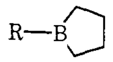
$R—B(CH_2CH_2CH_2CH_3)_2$

2



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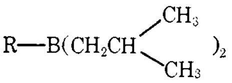
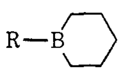


$R—B(CH_2CH(CH_3)_2)_2$

3



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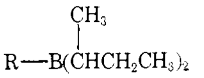
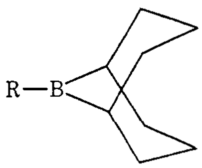


$R—B(CH(CH_3)CH_2CH_3)_2$

4



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tetraisopropyldiborane yielded extensively scrambled mixtures of all of the possible trialkylboranes.[5] Possibly in the present procedure the rapid *in situ* conversion of the dialkylborane intermediate into the more stable trialkylborane is primarily responsible for circumventing this difficulty.

The following procedure for the preparation of B-(*n*-pentyl)borinane and 1-(*n*-pentyl)cyclohexanol is representative. In a 300-ml three-necked flask equipped with a mechanical stirrer, a septum inlet, a thermometer well, and reflux condenser connected to a mercury bubbler were placed 7.0 g (100 mmol) of 1-pentene, 50 ml of THF, 2.28 g (20 mmol) of *n*-octane as a standard, and 24 ml of 1.38 *M* lithium aluminum hydride (33.3 mmol) in THF. To this was added over *ca.* 10 min 11.2 g (100 mmol) of B-methoxyborinane[6] at 25–30°. The uptake of 1-pentene was *ca.* 90% over in 1 hr. Two hours later, 6.9 g of 96% sulfuric acid (67 mmol) was slowly added at 0–10°, followed by the addition of *ca.* 5 ml of water and 25 ml of hexane. A clear supernatant solution resulted and the precipitate formed hail-like particles, allowing an easy transfer of the supernatant solution by means of a syringe. The precipitate was washed two–three times with hexane (10 ml each). Glpc examination of the combined solution on an SE-30 column indicated the presence of 89 mmol (89%) of B-(*n*-pentyl)borinane contaminated with *ca.* 5 mmol of B-*n*-pentyl-2-methylborolane.

One-half of the mixture was directly subjected to distillation to yield 5.4 g (71%) of *ca.* 95% pure B-(*n*-pentyl)borinane: bp 92–95° (20 mm); pmr (CCl_4, TMS) δ 0.83 (triplet, 3 H) and 1.0–1.8 (broad doublet-like multiplet, 18 H). The remaining mixture was carbonylated at 150° and 1000 psi after addition of 4.5 ml (*ca.* 75 mmol) of ethylene glycol. After a constant pressure was observed at 150° (*ca.* 3 hr), the reaction mixture was cooled and oxidized with 25 ml of 6 *N* sodium hydroxide, 25 ml of 30% hydrogen peroxide, and 25 ml of 95% ethanol at *ca.* 30° followed by heating at 50° for 1 hr. Glpc analysis indicated the presence of 1-(*n*-pentyl)cyclohexanol in 85% yield based on 1-pentene or B-methoxyborinane. 1-(*n*-Pentyl)cyclohexanol was obtained in a separate run using a distilled sample of B-(*n*-pentyl)borinane in 88% yield (95% by glpc): bp 83–85° (3 mm); $n^{20}D$ 1.4656; ir (neat) 3440 cm^{-1}; pmr (CCl_4, TMS) δ 0.9 (triplet, 3 H), 1.1–1.8 (doublet-like multiplet, 18 H), 2.2 (singlet, 1 H).

Consequently, the present results indicate that a wide variety of mixed organoboranes can be prepared and utilized without the complication of extensive disproportionation, thereby adding to the utility of the carbonylation reaction for the preparation of a wide variety of carbon structures.

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[5] R. Köster, G. Griaznow, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, **672**, 1 (1964).

[6] B-Methoxyborinane, bp 68–69° (90 mm), was prepared by the reaction of 1,5-bis(1′-borinyl)pentane, obtained by the hydroboration of 1,4-pentadiene followed by thermal treatment at 170°, with dry trimethyl borate in the presence of borane in THF (5 mol % in hydride) as catalyst at *ca.* 120°.[3c–e]

[7] Postdoctoral research associate on Grant No. DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

[8] Postdoctoral research associate on a research grant (GM 10937) supported by the National Institutes of Health.

