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Abstract

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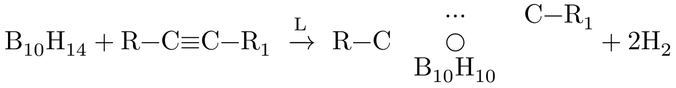
SYNTHESIS AND INVESTIGATION OF THE PROPERTIES OF A NEW CLASS OF ORGANOBORON COMPOUNDS: $B_{10}C_2H_{12}$ (BARENE) AND ITS DERIVATIVES

(Presented by Academician A. N. Nesmeyanov, 11 X 1963)

Shapiro and co-workers (^{1}) recently reported the preparation, in the reaction of pentaborane with acetylene in a glow discharge, of $B_3C_2H_5$, the simplest representative of a new class of organoboron compounds, the carboranes, and mentioned $B_4C_2H_6$ and $B_5C_2H_2$. However, Williams and Weiss (^{2}) found that, in the interaction of 2,6-dimethylpyridine, dihydrocarborane $B_4C_2H_6RR_1$ is obtained. We have made a detailed study of the reaction of decaborane with various acetylenic compounds and have found that, in the presence of substances forming complexes of the type $B_{10}H_{12}L_2$ with decaborane (L = ligand), a new class of organoboron compounds $B_{10}C_2H_{10}RR_1$ is formed.



$$B_{10}H_{14} + R{-}C{\equiv}C{-}R_1 \xrightarrow{L} R{-}C \underset{B_{10}H_{10}}{\overset{\cdots}{\bigcirc}} \overset{C-R_1}{} + 2H_2$$

We have named the first representative of this series, $B_{10}C_2H_{12}$, barene. The order of numbering of the boron atoms in barene remains the same as in decaborane, while the carbon atoms are designated by the numbers 11 and 12. The schematic representation of barene compounds by formula (1) follows from the structure of barenes proposed by us earlier (^{3}). It was shown that the reaction of formation of barenes from decaborane proceeds in two stages: first the complex $B_{10}H_{12}L_2$ is formed, which then reacts with the acetylenic compound with liberation of a molecule of hydrogen, release of the ligand, and formation of the barene derivative.

1. $B_{10}H_{14} + 2L \rightarrow B_{10}H_{12}L_2 + H_2$
2. $B_{10}H_{12}L_2 + RC{\equiv}CR_1 \rightarrow B_{10}C_2H_{10}RR_1 + 2L + H_2$,

where L = CH_2CN, $(C_2H_5)_2S$, $(C_2H_5)_3As$, $CHON(CH_3)_2$. The hydrogen molecule formed in the reaction of the complex is released at the expense of two bridging hydrogens that link $B_5{-}B_{10}$ and $B_7{-}B_8$ in the complex $B_{10}H_{12}L_2$.

As a result, a system of 12 atoms is formed (10 boron atoms and two carbon atoms), containing no bridging hydrogens. On the basis of X-ray structural analysis, IR spectra, and chemical properties, we believe that in the reaction of acetylenic compounds with $B_{10}H_{12}L_2$ two B—C σ-bonds arise (1.50 Å). The usual C=C bond is absent in barene, since the distance $C_{11}{-}C_{12} = 1.40$ Å; moreover, the two carbon atoms, in a state of sp^2 hybridization, contribute their π-electrons to common utilization with boron atoms 5, 7, 8, and 10, which apparently leads to the formation of a three-dimensional quasiaromatic system.

It should be noted that barene and its derivatives are distinguished by resistance to hydrolysis and high thermal stability, and are not changed by the action of mineral acids. Barene derivatives are prepared by heating acetylenic compounds in hydrocarbons either with decaborane in the presence of complexing agents or with decaborane complexes.

By this reaction we have obtained various classes of organoboron compounds: barene hydrocarbons, acetates of alcohols of the barene series

and dioxymethylbarene, haloalkyls and dihaloalkyls of barene, esters of acids and diacids of the barene series, ketones, ethers, etc.

The principal representatives of the various classes of the barene series are shown in Table 1.

