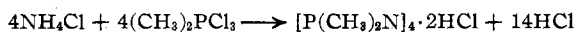
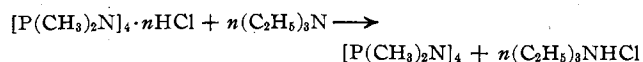


very cryptic.¹ In this reaction an enormous amount of HCl is produced, *viz.*

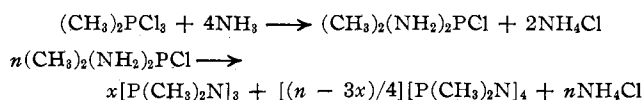


Our work indicates that it is crucial in order to obtain good yields that this HCl be efficiently removed. Hence the continuous sweeping with nitrogen followed by pumping are of vital importance. The removal of the remaining HCl by treatment with triethylamine is then very facile



It is also worth stressing that method I has the advantage of giving pure tetramer, uncontaminated with trimer.

Method II.—This method is new although the approach was suggested by previously reported direct ammonolysis reactions.^{8,9} It provides an efficient route to the intermediate $(\text{CH}_3)_2(\text{NH}_2)_2\text{PCl}$ which can then be used as previously described by Sisler and Frazier.² The equations are



This route differs from that in method I by providing, in roughly equimolar quantities, both the trimer and the tetramer, which can be separated by fractional crystallization.

Acknowledgment.—We are grateful to the National Science Foundation for financial support.

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The Preparation of Hexaborane(10) from Octahydropentaborate(1-) Salts

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The preparation and characterization of alkali metal octahydropentaborate(1-) salts have been described.¹⁻⁷ Addition of B_2H_6 to LiB_5H_8 is a potentially useful reaction in that it can yield B_6H_{10} and $\text{B}_{10}\text{H}_{14}$.⁸ We describe herein the preparation of B_6H_{10} in a procedure which offers substantial advantages over previously published methods.⁸⁻¹³

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Experimental Section

Methods and Materials.—Standard vacuum-line techniques were used in the manipulation of volatile materials. Nonvolatile materials were transferred in a drybox in a nitrogen atmosphere. Pentaborane(9) and diborane(6) were obtained from the Callery Chemical Co. and used directly. Solutions of LiCH_3 in diethyl ether were purchased from Foote Chemical Co. and had known concentrations in the range 1.5–1.7 *M*. Reagent grade diethyl ether was dried over LiAlH_4 and distilled and stored under vacuum in a glass bulb equipped with a Fisher-Porter Teflon valve. Dimethyl ether was obtained in a cylinder from the Matheson Co. and used directly.

Preparation of LiB_5H_8 Solutions.—In typical syntheses, 30-mmol quantities of LiB_5H_8 were prepared in $(\text{CH}_3)_2\text{O}$ or $(\text{C}_2\text{H}_5)_2\text{O}$ solutions. In a drybox, a carefully measured volume of LiCH_3 -ethyl ether solution (about 20 ml of a 1.5 *M* solution) was syringed into a 100-ml reaction flask which contained a Teflon-covered stirring bar (this vessel must be of adequate volume to contain the foam produced by the rapid evolution of methane in the reaction). The flask was fitted with a stopcock, placed on the vacuum line, cooled to -196° , and evacuated. In cases where $(\text{CH}_3)_2\text{O}$ was used, the $(\text{C}_2\text{H}_5)_2\text{O}$ was pumped away and an equal volume of $(\text{CH}_3)_2\text{O}$ was then distilled into the vessel. An amount of B_2H_6 , equimolar to the LiCH_3 present, was condensed into the reaction vessel at -196° . The vessel was opened to an evacuated section of the vacuum line of sufficient volume to contain the anticipated gas evolution and then warmed to -78° . With $(\text{C}_2\text{H}_5)_2\text{O}$ as the solvent, it was sometimes necessary to warm the reaction mixture to about -50° in order to melt the B_2H_6 which was frozen to the side of the bulb. On such occasions, the solution was then quickly cooled to -78° in order to prevent excessive foaming. By observing the increasing pressure in the system the extent of reaction was followed; as it neared completion, the mixture was stirred and allowed to warm briefly in order to hasten completion of the reaction. While it is not possible to isolate LiB_5H_8 free of solvent, solutions thus produced appeared to be stable at room temperature for periods up to 1 hr.

For the preparation of LiB_5H_8 in greater than 30-mmol quantities, the required amount of LiCH_3 solution was syringed into the reaction bulb, but it was prudent to add B_2H_6 in 20–30-mmol increments and allow complete reaction before the addition of each successive increment.

