

with an ordinary helium mass spectrometer leak detector. The study was begun in an effort to determine experimentally the effect of astronomical conditions on simple chemical compounds, and the implications of the present experiments concerning this were discussed.

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DECABORANE (16): ITS REARRANGEMENT TO DECABORANE (14) AND CLEAVAGE

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Decaborane (16), recently described,¹ is comparable with decaborane (14) among the known boron hydrides^{2, 3} in its thermal stability, ease of handling in

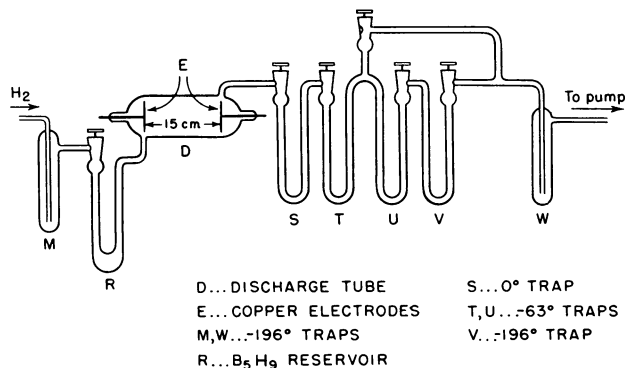


FIG. 1.—Preparation of $B_{10}H_{16}$. Pure gaseous H_2 is passed slowly over solid ($-78^\circ C$) B_5H_9 in R. The AC potential E is 2,800 volts. The $B_{10}H_{16}$ is trapped at -63° in T and U , while more volatile hydrides are caught in V . The 2 mg/hr of pure $B_{10}H_{16}$ represents less than 1% conversion, but the unused B_5H_9 is normally recirculated. If $E > 3,000$ volts some $B_{10}H_{14}$ is formed, but a separate distillation through a -10° trap retains $B_{10}H_{14}$ but passes $B_{10}H_{16}$.

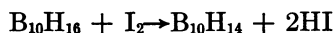
air, and separability from other hydrides. Its new structural feature, B atoms with no attached H atoms,⁴ strongly suggests that many new hydrides, intermediate between known hydrides and boron or the borides, may be discovered. We now report some of the reactions of $B_{10}H_{16}$, a few of which involve a remarkable rearrangement to $B_{10}H_{14}$. This rearrangement may be an important step in the formation of $B_{10}H_{14}$ in its syntheses from the lower boranes.

Preparation and Characterization of $B_{10}H_{16}$.—In Figures 1 and 2 we summarize

the details of preparation of $B_{10}H_{16}$ and its infrared spectrum. Besides large amounts of amorphous solids, there are a number of as yet unseparated crystalline boron hydrides formed under various conditions in the discharge process. X-ray powder diffraction photographic evidence has been obtained for several distinct but otherwise incompletely characterized new hydrides on which separations and further characterizations are being carried out.

In the following description of reactions all solids have been identified by comparison of X-ray powder patterns with authentic samples of known compounds. In addition, many products were also identified by comparison of infrared spectra.

Conversion of $B_{10}H_{16}$ to $B_{10}H_{14}$.—When $B_{10}H_{16}$ is heated in a sealed tube at $150^{\circ}C$ with a stoichiometric amount of I_2 , the reaction



occurs cleanly. However, an excess of I_2 yields $B_{10}H_{12}I_2$, possibly by direct reaction⁵ of I_2 with $B_{10}H_{14}$, and other derivatives. The reaction in the presence of excess $B_{10}H_{16}$ is discussed below.

A greater than 50 per cent yield of $B_{10}H_{14}$ results when $B_{10}H_{16}$ reacts with ethylene in the presence of $AlCl_3$ in dry CS_2 . H_2 is evolved, but other volatile and non-volatile products are formed and are still under investigation. A very nearly quantitative conversion of $B_{10}H_{16}$ to $B_{10}H_{14}$ without evolution of H_2 or HCl also occurs in very dilute CS_2 solutions in the presence of $AlCl_3$ only.

