2:2:1. This spectrum is consistent with either 2,3- or 2,4-$(CH_3)_2B_5H_7$.

In order to resolve this ambiguity, a low-temperature, single-crystal X-ray diffraction study has been completed. The probable space group is Pmcn, and there are four molecules in a unit cell having parameters $a = 12.55$, $b = 6.39$, and $c = 9.10$ A. At this stage the value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.11 for 343 independent observed diffraction maxima. The molecular structure (Figure 1c) shows conclusively that the methyl groups are attached to *adjacent* basal B atoms. These B atoms are 1.82 A apart, as compared with the three other B–B distances of 1.80 A. Thus, replacement of terminal H by CH_3 on basal B atoms seems to weaken B–B bonding. Hence, these distances, as well as those of 1.67 A from basal to apex B atoms, do not suggest that the local CH_3BBCH_3 unit has an abnormally strong B–B bond. Other features of interest are the normal C–B distance of 1.57 A and the value of 135° for the B(apex)–B(basal)–C angle, in agreement with the microwave value in B_5H_9 of 136° 10′ for $B_1B_2H_2$.[3]

We now accept the reasonable thermodynamic preference of electron-donating methyl for the positive boron at the basal position[4] and turn to steric considerations in $(CH_3)_2B_5H_7$ or in the negative ion $(CH_3)_2B_5H_6^-$. If no special features were present, we would expect the mechanism proposed earlier[1,5–7] to yield a 2:1 mixture of adjacent and opposite basal-substituted dimethyl products. However, the direct location of H atoms in the X-ray results indicates that the nearest H(methyl)···H(bridge) distances of 2.5 to 3.0 A are at least sufficiently short to fix the CH_3 orientation in a staggered configuration relative to H(bridge). Moreover, if the transition state has B···B distances of about 1.9 A in the equator of the trigonal bipyramid, the contraction of $B_2 \cdots B_4$ would produce H(methyl)···H(bridge) contacts as short as 2.0 A, provided that one adjacent pair of bridge H atoms (which need not rearrange) remains relatively fixed. Hence, it seems likely that the single product of this reaction probably arises from this steric feature of H···H repulsions in the transition state. Similar steric effects between H atoms on substituents and bridge H atoms in other boron hydrides may be expected to restrict the path of rearrangements in a somewhat similar fashion.

If, as has been suggested[7] for B_5H_9, the base removes a proton to leave $(CH_3)_2B_5H_6^-$ as the intermediate which rearranges, the exact steric interferences depend upon assumptions of the hydrogen atom positions. It seems more likely[8] that a bridge proton is lost than one from a terminal position, because then a BHB bond is merely converted to a BB bond, whereas loss of a terminal proton would leave a lone pair near an electron-deficient framework. If no other change than the loss of any one bridge H^+ occurs, the arguments given above for $(CH_3)_2B_5H_7$ also hold qualitatively for $(CH_3)_2B_5H_6^-$. Only if the $(CH_3)_2B_5H_6^-$ has two external terminal groups (H or CH_3) can the steric situation in the trigonal bipyramidal intermediate be somewhat relieved, but no closed polyhedral species of borane has yet been found in which this particular bonding situation occurs. Possibly a polyhedron with three bridge H atoms, in which one bridge is across equatorial B atoms, could exist as an intermediate, but this model would require a rather substantial H rearrangement, in comparison with a model based upon the least motion. If, on the other hand, rearrangement occurs in a base adduct of $(CH_3)_2B_5H_7$, the steric problems of the intermediate are even greater than those which are examined here for $(CH_3)_2B_5H_7$ or $(CH_3)_2B_5H_6^-$. Hence, it seems probable that this unique product is explainable on primarily steric grounds, but the preparation and structure determination of a salt of the $(CH_3)_2B_5H_6^-$ ion would be of interest in further elucidation of this mechanism.[9]

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(9) The structural and, to some extent, mechanistic implications in the present work may also apply to the dibasal isomer obtained from the thermal rearrangement of 1,2-dimethylpentaborane. The base-catalyzed and thermally rearranged products have identical infrared patterns in the examined region of 2–15 μ. Identical ^{11}B and ^1H nmr patterns and chemical shifts are also observed but these are, perhaps, less reliable in establishing coidentity than is the infrared comparison.

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Preparation of Acyl Halides under Very Mild Conditions

Sir:

Acyl halides are valuable intermediates in a variety of reactions and are generally readily prepared from the parent acid. The usual reagents (*e.g.*, thionyl chloride, phosphorus pentachloride) can be replaced by slightly less vigorous ones (*e.g.*, oxalyl chloride, phosgene) when sensitive acids are being halogenated, but more or less vigorous acidic conditions are needed in all these cases.

In connection with some work on sugars and terpenes, we needed some acid chlorides which were obtainable only in poor yield by the standard methods.

We considered that a triaryl- or trialkylacyloxyphosphonium halide (I) would probably readily decompose to give the corresponding acyl halide and the phosphine oxide and confirmed this by examination of the reaction of triphenylphosphine and carbon tetrachloride with various acids.[1]

For example, acetic acid (1 mole) and triphenylphosphine (1 mole) in carbon tetrachloride reacted very rapidly to produce acetyl chloride, triphenylphosphine oxide, and chloroform in good yield. A range of acids was treated in this way and in each case good yields of acyl chloride were obtained. The over-all reaction may be written

$$RCOOH + (C_6H_5)_3P + CCl_4 \longrightarrow RCOCl + (C_6H_5)_3PO + HCCl_3$$

It can be seen that, in the absence of hydrolysis, the acid is rapidly converted to the neutral halide with no generation of any strongly acidic material.