Preparation of B_6H_{10} .—In a typical procedure, a 30-mmol quantity of B_2H_6 was allowed to expand into a reaction bulb at -78° which contained a dimethyl ether solution of 30 mmol of LiB_5H_8 that had been prepared by the method described above. The B_2H_6 was completely absorbed in 1–2 hr when the solution was stirred vigorously. Then the reaction vessel was opened to a U trap at -196° and the bulk of the solvent distilled from the reaction vessel at -78° . At this point the remaining material was white and solid at -78° . While constantly pumping through the U trap at -196° , this solid was stirred and slowly warmed to -15° over a period of several hours. The solid liquefied and thickened, first turning yellow and then yellow-brown, as H_2 was given off. The mixture was maintained at -15.3° (benzyl alcohol slush) until removal of volatile material to the U trap became prohibitively slow (several hours for the scale of reaction described herein). Then the mixture was slowly warmed to room temperature over several additional hours while continuously pumping volatile material into the U trap at -196° . The nonvolatile residue which remained consisted of LiBH_4 (identified by X-ray powder diffraction and boron-11 nmr), plus unidentified material.

Hexaborane(10) was isolated from the material which was collected in the U trap. This was accomplished by warming the trap to -45° and slowly distilling its contents through a series of traps which were maintained at -78 , -95 , and -196° . The fractionation process was continued until the material which collected in the -78° trap was shown to have a constant vapor pressure, 7.5 mm at 0° , in excellent agreement with an earlier report for B_6H_{10} .¹⁴ The yield of B_6H_{10} from the -78° trap was about 6.5 mmol. The fraction which collected in the -95° trap consisted primarily of B_6H_9 but also contained some B_5H_{10} . Fractionating this material at -78° yielded another 1.0 mmol of B_6H_{10} , giving a total yield of 25% of the theoretical yield.

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TABLE I
REPRESENTATIVE YIELDS OF B_6H_{10} FROM THE
REACTION $LiB_5H_8 + B_2H_6$

Solvent	Scale, mmol	B_6H_{10} yield, mmol (%)	$B_{10}H_{14}$ yield, mmol
$(C_2H_5)_2O$	7.2	1.56 (21.7)	0.16
$(C_2H_5)_2O$	30	6.45 (21.5)	Not measd
$(CH_3)_2O$	30	9.20 (30.7)	2.0
$(CH_3)_2O$	30	7.50 (25.0)	1.6
$(CH_3)_2O$	150	37.8 (25.1)	8.96

The identity and purity of the product were established by its molecular weight by vapor density (calcd for B_6H_{10} , 75.95; found, 76.3), vapor pressure,¹⁴ mass spectrum,¹⁵ infrared spectrum,¹⁴

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and boron-11 nmr spectrum,¹⁶ all of which were in excellent agreement with published reports.

Decaborane(14) was isolated from the fraction remaining at -45° by warming to room temperature and fractionating through a U trap maintained at -15° (benzyl alcohol slush). Decaborane(14) was identified by its melting point⁸ and its boron-11 nmr spectrum.¹⁶

The preparation of B_6H_{10} can be conveniently scaled up. Typical yields for several scale reactions are given in Table I.

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Correspondence

Reply to the Paper by F. A. Cotton and T. J. Marks, "Interpretation of a Spin-Tickling Experiment on (Monohaptocyclopentadienyl)-(methyl)(dichloro)silane"¹

Sir:

The assignment made by Cotton and Marks while analyzing our spin-tickling data for the compound $C_5H_5SiCH_3Cl_2$ ² is absolutely correct. However, 3 months before Cotton and Marks published their paper we published the correction in ref 3, in which this correct assignment was already made. Perhaps Cotton and Marks were not aware of our correction.

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The Acidities of Germane and the Phenylgermanes

Sir:

Generally, a phenyl derivative of a nonmetal hydride, $C_6H_5MH_{x-1}$, is more acidic than the parent hydride,

MH_x .^{1,2} For example, phenylarsine is a stronger acid than arsine, and diphenylarsine is a stronger acid than phenylarsine.² However, germane and the phenylgermanes constitute a puzzling exception to this rule. The phenylgermanes are weaker acids than germane—the weakness increasing with increasing phenyl substitution.^{3,4} Although the exceptional acidities of the phenylgermanes have been cited as evidence for $p\pi-d\pi$ bonding,³ no explanation was offered for the implied greater importance of such bonding in the phenylgermanes than in, say, the phenylarsines. The purpose of this communication is to show that the data may be explained in terms of two opposing effects of phenyl substitution: an acid-weakening effect (which we ascribe to $p\pi-d\pi$ bonding) and an acid-strengthening effect (mainly due to $p\pi-p\pi$ bonding).

The phenyl group in the molecule $C_6H_5MH_x$ can exert an acid-weakening effect if the atom M has empty valence $d\pi$ orbitals which interact with the filled $p\pi$ molecular orbitals of the phenyl ring. Such $d\pi$ orbitals are available when M is from the second or third row of the periodic table.⁵ The acid-weakening effect may

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