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Preliminary communication

A simple synthesis of bis(3,5-dimethyl)borinane and bis(3,6-dimethyl)-borepane as new valuable reagents via cyclic hydroboration

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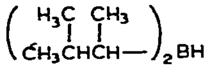
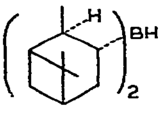
In the past decade various dialkylboranes, such as disiamylborane (I), diisopinocampheylborane (II), and 9-borabicyclo[3.3.1]nonane (9-BBN) (III), have been developed as useful reagents[1,2]. All of these dialkylboranes (I–III) have two secondary alkyl groups attached to the boron atom. Certain new developments in our laboratories made it desirable to have relatively unhindered dialkylboranes with two primary alkyl groups attached to a boron atom.

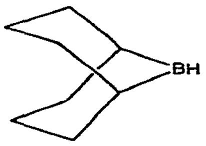


$(CH_3CH(CH_3)CH(CH_3)-)_2BH$

(I)

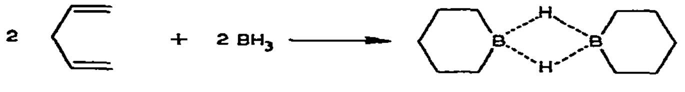


(II)



(III)

Recently, we reported a convenient synthesis of such a dialkylborane, bisborinane (IV)[3]. Although the preparation is relatively simple, it does require an isomerization of the organoborane intermediate at an elevated temperature (170°)[3]. It would be nice to avoid such a stage. Various attempts to realize a simple cyclic hydroboration of 1,4-pentadiene to form IV, as shown in eq. 1, have been unsuccessful.



(1)

(IV)

Similar difficulties have also been encountered with 1,5-hexadiene. In these systems the problem apparently arises from the fact that closure of the ring proceeds to attach the

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TABLE 1

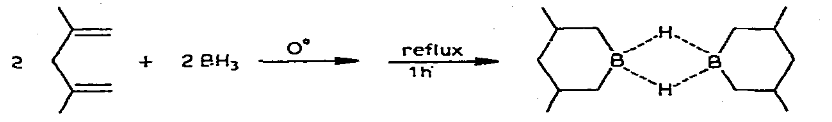
CHARACTERIZATION OF BIS(3,5-DIMETHYL)BORINANE, BIS(3,6-DIMETHYL)BOREPANE, AND THEIR ALKOXY DERIVATIVES

Bisbora-cyclane [a]	Yield [b] (%)	B.p.(°C/mm)	$\nu(\supseteq B \overset{H}{\underset{H}{\cdots}} B \subseteq)$ (cm^{-1})	*B*-Methoxy-boracyclane [a,c] B.p. (°C/mm)	*B*-(2-Dimethyl-aminoethoxy)-boracyclane [a,c,d] B.p.(°C/mm)	n_D^{20}
3,5-DMB-6 [c]	94(87) [e]	79–82(1)	1565	59–60(18)	110(3)	1.4835
3,6-DMB-7 [f]	84 [g]	–	1560	76–79(20)	104–105(1)	1.4825

[a] Presumably a mixture of *cis* and *trans* isomers. No attempt was made to determine the *cis*-to-*trans* ratio. [b] By GLC analysis of the reaction mixture after methanolysis. [c] The compound yielded satisfactory spectral data. [d] Correct elemental analyses were obtained. [e] By isolation. [f] The compound was not isolated. [g] The figure indicates the total yield of the cyclic products which contain ~6% of a ring-contracted isomer.

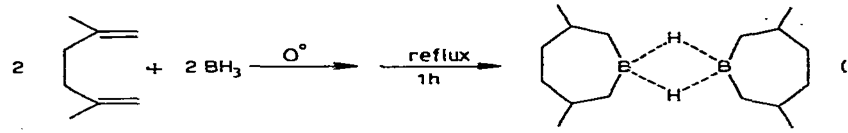
boron atom to a considerable extent at the secondary position[4].

It occurred to us that this problem might be circumvented by utilizing the greater directive effect of the $-C(CH_3)=CH_2$ moiety in hydroboration[1]. Indeed, the hydroboration of commercially available 2,4-dimethyl-1,4-pentadiene[★] and 2,5-dimethyl-1,5-hexadiene[★] with borane in THF followed by heating under reflux (~ 70°) for 1 h provides cleanly and in excellent yields bis(3,5-dimethyl)borinane (3,5-DMB-6) (V)[★★] and bis(3,6-dimethyl)borepane (3,6-DMB-7) (VI), respectively (eq. 2 and 3).