Both pyridine and 2,6 lutidine react with $B_{10}H_{16}$ to yield the same solid derivatives as are obtained when $B_{10}H_{14}$ reacts with these bases, as has been established from X-ray powder patterns and infrared spectra. No more than a trace of H_2 is produced, but the reactions are complicated by a variety of products. For example, the $B_{10}H_{14}$ -pyridine reaction,⁶⁻¹⁰ yields a 2:1^{6,10} or a 3:1⁹ complex.

The mechanism of the rearrangement of $B_{10}H_{16}$ to $B_{10}H_{14}$ is not yet established, but a possible path consistent with the present theory of bonding¹² in boron hydrides is shown in Figures 3 and 4, and may be tested with the use of B^{10} , D or CH_3 (for H) as tracers. This rearrangement may occur in the discharge or in pyrolysis methods of production of $B_{10}H_{14}$ from the lower hydrides. The steps in these reactions appear¹² to require fairly direct conversions of B_5 hydrides to $B_{10}H_{14}$, with the hydrides in the B_6 to B_9 range regarded as by-products rather than intermediates. This step is different from the sequence suggested by Hillman, Mangold,

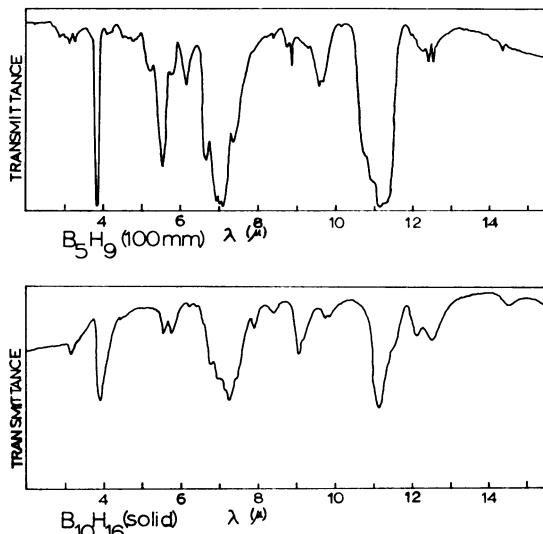


FIG. 2.—Similarity of infrared spectra of B_5H_9 (gas) and $B_{10}H_{16}$ (KBr disk). The 9.02μ peak is presumed to be B-B stretch in $B_{10}H_{16}$, and the large peak centered around 11.1μ cannot be wholly due to apical B-H bend since it occurs in both compounds.

and Norman,¹³ who, however, have shown experimentally that when B_2H_6 is pyrolyzed with B^{10} isotopically labeled B_5H_9 , the resulting $B_{10}H_{14}$ has half of its B atoms from the labeled B_5H_9 . It is therefore conceivable that the B_2H_6 polymerizes to a B_5 hydride, which may react with B_5H_9 to produce $B_{10}H_{16}$ which then goes to $B_{10}H_{14}$ with loss of H_2 .

Other Reactions of $B_{10}H_{16}$.

—At room temperature HI slowly cleaves the central B—B bond of $B_{10}H_{16}$ to yield B_5H_9 and B_5H_8I . At $100^\circ C$ the yield of B_5H_9 is quantitative, but the B_5H_8I produces polymeric sub-