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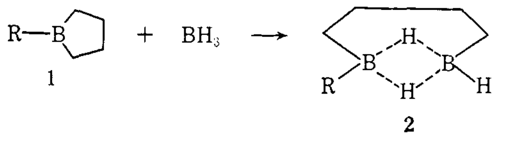
A Facile Opening of the Borolane Ring with Borane. A Simple Entry into 1,2-Tetramethylenediboranes

Sir:

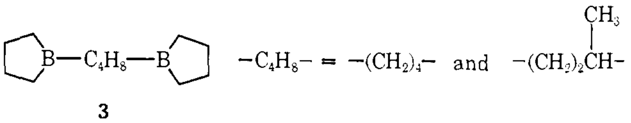
We wish to report a remarkably facile opening of the borolane ring of B-alkylborolanes (**1**) with borane (eq 1). The reaction not only indicates an unusual chemical reactivity of the borolane ring, but also provides a simple route to a novel class of compounds, the 1-alkyl-1,2-tetramethylenediboranes (**2**), with unusual and unique properties.



(1)

a, R = $n\text{-}C_4H_9$–
b, R = $n\text{-}C_8H_{17}$–

During a detailed examination of the hydroboration of 1,3-butadiene, it was discovered that the 1:1 product obtained by the addition of 1 mol of borane in tetrahydrofuran (THF) to an equimolar quantity of 1,3-butadiene is almost entirely polymeric.[1] On the other hand, the 3:2 product obtained by using only the theoretical quantity of borane, two-thirds of that utilized above, is largely a mixture of monomeric dumbbell-shaped compounds (**3**).[2] These results suggested that **3** must be susceptible to the action of borane. This observation, coupled with a new simple entry[3] into the B-alkylborolanes, led us to study this reaction of B-alkylborolanes (**1**) with borane in detail.



$-C_4H_8- = -(CH_2)_4-$ and $-(CH_2)_2CH(CH_3)-$

3

Treatment of B-(*n*-butyl)borolane (**1a**) with an equimolar quantity of borane in THF at 25° resulted in the essentially complete reaction of borane within 15 min, as revealed by the disappearance of the strong

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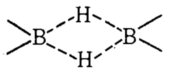
[1] (a) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962); (b) E. Breuer and H. C. Brown, *ibid.*, **91**, 4164 (1969).

[2] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460 (1970).

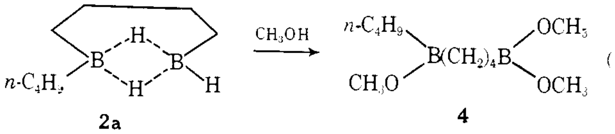
[3] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 6648 (1970).

band at 2400 cm^{-1} of borane in the infrared spectrum of the reaction mixture.[4] An extensive formation of the double hydrogen bridge



was indicated by the presence of a strong band at 1570 cm^{-1}, a band which was totally absent in the spectrum of either **1a** or borane in THF. A medium absorption at 2510 cm^{-1} for a single terminal B–H bond was also observed.

Glpc examination[5] of the reaction mixture after quenching with 100% molar excess of methanol at 25° indicated the presence of essentially one peak. Upon distillation of the methanolysis product, 1-(*n*-butyl)-methoxyboryl-4-dimethoxyborylbutane (**4**) was obtained in 85% yield (94% by glpc): bp 74–75° (0.5 mm); $n^{20}D$ 1.4285; ir (neat) 1330 cm^{-1} (s) with a shoulder at 1360 cm^{-1}; pmr (CCl$_4$) δ 0.6–1.1 (multiplet, 9 H), 1.1–1.6 (multiplet, 8 H), 3.50 (6 H), and 3.68 (3 H) ppm. *Anal.* Calcd for $C_{11}H_{26}B_2O_3$: C, 57.96; H, 11.50; B, 9.48. Found: C, 58.03; H, 11.48; B, 9.23.

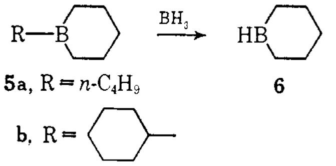


2a **4** (2)

These results clearly support the formulation given in eq 1, and rule out the alternative reaction path to form borolane (eq 3). Similar observations were made also with B-(*n*-octyl)borolane (**1b**).

(3)

In marked contrast, the reaction of B-alkylborinanes (**5**) with borane does not involve an opening of the borinane ring. Instead, the alkyl group migrates to the borane moiety. Thus, reaction of either B-(*n*-butyl)borinane (**5a**) or B-cyclohexylborinane (**5b**) with



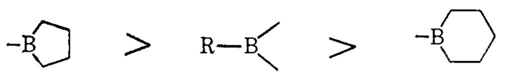
(4)

5a, R = *n*-C_4H_9 **6**

b, R =

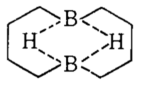
an equimolar quantity of borane at 25° results in nearly complete disappearance of the starting B-alkylborinanes with quantitative formation of borinane (**6**), observed by glpc as B-methoxyborinane after treatment with methanol. Completion of the reaction requires approximately 3 hr with **5a** and 6 hr with **5b**.