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(1) *Cf.* P. C. Crofts and I. M. Downie, *J. Chem. Soc.*, 2559 (1963).

The reaction is obviously a several-step process, and it is suggested that initially formation of II (triphenyltrichloromethylphosphonium chloride) occurs, with further reaction yielding chloroform and the ion I. Other examples of this reaction are given in Table I.

Table I

Acid	Halides,[a] bp, °C	Derivative, mp, °C
Acetic	50–53	Anilide, 114–115
Propionic	80–84	Anilide, 100–102
n-Butyric	101–107	*p*-Toluidide, 57–59
Phenylacetic	206–211	Anilide, 110–112
Benzoic	195–200	Anilide, 163–165
Chloroacetic	106–109	Anilide, 127–128
n-Heptylic	123–125	*p*-Toluidide, 78–79
Pelargonic	210–218	*p*-Toluidide, 81–82
2,3-O-Isopropylidene-glyceric	80–83° (20 mm)	

[a] Confirmed by comparison by gas–liquid partition chromatography and by spectral comparison with authentic material.

Work is proceeding to elucidate the reaction details and to determine its scope and limitations.

$$(C_6H_5)_3P + CCl_4 \xrightarrow[\text{stages?}]{\textit{via}\ \text{radical}} \underset{\text{II}}{(C_6H_5)_3\overset{+}{P}CCl_3\,Cl^-}$$

$$\text{I} + RCOOH \longrightarrow \underset{\text{I}}{RCOO\overset{+}{P}(C_6H_5)_3} + HCCl_3$$

$$\text{I} \longrightarrow RCOCl + (C_6H_5)_3PO$$

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Preparation and Properties of Sodium Decaboranate(12,2−)[1]

Sir:

We wish to report the preparation of sodium decaboranate(12,2−), $Na_2B_{10}H_{12}$. Several previous investigations[2–4] have demonstrated the initial reaction of sodium hydride with decaborane(14) in ethyl ether to yield $NaB_{10}H_{13}$, but evidence of a second acid hydrogen on the $B_{10}H_{13}^-$ anion reacting with NaH was not presented. We have found that the reaction with excess sodium hydride proceeds slowly in ethyl ether with liberation of hydrogen and formation of the salt $Na_2B_{10}H_{12}$. The over-all reaction is

$$B_{10}H_{14} + 2NaH \xrightarrow{(C_2H_5)_2O} Na_2B_{10}H_{12} + 2H_2$$

The reaction could be accelerated by warming to 45°; this was accomplished in a stainless steel bomb reactor. Starting with 7.9 mmoles of NaH and 0.90 mmole of $B_{10}H_{14}$, 89% of the hydrogen expected for formation of $Na_2B_{10}H_{12}$ was evolved in 68 hr. In separate experiments it was shown that the reaction proceeds, although very slowly, even at 0°. Approximately 75% of the expected hydrogen was evolved in 6 days at 0° when excess NaH was used.

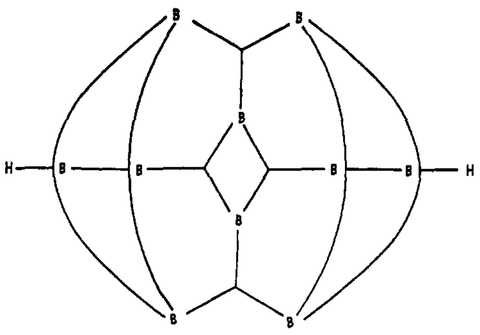

Figure 1. Proposed structure of 0822 $B_{10}H_{12}^{2-}$ (a terminal H on each boron atom is omitted).

Sodium decaboranate(12,2−) is a white solid insoluble in ethyl ether. This allows easy separation from $NaB_{10}H_{13}$, which is highly soluble in ethyl ether. When slightly less than two formula weights of sodium hydride was used per mole of decaborane(14), the reaction allowed to continue until hydrogen evolution ceased, and the resulting mixture filtered and washed with ethyl ether, solid nonsolvated $Na_2B_{10}H_{12}$ was obtained. The only previous report of a $B_{10}H_{12}^{2-}$ species is that of the solvated Grignard reagent, $B_{10}H_{12}(MgX)_2 \cdot (C_2H_5)_2O$, which was characterized by analysis.[5]

Analytical results on sodium decaboranate(12,2−) and its molecular weight obtained by freezing-point depression in liquid ammonia support the formula $Na_2B_{10}H_{12}$. *Anal.* Calcd for $Na_2B_{10}H_{12}$: Na, 27.6; B, 65.1; H, 7.28; mol wt, 166. Found: Na, 25.4; B, 67.9; H, 7.49; mol wt, 180 ± 20.

The infrared spectrum shows strong ν(B–H) bands at 2440, 2380, and 2310 cm^{-1} but no absorption in the region 2000 to 1700 cm^{-1} generally ascribed to bridging hydrogens. The description provided by the valence theory proposed by Lipscomb[6] would be 0822, which is shown as a planar projection in Figure 1. In three dimensions, the boron atoms differ little in location from those in $B_{10}H_{14}$.

Further support of the close structural relationship of the ion to decaborane(14) may be drawn from the results of the reaction of $Na_2B_{10}H_{12}$ with dilute aqueous HCl at 100°. The principal product of this reaction is decaborane(14), which was obtained in 67% yield. $Na_2B_{10}H_{12}$ was found to be hygroscopic and decomposed on handling in moist air, apparently because of the ready protonation of the anion to yield $B_{10}H_{13}^-$ or $B_{10}H_{14}$. The salt is stable for at least several days at room temperature in a dry inert atmosphere.

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[7] P. H. W. appreciates financial support by the Astronuclear Laboratory of the Westinghouse Electric Corporation under its Doctoral Assignment Program.