(V)

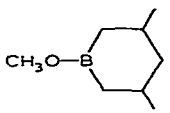
(2)



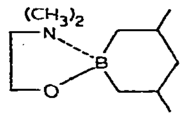
(VI)

(3)

The preparations of 3,5-DMB-6 and 3,6-DMB-7 are exceedingly simple, as indicated by the following procedure for 3,5-DMB-6. To 55.6 ml (200 mmoles) of 3.61 *M* borane in THF and 16 ml of THF in a 200 ml flask was added 19.2 g (200 mmoles) of 2,4-dimethyl-1,4-pentadiene at 0°. The reaction mixture was then refluxed at ~ 70° for 1 h[★★★]. The resultant mixture contained 94 mmoles (94% by GLC after methanolysis) of 3,5-DMB-6 and was used as its stock solution, A 25 ml (25 mmoles) aliquot was distilled to yield 4.8 g (87%) of 3,5-DMB-6. The substance was fully identified by the analyses of the oxidation products (2,4-dimethyl-1,5-pentanediol and boric acid), the active hydride analysis by methanolysis, the GLC analysis of the resultant *B*-methoxy-3,5-DMB-6 (VII), and the conversion into a stable derivative VIII which yielded the correct elemental analyses.



(VII)



(VIII)

The preparation of 3,6-DMB-7 was carried out in a similar manner. Although 3,6-DMB-7 was not isolated, it was fully characterized. The data for 3,5-DMB-6, 3,6-DMB-7, and their alkoxy derivatives are summarized in Table 1.

[★] Chemical Samples Co., Columbus, Ohio 43221 (U.S.A.)

[★★] It has been previously obtained by the hydroboration of 2,4-dimethyl-1,3-pentadiene with a certain dialkylborane followed by thermal isomerization and treatment with diborane[5].

[★★★] Although the hydroboration was over as soon as the addition of the diene was complete, GLC examination after methanolysis indicated the presence of 3,5-DMB-6 in only ~50% yield. It required 24 h at 25° to observe a yield of 89%, or 1 h at 70° for a yield of 94%.

The hydroboration of many representative olefins, such as 1-hexene, 1-octene, isobutylene, 2-butene, 2-methyl-2-butene, cyclopentene, and norbornene, with a modest excess (25–50% in active hydride) of a solution containing 3,5-DMB-6 or 3,6-DMB-7 was quite rapid, being essentially over within 1–2 h at 25°. After the usual oxidation with 30% hydrogen peroxide and 3 *N* sodium hydroxide, the corresponding alcohols were obtained in 95–100% yields (by GLC). The isomeric purity of 1-hexanol and 1-octanol obtained in this manner was ~ 99%, indicating that both 3,5-DMB-6 and 3,6-DMB-7 provide considerable control over the direction of hydroboration. With less reactive olefins, such as cyclohexene and 2,3-dimethyl-2-butene, the hydroboration was slower, requiring 4–8 h with cyclohexene and 16–24 h with 2,3-dimethyl-2-butene.

It is important to note that the hydroboration of olefins with 3,5-DMB-6 or 3,6-DMB-7 is essentially free of disproportionation, yielding the corresponding *B*-alkylboracyclanes in nearly quantitative yields. This is indicated by the results realized in hydroborating 1-hexene and cyclopentene with 3,5-DMB-6 and 3,6-DMB-7 (Table 2).

TABLE 2

SYNTHESIS OF *B*-ALKYL-3,5-DIMETHYLBORINANES AND *B*-ALKYL-3,6-DIMETHYLBOREPANES

B-Alkylboracyclane [a]	Yield (%)		
	GLC	Isolated	B.p. (°C/mm)
B-(n-Hexyl)-3,5-dimethylborinane [b]	95	90	122–124(17)
B-Cyclopentyl-3,5-dimethylborinane [b]	93	84	112–114(17)
B-(n-Hexyl)-3,6-dimethylborepane [c]	97	89	108–112(3)
B-Cyclopentyl-3,6-dimethylborepane [c]	98	91	96–100(3)

[a] Identified by GLC analyses of the oxidation products. Satisfactory PMR and IR spectra were also obtained. [b] The compound contains ~ 1% of a ring-contracted isomer. [c] The compound contains ~ 10% of a ring-contracted isomer.

Therefore these readily available bisboracyclanes, V and VI, are highly selective hydroborating agents, allowing quantitative conversion of olefins into the desired anti-Markovnikov alcohols or into the corresponding *B*-alkylboracyclanes. The latter are applicable as highly useful intermediates in various reactions where the corresponding *B*-alkyl-9-BBN cannot be applied[6].

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