In the course of the investigation of chemical properties, interesting reactions were found. For example, both barene and its alkyl and aryl derivatives react with C_4H_9Li to give lithium derivatives, the carbonation of which leads to acids of the barene series.

$$\mathrm{R{-}C{-}CH} + \mathrm{C_4H_9Li} \longrightarrow \mathrm{R{-}C{-}C{-}Li}$$

$$\mathrm{R{-}C{-}C{-}Li} \xrightarrow{\mathrm{CO_2}} \mathrm{R{-}C{-}C{-}COOH}$$

The absence of hydrogen bridges in barene makes it possible, without disrupting its structure, in principle to replace all hydrogen atoms at boron and carbon by halogen. Thus, on chlorination and bromination of barene and its derivatives, mono-, di-, tri-, and polyhalogen derivatives were obtained. Alcohols of the barene series were obtained by acid methanolysis of the corresponding acetates.

$$\mathrm{HC{-}C{-}(CH_2)_n{-}COOCH_3} \xrightarrow[\mathrm{CH_3OH}]{[\mathrm{H^+}]} \mathrm{HC{-}C{-}(CH_2)_n{-}OH}$$

$$n = 1, 2, 3$$

Alkaline hydrolysis is accompanied by the formation of by-products. Oxidation of the alcohols with CrO_3/H_2SO_4 gives the corresponding acids of the barene series.

$$\mathrm{HC{-}C{-}(CH_2)_n{-}CH_2OH \xrightarrow[H_2SO_4]{CrO_3} HC{-}C{-}(CH_2)_n{-}COOH}$$

On oxidation of oxymethylbarene with $KMnO_4$, barene is obtained:

$$\mathrm{HO{-}CH_2{-}C{-}C{-}CH_2OH \quad \overset{KMnO_4}{\longrightarrow} \quad HC{-}C{-}CH_2OH \quad \longrightarrow \quad HC{-}CH}$$

Haloalkyls of the barene series react with magnesium in tetrahydrofuran and in ether to give a Grignard reagent.

$$\mathrm{HC{-}C{-}(CH_2)_{nX} + Mg \longrightarrow HC{-}C{-}(CH_2)_n{-}MgX}$$

$$\mathrm{HC{-}C{-}(CH_2)_n{-}MgX \xrightarrow{C_6H_5CHO} HC{-}C{-}(CH_2)_n{-}CH(OH){-}C_6H_5}$$

$$\mathrm{HC{-}C{-}(CH_2)_n{-}MgX \xrightarrow{H_2O} HC{-}C{-}(CH_2)_{n-1}{-}CH_3}$$

Table 1

Compounds of the type $R{-}C{-}C{-}R_1$ with $B_{10}H_{10}$

R	R_1	M.p., °C	C, %	H, %	B, %	Halide
H	H	294,5–295,0	17,02	8,42	75,24	
CH_3–	H	217–218	22,53	8,60	68,03	
C_2H_5–	H	52–53	27,41	9,39	62,82	
$CH_2{=}CH$–	H	76–78	28,52	8,27	63,12	
n-C_3H_7–	H	68–69	32,62	9,75	58,12	
n-C_4H_9*	H	11,2–11,3	36,58	10,01	53,01	
$CH_2{=}C(CH_3)$–	H	46,0	32,97	8,80	58,14	

R	R_1	M.p., °C	C, %	H, %	B, %	Halide
$(CH_3)_2C$ —**	H	–14,5	32,40	9,56	57,65	
C_6H_5 —	H	67,5–67,9	43,52	7,18	49,12	
HOH_2C —	H	229–230	21,11	8,24	61,46	
HOH_2CH_2C —	H	51–52	24,99	8,97	57,35	
ClH_2C —	H	91,5	18,39	6,75	56,40	18,59
ClH_2CH_2C —	H	82	23,47	7,40	51,59	17,59
BrH_2C —	H	31,5	15,02	5,97	44,43	34,44
BrH_2CH_2C —	H	110	19,19	5,11	43,25	31,64
JH_2CH_2C —	H	130,5–131	16,29	5,32	36,18	42,25
$HOCH_2$ —	$HOCH_2$	299–300	23,49	7,91	52,72	
ClH_2C —	ClH_2C	113–114	20,14	5,83		27,94
BrH_2C —	BrH_2C	67–67,5	14,81	4,32	32,64	48,69
Br–C_6H_4 —	H	134,5–134,1	26,30	5,12	36,14	
$R=H_5C_2COO$ —	$R_1=H$	61,5–62	27,76	7,88	49,21	
C_6H_5	— $CH_2OC_2H_5$	59–60	47,40	7,92	38,27	
HC=C-CH_2-O-$CH_2B_{10}H_{12}$	H	344	21,84	7,86	65,40	
$R=COOH$***	$R_1=H$	151–150,5	19,46	6,51	57,00	
COCl	H	39–41	–	–	–	17,21
$CONH_2$	H	114,5–115	19,30	7,03	57,43	
CH_2–COOH	H	192–193	24,09	7,02	53,20	
CH_2OOCCH_3	H	46–47	27,47	7,40	49,84	
$COCH_3$	C_6H_5	68–69	45,56	7,01	41,10	