These results clearly establish the following order of reactivity of various types of B–C bonds toward borane.



R = alkyl

Ordinary mono- and dialkylboranes react readily with both methanol and terminal olefins. Indeed, 1,6-diboracyclodecane (**7**)[1b] was originally assigned its unusual structure because of its unique inertness in these reactions. Quite interestingly, treatment of **2b** at 25° with the calculated quantity of 1-octene to achieve complete hydroboration resulted in a reaction which proceeds rapidly to 33% completion. The uptake of 1-octene then becomes quite slow. On the other hand, the reaction of **2b** with water or methanol is rapid and complete for all three hydrides, the reactions being essentially complete in 15 min at 25°. These unusual results may be best interpreted in terms of the usual rapid addition of the terminal B–H bond to 1-octene to form **8**, followed by a very sluggish further reaction of the olefin with the B–H bonds of the double hydrogen bridge. Thus this monocyclic diborane derivative (**8**) is approaching the great inertness of the bicyclic derivative **7**.



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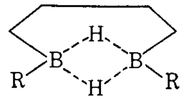

8, R = alkyl

The facile opening of the borolane ring with borane as well as the unusual reactivity exhibited by the ring-opened product have proved to be major factors in understanding the fascinating phenomena encountered in the hydroboration of 1,3-butadiene, pentadienes, and other related dienes, phenomena which have been highly puzzling in the past.

The borolane ring is highly reactive in many other reactions. Thus, the reaction of B-phenylborolane with isobutyl alcohol or with *n*-butyl mercaptan ruptures the borolane ring to form the corresponding derivatives of *n*-butylphenylborane.[6a] Similarly, bromine opens the borolane ring in B-(*n*-butyl)borolane pyridinate.[6b] Moreover, in contrast to other trialkylboranes, **3** is highly susceptible to water and other protic solvents.[2] Subsequent studies have established that the facile solvolysis is a consistent property of the B-alkylborolanes. For example B-(*n*-butyl)borolane (**1a**) is hydrolyzed completely to di-*n*-butylborinic acid within 3 hr by refluxing in THF with 10 molar excess of water.[2] On the other hand, representative B-alkylborinanes, such as **5a** and **5b**, are quite stable and do not react with water to any detectable extent in 24 hr in THF under the same conditions.

It is now clear that the borolane ring moiety of B-alkylborolanes (**1**) possesses high reactivity toward various reagents. This reactive nature must be taken into consideration in utilizing the B-alkylborolanes in various syntheses, such as the carbonylation reaction

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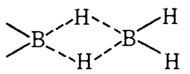
[4] A peak near 2600 cm^{-1} due to the double terminal B–H bonds of a substituted diborane



was also absent. For detailed information on the infrared spectra of alkyldiboranes and borane, see (a) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, 17, 396 (1961); (b) G. J. Klender, Ph.D. Thesis, Purdue University, 1961.

[5] Glpc examination was carried out on a 2-ft SE-30 column using a block temperature of 150°.

[6] (a) B. M. Mikhailov and V. A. Dorokhov, *Dokl. Akad. Nauk SSSR*, 133, 119 (1960); (b) B. M. Mikhailov and L. S. Vasil'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2586 (1967).

and the 1,4-addition reaction with α,β-unsaturated carbonyl compounds,[7] as well as in their preparation.[3]

Although we have not established the precise physical basis for these facile ring opening reactions, the strain present in the borolane ring, attributable largely to the sp^2 hydridization of the boron atom, appears to be primarily responsible for the greater reactivity. However, the possibility must also be considered that the additional stability of the double hydrogen bridge of 1,2-tetramethylenediboranes (**2** and **8**), as evidenced by its relatively low reactivity toward terminal olefins, may also be playing an important role in the ease of the ring opening reaction with borane.

(7) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, E. Negishi, and S. K. Gupta, *Chem. Commun.*, 1009 (1969).

(8) (a) Postdoctorate research associate on a research grant (DA 31-124 ARO(D) 453) supported by the U. S. Army Research Office (Durham). (b) Graduate assistant on a research grant (GM 10937) supported by the National Institutes of Health.

