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Abstract

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On the Conversion of Barenes into Salts of Dicarbaundecaborane Derivatives under the Action of Amines

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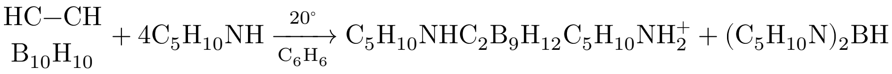
Recently Grafstein and co-workers reported (1) the preparation, under the action of certain amines on barenes, of stable adducts of composition (amine)$_2\cdot$barene, which, according to their data, are coordination-covalent compounds rather than compounds with a lower boron content, and in which the nitrogen atoms are directly bonded to boron atoms. In contrast to the American investigators, we found that the interaction of amines with barenes proceeds with cleavage of the barene nucleus and formation of salts of dicarbaundecaborane derivatives (1,3). Thus, in the reaction of barene with piperidine there are formed an adduct of piperidine with the piperidinium salt of dicarbaundecaborane (2) (I) and bis-(piperidino)-borine:



$$\begin{matrix}HC-CH\\B_{10}H_{10}\end{matrix} + 4C_5H_{10}NH \xrightarrow[C_6H_6]{20^\circ} C_5H_{10}NHC_2B_9H_{12}C_5H_{10}NH_2^+ + (C_5H_{10}N)_2BH$$

(*I*)

What is surprising is the ease with which this reaction proceeds; in benzene solution at 20° it is complete within a few minutes. The preparation by us of I also shows the possibility of the existence of anions of composition $C_2B_9H_{12}X^-$.

It was found that, just as readily, in benzene or hexane solution, piperidine interacts with mono- and disubstituted barenes: phenylbarene, *p*-nitrophenylbarene, vinylbarene, 1-methyl-2-phenylbarene, 1-chloro-2-phenylbarene, and 2-propenyl-3,4-barenotetrahydrofuran. Phenylbarene and vinylbarene react readily with butylamine. It was established that in the reaction of an amine with unsymmetrically substituted barenes (mono- and disubstituted), only one anion of the corresponding dicarbaundecaborane is formed, and not a mixture of isomeric anions. It follows from this that, under the action of an amine, a boron atom is removed from a definite position in the barene nucleus. The formation of only one anion also makes it possible to put forward certain assumptions concerning the position of this boron atom in the barene nucleus. We have previously

Fig. 1. Icosahedral structure of barene B10H10C2H2. 1—C atoms, 2—B atoms (H atoms not shown)

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shown (4) that in the dicarbaundecaborane anion the adjacent arrangement of the carbon atoms is retained (there is a C—C bond). Taking into account the ease of conversion of the barene molecule under the action of an amine into the dicarbaundecaborane anion with retention of the C—C bond, one may consider with sufficient confidence that, in this conversion, no rearrangement of the skeleton of boron atoms occurs, but only the removal of one boron atom and the formation of new bonds take place. Therefore, the formation of only one anion from an unsymmetrically substituted barene indicates that the departing boron atom must be situated symmetrically with respect to both carbon atoms of the barene nucleus*.

In barene, for which the icosahedral structure is most probable (5) (Fig. 1), there are only two pairs of boron atoms situated symmetrically with respect to both carbon atoms (they lie in the plane of symmetry, pro-perpendicular to the C—C bond line); these are boron atoms 3, 6 and 8, 10. In choosing which of the boron atoms 3(6) or 8(10) is removed from the barene nucleus, the following considerations seem justified to us. It is assumed that, in the transition from decaborane to barene, the boron skeleton of decaborane is not changed, but is only completed by two carbon atoms to an icosahedron. Therefore, as a rough approximation one may assume that in the barene molecule (taking into account that there is considerable electron density on the carbon atoms, which accounts for the proton mobility of the hydrogen atoms bound to them) the same order of distribution of electron density on the boron atoms is retained as in the decaborane molecule. As has been established (6), the boron atoms of decaborane (Fig. 2) are arranged in the following order of increasing negative charge: 6, 9 $<$ 5, 7, 8, 10 $<$ 1, 3 $<$ 2, 4. Therefore, the boron atoms in positions 2, 4, 1, and 3 are most readily attacked by electrophilic reagents, and the boron atoms in positions 6 and 9 by nucleophilic reagents.

Fig. 1. Icosahedral structure of barene $B_{10}H_{10}C_2H_2$. 1—C atoms, 2—B atoms (H atoms not shown)

One may assume that in barene the boron atoms in positions 8, 9, 10, and 12 have the greatest negative charge and will be the first to be attacked by electrophilic reagents, while the boron atoms in positions 3 and 6 have the lowest electron density and will be the first to be attacked by nucleophilic reagents (for

* The formation of only one dicarbaundecaborane anion is in better agreement with the icosahedral structure of barene than with a structure in which a bridge of two carbon atoms connects the 6 and 9 boron atoms of the decaborane skeleton.