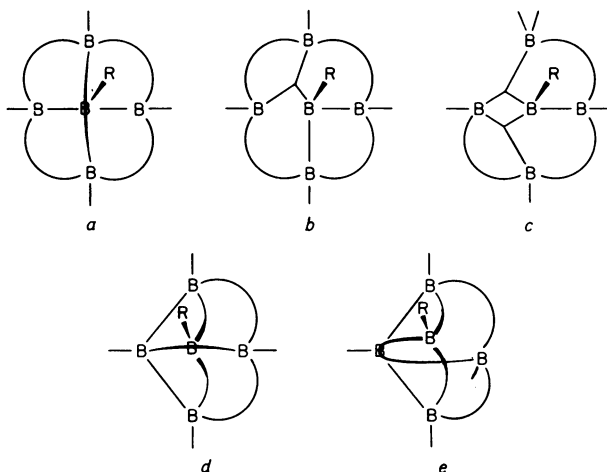


FIG. 3.—Proposed rearrangement of $1-RB_5H_8$ (apical) to $2-RB_5H_8$ (basal) based upon experimental results of Onak.¹¹ Note that we assume that the B—C bond is not broken, but that a different B atom becomes the new apex. A curved line through a B atom is an open three-center bond. Other curved lines are bridge H atoms. The role of an electron pair donor in promoting these H-atom rearrangements has been omitted. This donor presumably would bond to an orbital freed by the conversion of a three-center bond to a two-center bond.

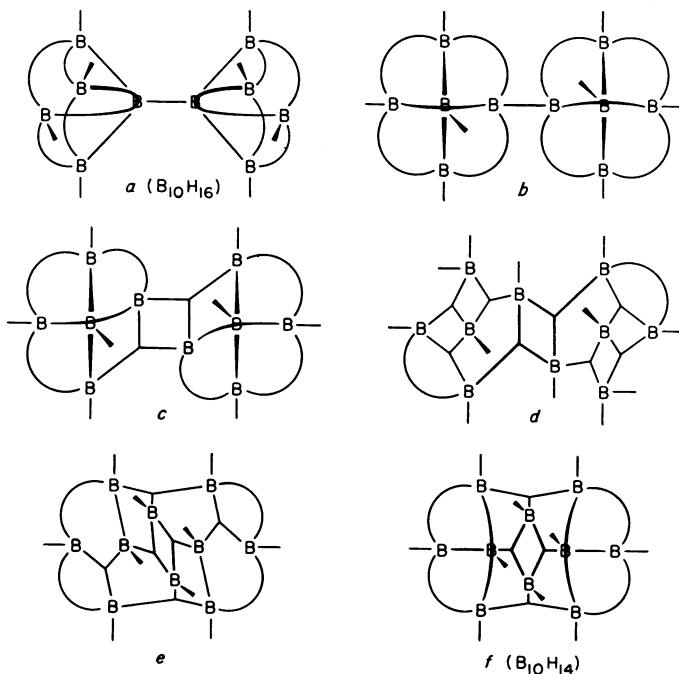


FIG. 4.—A plausible path for the $B_{10}H_{16}$ transformation to $B_{10}H_{14}$ with loss of H_2 . After the apex-to-base rearrangements have occurred a minimum of atomic motion is required. Again the role of the electron pair donor has been omitted. In the discharge preparation of $B_{10}H_{14}$ a wall or surface may supply the electron pair donor.

stances. Similar reactions occur at somewhat higher temperatures when HBr cleaves $B_{10}H_{16}$. When an excess of $B_{10}H_{16}$ reacts with I_2 , the reaction produces $B_{10}H_{14} + HI$ as mentioned earlier at $150^\circ C$, but the excess $B_{10}H_{16}$ then reacts with HI as described above.

Iodine and bromine do not react with $B_{10}H_{16}$ at room temperature in dry CCl_4 or $CHCl_3$ in the absence of air, but a trace of moisture is sufficient to produce HI or HBr from equimolar mixtures of $B_{10}H_{16}$ and halogen in CCl_4 , with evolution of HI or HBr. The initial boron-containing products are so quickly hydrolyzed to boric acid that they have not been identified as yet.

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RADIATION DAMAGE IN ORGANIC CRYSTALS: AUFBAU PROCESSES*

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A great variety of long-lived oriented free radicals have been produced in organic single crystals by high energy radiation.¹⁻⁹ Practically all of the many examples studied thus far have involved *abbau processes*; that is, the long-lived oriented free radical is derived from the parent (undamaged) molecule by loss of a hydrogen atom, a carboxyl group, etc. The purpose of this note is to point out that in some systems long-lived oriented free radicals can be formed by *aufbau* processes, in particular by H-atom addition. Thus, for example, the spin resonance of X-irradiated tiglic acid ($CH_3CH=C(CH_3)COOH$) suggests a single stable long-lived π -radical