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Nuclear Magnetic Resonance in Paramagnetic Solution. Carbon-13 Contact-Shift Studies of Pyridine, Aniline, and Triphenylphosphine Complexed with Nickel(II) Acetylacetonates

Sir:

Recently nmr contact shifts have been extensively studied for various paramagnetic systems, including transition metal complexes and organic free radicals.[1] Most of these studies have dealt with the proton shift, and major problems in this area involve the interpretation of the mechanism of electron spin delocalization onto the ligand molecule and the determination of the sign and magnitude of the electron spin density on the proton. The present report deals with the ^{13}C contact shifts for pyridine- and aniline-type bases, induced by the formation of complexes with paramagnetic nickel(II) acetylacetonate (Ni(AA)$_2$). These molecules have been shown by proton contact-shift studies to be typical σ- and π-type bases,[1d,2] respectively. It is hoped that ^{13}C contact-shift studies will yield useful information about the electron spin distribution on the carbon skeleton, thus providing a powerful new tool for investigating the molecular and electronic structures of paramagnetic complexes.

We have observed ^{13}C chemical shifts for the σ-type bases pyridine, methyl-substituted pyridines, and piperidine, and for the π-type bases aniline and triphenylphosphine, perturbed by Ni(AA)$_2$. The perturbation of the ^{13}C nmr spectra of pyridine and triphenylphosphine by Ni(AA)$_2$ is shown in Figures 1 and 2. The spectra were measured at room temperature on a JEOL-C60-HL spectrometer at 15.1 MHz using a fully proton-decoupled ^{13}C nmr technique.[3] In the spectra of the diamagnetic solution a, each carbon

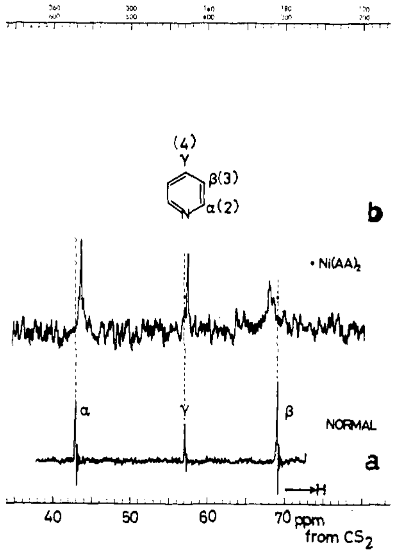

Figure 1. Proton-decoupled ^{13}C nmr spectra (at 15.1 MHz) of pyridine: (a) pyridine alone (single scan), (b) in the presence of Ni(AA)$_2$ (0.3 *M*).

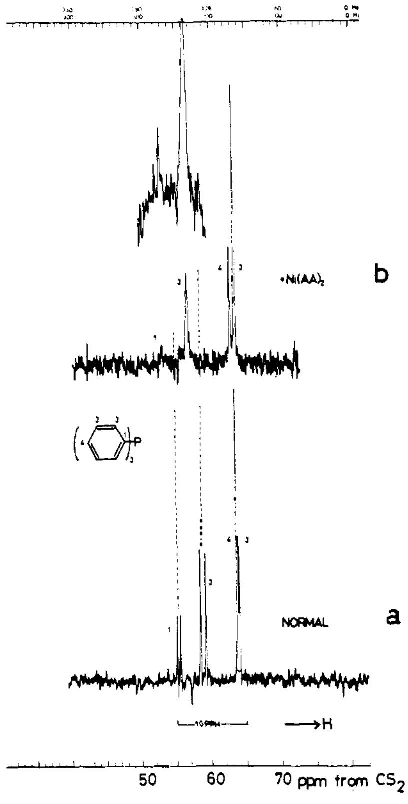

Figure 2. Proton-decoupled ^{13}C spectra (at 15.1 MHz) of triphenylphosphine in CDCl$_3$: (a) the diamagnetic solution (3 *M* in CDCl$_3$, single scan) [the splittings are due to P–C spin coupling ($J_{\text{P-C}_1} = 10, J_{\text{P-C}_2} = 16, J_{\text{P-C}_3} = 5$, and $J_{\text{P-C}_4} = 0$ Hz]; (b) in the presence of 0.3 *M* Ni(AA)$_2$ (single scan) (the P–C couplings disappear due to decoupling by paramagnetic complex formation).

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(1) (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) E. De Boer and H. Nan Willigen, "Progress in NMR Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1967, p 111; (c) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jap*, **43**, 379 (1970); (e) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, in press.

(2) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

(3) Completely proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a JEOL-C60-HL spectrometer equipped with an IS-60 field-frequency synchronous sweep system of the proton irradiation frequency and an SD-HC heteronuclear spin decoupler. Spectra were also measured with the external field locking mode. Samples were made in 50% (v/v) CDCl$_3$ solution in 8-mm sample tubes. For the