Fig. 2. Boron skeleton of decaborane B10H14

Figure 2: Fig. 2. Boron skeleton of decaborane B10H14

example, amines). This qualitative consideration of the distribution of electron density in the barene molecule agrees with calculations previously carried out by Hoffmann and Lipscomb ([7]), which predicted the distribution of electron density in barene and its isomers. According to their calculations, the greatest electron density (with the exception of the carbon atoms) in barene is located on boron atoms 8, 9, 10, and 12, and the lowest electron density on boron atoms 3 and 6. Therefore it may be assumed that, when the barene molecule is converted under the action of an amine into the anion of dicarbaundecaborane, a boron atom is removed from positions 3 and 6. Wisbock and Hawthorne ([3]) also came to a similar conclusion; they found that, when phenylbarene labeled with deuterium in positions 8, 9, 10, and 12 is converted under the action of alcoholic alkali into the phenyl-dicarbaundecaborane anion, only pure hydrogen is evolved. In their opinion, this indicates that the boron atoms in these positions are not removed in the reaction.

Fig. 2. Boron skeleton of decaborane $B_{10}H_{14}$

We found that the reaction of amines with barenes is also strongly influenced by the solvent. Thus, it turned out that the interaction of piperidine with barene in ethanol proceeds more slowly than in benzene: at the boiling temperature of the alcohol the reaction is completed only after 4 h; at 20° the reaction practically does not occur. Introduction of a substituent into the barene molecule facilitates, in a number of cases, the cleavage reaction of the barene nucleus. This was studied in more detail using the interaction of phenylbarene with various amines in alcoholic solution as an example. It was found that ammonia, *n*-butylamine, diethylamine, and triethylamine, upon heating in an alcoholic solution cause its conversion into the phenyldicarbaundecaborane anion. Aniline under these conditions does not react with phenylbarene. Ammonia and triethylamine also practically do not react with barene in alcoholic solution. It may be assumed that, in the reaction of an amine with barene, an unstable diadduct of the type $(\text{amine})_2$-barene is formed as an intermediate, in which the nitrogen atoms are bound by donor bonds to the 3 and 6 boron atoms. Therefore, it may be expected that introduction of negative substituents at the carbon atoms, by decreasing the electron density on these boron atoms, will increase the ease of coordination and, consequently, the ease of cleavage of the barene molecule to the dicarbaundecaborane anion. In a similar way, coordination will increase with increasing basicity of the amine and with decreasing steric hindrance.

Experimental Part

Interaction of barenes with piperidine in a hydrocarbon solution. To a solution of the barene compound in benzene or hexane, piperidine was added in slight excess at room temperature. When carefully dried reagents were used, no hydrogen was evolved during the reaction. On mixing the reagents, slight heating occurred; after several minutes the solution became turbid and two layers formed. When the reaction was carried out in benzene, hexane was added to the reaction mixture. The upper hydrocarbon layer was decanted, and the residue was washed with hexane. On addition of ethyl alcohol to the decanted hydrocarbon solution, vigorous evolution of hydrogen occurred in an amount of one mole of hydrogen per mole of barene compound. The solvent was completely removed in vacuo from the residue washed with hexane. The residue was then dissolved in aqueous alcohol, and an aqueous solution of methylpyridinium iodide was added to the solution. A methylpyridinium salt precipitated; it was filtered off and recrystallized from aqueous alcohol. The yield of salt was practically quantitative. In this way methylpyridinium salts of dicarbaundecaboranes were obtained:

From barene, m.p. > 300°.

$C_8H_{20}B_9N$. Found, %: C 42.30; H 8.98; B 42.65; N 6.21
Calculated, %: C 42.41; H 8.81; B 42.80; N 6.17

From vinylbarene, m.p. > 300°.

$C_{10}H_{22}B_9N$. Found, %: C 47.38; H 8.54; B 38.49; N 5.41
Calculated, %: C 47.45; H 8.70; B 39.35; N 5.53

From phenylbarene, m.p. 122–123°.

$C_{14}H_{24}B_9N$. Found, %: C 55.08; H 7.92; B 32.48; N 4.94
Calculated, %: C 55.45; H 7.92; B 32.10; N 4.73

From *n*-nitrophenylbarene, m.p. 155–156°.

$C_{14}H_{23}B_9N_2O_2$. Found, %: N 8.03
Calculated, %: N 8.04

From 1-methyl-2-phenylbarene, m.p. 154–155°.

$C_{15}H_{26}B_9N$. Found, %: N 4.43
Calculated, %: N 4.42

From 1-chloro-2-phenylbarene, m.p. 126–128°.

$C_{14}H_{23}B_9ClN$.
Found, %: N 4.30
Calculated, %: N 4.15

From 2-propenyl-3,4-barenotetrahydrofuran, m.p. 139–140°.

$C_{13}H_{26}B_9NO$.
Found, %: N 4.57
Calculated, %: N 4.53

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Note: Figure translations are in progress. See original paper for figures.

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