of oxygen above the solution and the rate of stirring. The same products were obtained in the absence of the thallium compound, except that the alkylmercuric salt was formed as the hydroxide or alkoxide. *sec*-Butylmercuric bromide yields the same types of products when subjected to air or oxygen under these conditions, but the reaction is slower than with di-*sec*-butylmercury. We were unable to reproduce the kinetic data of Hart and Ingold, and the substantial agreement within their data was apparently fortuitous.

In marked contrast to this behavior under an air atmosphere, when the reagents were brought together in the absence of oxygen (nitrogen atmosphere) no reaction occurred. No gas was taken up or evolved, and after three half-lives (Hart and Ingold's half-lives) the diethylthallium bromide and di-*sec*-butylmercury were recovered in ~100 and >90% yields, respectively.

An important part of the discussion in Hart and Ingold's paper was in respect to the postulated alkyl group exchanges (eq 1–4). In order to ascertain the validity of these postulates, two samples were prepared in nmr tubes under Hart and Ingold's conditions but under an inert atmosphere; one sample contained diethylmercury and di-*sec*-butylthallium chloride and the other contained di-*sec*-butylmercury and diethylthallium bromide, along with the appropriate amounts of water, cyclohexene, and DMF as solvent. The tubes were placed in a bath at 70° and were removed from time to time to record the nmr spectrum of the contents. Since no interchange occurred after 1 week, as evidenced by the constancy of the peak positions, it is concluded that the postulated alkyl exchange does not occur.

Detailed studies of the reaction of diisopropylmercury with oxygen under conditions comparable to those of Hart and Ingold have been carried out by Aleksandrov, *et al.*[2] From their studies, they concluded that the reaction of diisopropylmercury and oxygen occurs by a free radical chain process and our results indicate the same for di-*sec*-butylmercury. In both reactions an induction period is observed, the reactions are subject to inhibition, the kinetics tend to be erratic, and the product distributions vary with the concentration of oxygen. Some possible chain propagating steps are shown in eq 5–8.

$$RHgO_2R \longrightarrow RO\cdot + RHgO\cdot \tag{5}$$

$$RO\cdot + R_2Hg \longrightarrow RHgOR + R\cdot \tag{6}$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{7}$$

$$RO_2\cdot + R_2Hg \longrightarrow RHgO_2R + R\cdot \tag{8}$$

Acknowledgment. This work was supported by the National Science Foundation under Grant No. GP-3538.

Frederick R. Jensen, Duane Heyman
Department of Chemistry, University of California
Berkeley, California 94720
Received May 23, 1966

Rearrangement of 1,2- to 2,3-Dimethylpentaborane(9)

Sir:

The base-catalyzed rearrangement of $1,2\text{-}(CH_3)_2B_5H_7$ (apex, basal) is shown here by X-ray diffraction methods to yield only one isomer, $2,3\text{-}(CH_3)_2B_5H_7$, in which methyl groups are attached to adjacent B atoms. Absence of the 2,4 isomer is attributed to H(methyl)··· H(bridge) repulsions in a more detailed development of a probable nearly trigonal bipyramidal transition state of $(CH_3)_2B_5H_7$ (Figure 1), or of a possible closely related intermediate $(CH_3)_2B_5H_6^-$.

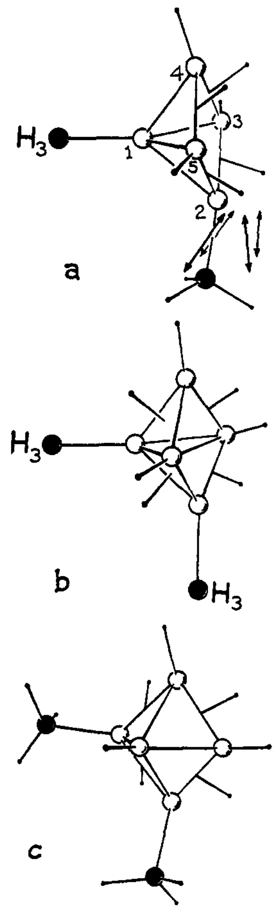

Figure 1. Proposed dimethylpentaborane rearrangement mechanism: a to b to c. Although H-atom positions are highly tentative, it seems likely that the H(methyl)···H(bridge) contacts indicated by double arrows in a may hinder B2···B4 approach. Hence, the transition state b formed by B3···B5 approach (and B2···B4 expansion) is favored.

Earlier studies have established that $1\text{-}CH_3B_5H_8$ rearranges under base catalysis[1] (possibly with proton abstraction or complexing) and thermally[2] at 200° (possibly with intermolecular H exchange) to give $2\text{-}CH_3B_5H_8$. In the present study, Friedel–Crafts methylation of $2\text{-}CH_3B_5H_8$ yielded $1,2\text{-}(CH_3)_2B_5H_7$. The dibasal substituted isomer was prepared by allowing a 4:1 mixture of 2,6-dimethylpyridine and 1,2-dimethylpentaborane to stand under ambient conditions for 5 days. Two vacuum fractionations through a trap cooled to −45° removed the catalyst, and glc gave the isomer of the dibasal substituted dimethylpentaborane. *Anal.* Calcd for $C_2H_{13}B_5$: C, 26.3; H, 14.3; mol wt, 91.2. Found: C, 26.0; H, 14.4; mol wt, 92.5 (gas density). The ^{11}B nuclear magnetic resonance spectrum exhibits a singlet [δ +1.2 ppm ($BF_3 \cdot C_2H_5O$ = 0)] and two doublets (δ +19.6 ppm, J = 160 cps; δ +50.4 ppm, J = 178 cps) with relative areas of

---

(1) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).
(2) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).

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)$\cdots$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$\cdots$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)$\cdots$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$\cdots$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]

---

(3) H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, **22**, 262 (1954).

(4) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

(5) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(6) R. N. Grimes and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 496 (1962).

(7) W. V. Hough, L. J. Edwards, and A. F. Stang, *J. Am. Chem. Soc.*, **85**, 831 (1963).

(8) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963.

(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 ^{1}H nmr patterns and chemical shifts are also observed but these are, perhaps, less reliable in establishing coidentity than is the infrared comparison.

Thomas Onak
Department of Chemistry, California State College
Los Angeles, California 90032

Lawrence B. Friedman, Jean A. Hartsuck, William N. Lipscomb
Department of Chemistry, Harvard University
Cambridge, Massachusettts 02138

Received April 1, 1966

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.

---

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