pressure. Addition of BMS now generates borinane (eq 10).



(10)

Since borinane also exhibits high regioselectivity in hydroboration, no other isomeric products are formed. By this method, two moles of borinane are converted into three. In several cycles, the minor amount of 9-BBN in solution becomes negligible

EXPERIMENTAL SECTION

The IR spectra were recorded on a Perkin-Elmer 700 spectrophotometer. The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer and all chemical shifts are relative to $BF_3 \cdot OEt_2$ (0 ppm). GC analysis was performed on a Hewlett-Packard 5750 research chromatograph using a 6' x 1/4" 10% Apiezon L on Chromosorb W 60/80 column. Diols were analyzed as their bis-silyl ethers. 9-BBN was obtained from the Aldrich Chemical Company; 1,4-pentadiene was obtained from ChemSampCo and used without further purification. Triethylamine was distilled from calcium hydride and stored under nitrogen. *n*-Hexane was stirred over conc. sulfuric acid for several days and distilled from a small amount of lithium aluminum hydride and stored under nitrogen.

Method: An oven-dried, 50-mL centrifuge vial containing a magnetic stirring bar was capped with a rubber septum and cooled under nitrogen. The tube was charged with 3.1 g of solid 9-BBN (25 mmol). The vial was immersed in a water bath kept at 25°C and 10 mL of *n*-hexane and 1.29 mL of 1,4-pentadiene (12.5 mmol) was added. In the beginning, most of the 9-BBN was out of solution, but as the reaction proceeded, a homogeneous solution resulted. After 6 h, 1.3 mL of 9.6 *M* BMS (12.5 mmol) was added. As the reaction proceeded, 9-BBN started to come out of the solution. The reaction was allowed to proceed for 18 h. Triethylamine (3.48 mL, 25 mmol) was now added to the vial and it was cooled to -78°C in a Dry Ice-acetone bath. After 1 h, the vial was centrifuged quickly, reimmersed in the cooling bath, and the supernatant solution decanted with a double-ended needle. The residue was washed at -78°C once with a small amount of *n*-hexane and the washings transferred to the mother liquor. The residue was dried and weighed: 3.03 g (98%). A small amount of residue was oxidized by the standard method and the diol analyzed by GC. It showed only 1,5-cyclooctanediol.

Regeneration of Borinane. Method I: To the mother liquor so obtained was added 3.08 mL of $BF_3 \cdot OEt_2$ (25 mmol). After 5 min, the vial was cooled to 0°C and the clear upper layer was decanted using a double-ended needle. Evaporation of the solvents gave 1.02 g of a solid. It was analyzed by GC after oxidation and found to contain 96% 1,5-pentanediol and 4% 1,5-cyclooctanediol.

Method II: To the mother liquor 0.64 mL of 1,4-pentadiene (6.2 mmol) was added. After 1 h, the solvent and Et_3N were pumped off at 10 mm pressure. *n*-Hexane (5 mL) was added to the flask, followed by 0.66 mL of 9.6 *M* BMS (6.3 mmol). After 24 h, the reaction mixture was transferred to a 25-mL standard with *n*-hexane and made up to the mark. Hydride estimation established the strength of the solution to be 0.75 *M*. ^{11}B NMR showed a peak at δ 27. Addition of Et_3N shifted this peak to δ -2, leaving a small hump at δ 27. Oxidation and GC analysis showed 1,5-pentanediol and a small amount ($\sim$ 3%) of 1,5-cyclooctanediol. A sample of the borinane was sublimed: mp 52-55°; IR (*n*-

hexane): 1560 cm^{-1}.

ACKNOWLEDGEMENT

Financial support from the National Institutes of Health (GM 10937-19) is gratefully acknowledged.

REFERENCES

1. H. C. Brown and C. F. Lane, Heterocycles, 1977, **7**, 453; G. W. Kramer and H. C. Brown, Heterocycles, 1977, **7**, 487.
2. R. Köster, Angew. Chem., 1960, **72**, 626; R. Köster, Advan. Organometal. Chem., 1964, **2**, 257; E. Negishi and H. C. Brown, J. Am. Chem. Soc., 1973, **95**, 6757.
3. H. C. Brown and E. Negishi, J. Organomet. Chem., 1971, C67; E. Negishi, P. L. Burke, and H. C. Brown, J. Am. Chem. Soc., 1972, **94**, 7431.
4. P. L. Burke, E. Negishi, and H. C. Brown, J. Am. Chem. Soc., 1973, **95**, 3654.
5. H. C. Brown and K. K. Wang, Rec. Trav. Chim. Pays-Bas, 1979, **98**, 117.
6. In THF solution there is about 15% association. H. C. Brown and S. U. Kulkarni, Inorg. Chem., 1977, **16**, 3090.
7. H. C. Brown and G. G. Pai, J. Org. Chem., submitted.
8. In general, quantitative integration of peaks is not possible in ^{11}B NMR. However, in this case, the ^{11}B result was found to be in agreement with the value obtained by GC analysis of the diols.

Received, 20th July, 1981