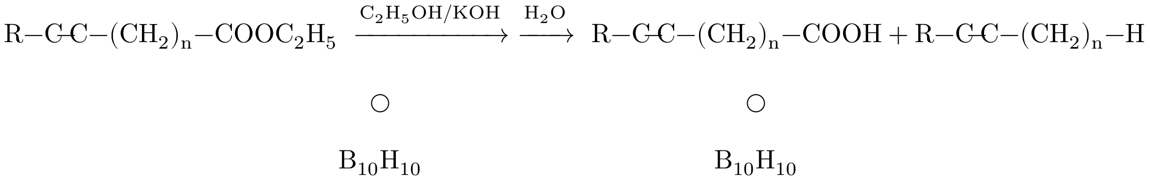
R	*R*$_1$	M.p., °C	C, %	H, %	B, %	Halide
CH_3–C–C–H; $B_{10}H_8Br_2$	(two isomers)	1) 153,5–154	11,61	3,73	34,35	50,77
CH_3–C–C–H; $B_{10}H_8Br_2$	(two isomers)	2) 96–97	11,86	3,76	34,23	50,52
$B_{10}H_{10}$-substituted fused cyclic ketone structure [[unclear: structural formula]]		165,5–166	44,20	5,84	43,63	
–H_2C–CH_2–N(C_2H_5)$_2$	R_1=H	46,5–48	40,82	10,42	43,42	

* B.p. 105–106° at 1–1,5 mm; $n_D^{20} = 1{,}5310$, $d_4^{20} = 0{,}9106$.

** B.p. 98–100° at 1–1,5 mm; $n_D^{20} = 1{,}5397$, $d_4^{20} = 0{,}9265$.

*** Acids of the barene series were described in a preliminary communication (*Izvestiya AN SSSR*, chemical series, No. 12).

Acids of the barene series were obtained by alkaline and acid hydrolysis of the corresponding ethyl esters. It was found that decarboxylation also takes place during hydrolysis.



$$R{-}\underset{\substack{\bigcirc\\ B_{10}H_{10}}}{C{-}C}{-}(CH_2)_n{-}COOC_2H_5 \xrightarrow{C_2H_5OH/KOH} \xrightarrow{H_2O} R{-}\underset{\substack{\bigcirc\\ B_{10}H_{10}}}{C{-}C}{-}(CH_2)_n{-}COOH + R{-}C{-}C{-}(CH_2)_n{-}H$$

Decarboxylation is observed when $R = C_6H_5, C_6H_5CH_2, C_6H_5(CH_2)_2$ at $n = 0$, and when $R = H$ at $n = 0, 1$. The mechanism of the alkaline hydrolysis of esters of barenecarboxylic acids has been studied. An interesting intramolecular cyclization was discovered in the reaction of the acid chloride of phenylpropiolic acid with the decaborane complex:

$$\mathrm{C_6H_5{-}C{\equiv}C{-}COCl + B_{10}H_{12}L_2} \longrightarrow \begin{array}{c}\text{cyclic product containing } \mathrm{B_{10}H_{10}}\\ \text{fused to the benzene ring and C=O}\end{array}$$

$$\mathrm{ClOC{-}C{-}C{-}C_6H_5} \xleftarrow{\mathrm{AlCl_3}} \begin{array}{c}\text{cyclized benzobarene ketone}\\ (\mathrm{B_{10}H_{10}})\end{array}$$

Studies of the signals of nuclear quadrupole resonance of n-bromophenylbarene purified by zone melting show that the barene nucleus is an electron-acceptor substituent—weaker than a nitro group and stronger than a carboxyl group.

$$\mathrm{O_2N{-}C_6H_4{-}Br}$$

$$\mathrm{H{-}C{-}C{-}C_6H_4{-}Br} \qquad \begin{array}{l}\text{278.582 MHz at 77°K for } Br^{79}\\ \text{274.174 MHz at 77°K for } Br^{79}\\ \text{271.093 MHz at 77°K for } Br^{79}\end{array}$$

$$\mathrm{B_{10}H_{10}}$$

$$\mathrm{HOOC{-}C_6H_4{-}Br}$$

After our investigation had been carried out, an American patent appeared in print (4) for the preparation of isopropenylidenedecaborane (isopropenylbarene) from diacetonitriledecaborane and isopropenylacetylene.

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