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Preliminary communication

A simple synthesis of bisborinane and its applicability in hydroboration for the preparation of *B*-alkylborinanes

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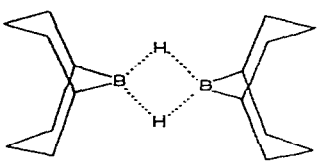
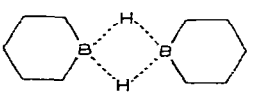
The hydroboration of 1,5-cyclooctadiene provides a convenient route to 9-borabicyclo[3.3.1]nonane (9-BBN) (I)[1] and this reagent has proven very valuable in applying the new chemistry of organoboranes for synthetic requirements[2]. Certain new developments in our laboratories made it desirable to have bisborinane (II) readily available as a reagent for certain reactions where 9-BBN was not applicable.

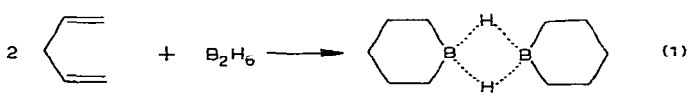


(I)



(II)

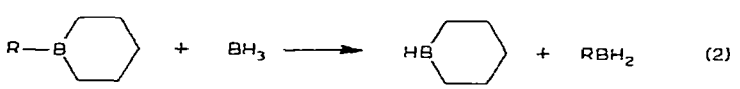
It has been reported that bisborinane can be prepared by the hydroboration of 1,4-pentadiene[3,4] (eq. 1). Unfortunately, no details have been reported. In our hands the



(1)

method was unsatisfactory, yielding only ~ 40% of bisborinane. Apparently hydroboration of the diene proceeds preferentially to give the five-membered heterocycle[5].

An alternative route would be the treatment of *B*-alkylborinane with borane[6] (eq. 2). This approach has been used for certain related conversions of *B*-alkylboracyclanes



(2)

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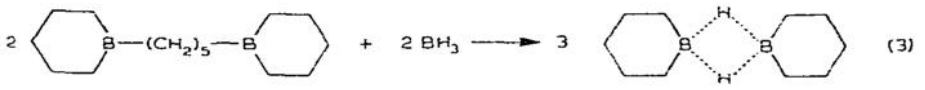
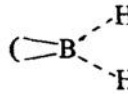
to the corresponding boracyclanes[4]. However, in order to utilize the boracyclane for hydroboration, it is often essential to separate it from the alkylboranes formed simultaneously. This introduces major difficulty into the procedure.

It occurred to us that this difficulty might be avoided by utilizing 1,5-bis(1'-borinyl)pentane (III)[7]. If the chain moiety readily cyclized to form bisborinane, there would be no active hydroborating side-product to be separated (eq. 3). Indeed, this procedure works quite satisfactorily.



(3)

(III)

A convenient route to III involves hydroboration of 1,4-pentadiene with borane in tetrahydrofuran (THF) in the 3/2 molar ratio, followed by isomerization for 3 h at 170° ★. The product III was then treated with the theoretical quantity of borane in THF at 25°. A rapid exchange reaction took place as indicated by the disappearance of the strong band at 2400 cm^{-1} (BH_3/THF) as well as by the appearance of a strong band at 1560 cm^{-1} (). The reaction reached a steady state in 3 h and no further detectable change was observed for at least 72 h at 25°. GLPC examination of a methanolyzed aliquot indicated the formation of *B*-methoxyborinane in 80% yield. Evaporation of the solvent yielded a crystalline material. Pure bisborinane was obtained by sublimation, m.p. 52–54°. The substance was identified by analyses of the oxidation products (1,5-pentanediol (94%) and boric acid (101%)), analysis of active hydride by methanolysis (95%) and GLPC analysis of the resultant *B*-methoxyborinane (97%), and IR (1560 s cm^{-1}).

No difficulty was encountered in preparing various *B*-alkylborinanes in excellent yields by the hydroboration of olefins with bisborinane at 25°. The hydroboration products were identified by the comparison of GLPC retention times with those of authentic samples prepared and fully identified earlier[8]. The results of preparation of *B*-alkylborinanes are summarized in Table 1.

In cases in which *B*-alkylborinanes are required as intermediates, isolation of neither bisborinane nor *B*-alkylborinanes is necessary. The crude product in the reaction mixture appears to contain approximately 20% of impurities. Loss of olefin through side reaction with these impurities can be avoided by using a modest excess (25–50%) of the solution containing bisborinane. Apparently the hydrides in the impurities are less reactive, so that the olefins react preferentially with the bisborinane to form the corresponding *B*-alkylborinanes in nearly quantitative yields based on the olefins without being contaminated with the isomeric impurities. Excess reagent is conveniently destroyed with water or alcohol prior to isolation or further use of the *B*-alkylborinanes.

The following procedure has been employed for the preparation of bisborinane

★ On oxidation, 1,5-pentanediol was obtained in 80% yield. Minor quantities of 1,4-pentanediol and 1-pentanol were also obtained.

TABLE 1

SYNTHESIS OF *B*-ALKYLBORINANES

B-Alkylborinane	Yield (%) [a]		B.p. (°C (mm))
	GLPC	Isolated	
B-(n-Butyl)borinane	90	79	78–81 (18)
B-(n-Pentyl)borinane	93	81	92–95 (20)
B-(sec-Butyl)borinane	88	73	64–67 (20)
B-Cyclopentylborinane	91	75	97–100 (19)
B-Cyclohexylborinane	93	90	115–118 (20)
B-(*exo*-Norbornyl)borinane	91	76	128–130 (20)

[a] Based on olefins.

solution in THF. In a distillation set-up with a 300-ml three-necked flask which had a septum inlet, a magnetic stirrer, and a thermometer-well were placed 20.4 g (300 mmoles) of 1,4-pentadiene and 100 ml of THF. Borane in THF (2.2 *M*, 91 ml, 200 mmoles) was added over 30 min at 0°. One hour later the solvent was evaporated at a diminished pressure and the residue heated at 170° (bath temperature) for 3 h. After cooling 45.5 ml of 2.2 *M* borane (100 mmoles) was added at room temperature and the concentration was adjusted to 2.0 *M* in active hydride by the addition of THF. In a typical hydroboration experiment, 2.46 g (30 mmoles) of cyclohexene in 30 ml of THF was added to 20 ml of the above-obtained 2.0 *M* bisborinane solution at 20–25°. After stirring the reaction mixture at 25° for 2 h, the residual hydride was destroyed with 0.18 ml (10 mmoles) of water. GLPC examination indicated the presence of 29 mmoles (93% based on cyclohexene) of *B*-cyclohexylborinane which was essentially free from isomeric impurities. Distillation provided 4.4 g (90%) of *B*-cyclohexylborinane, b.p. 115–118° (20 mm).

The present simple synthesis of bisborinane not only permits a convenient and general synthesis of *B*-alkylborinanes but provides the basis for a further study as to its utility as a valuable new reagent for syntheses via hydroboration and for selective reductions.

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