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Abstract

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Nitration of Phenylbarene, Phenylbarenecarboxylic Acid, and Phenylneobarene

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In papers (1-3) it was shown that the barene system possesses a strong inductive electron-acceptor effect. To establish the directing influence of the barene nucleus on electrophilic substitution in the benzene ring, we studied the nitration of phenylbarene and phenylbarenecarboxylic acid. In addition, for comparison, nitration of phenylneobarene (phenylneocarborane)* was carried out. Nitration of phenylbarene was performed with a nitrating mixture (HNO_3 : H_2SO_4 = 1 : 3) at room temperature in CCl_4 solution. Under these conditions phenylbarene is nitrated only in the benzene ring, giving, practically in quantitative yield, a mixture of two mononitrophenylbarenes: *p*-nitrophenylbarene and *m*-nitrophenylbarene:

$$C_6H_5C{-}CH\begin{pmatrix}\text{barene cage}\\ B_{10}H_{10}\end{pmatrix} + HNO_3 \xrightarrow[20^\circ]{H_2SO_4} O_2N{-}C_6H_4{-}C{-}CH\begin{pmatrix}\text{barene cage}\\ B_{10}H_{10}\end{pmatrix} + O_2N{-}C_6H_4{-}C{-}CH\begin{pmatrix}\text{ba}\\ \end{pmatrix}$$

From the resulting mixture, *p*-nitrophenylbarene (m.p. 165-165.5°), which is formed in larger amount than the *m*-isomer, can readily be isolated by crystallization.

$C_8H_{15}B_{10}NO_2$. Found, %: C 36.03; H 5.93; B 40.68; N 5.33
Calculated, %: C 36.21; H 5.70; B 40.77; N 5.28

It was not possible to isolate *m*-nitrophenylbarene from the mixture in pure form because of the close solubilities of the two isomers in most solvents. The ratio of isomers in the mixture was established by thin-layer chromatography on alumina. The ratio of *p*-nitrophenylbarene to *m*-nitrophenylbarene proved to be approximately 7:4. On nitration of phenylbarene with 100% nitric acid,** a mixture of the para and meta isomers is likewise formed, also in approximately the ratio 7:4. *o*-Nitrophenylbarene was not detected among the nitration products of phenylbarene. The structure of *p*-nitrophenylbarene was proved by oxidizing it to *p*-nitrobenzoic acid by the method proposed by us (5): on treatment with alcoholic alkali it was converted into the anion of *p*-nitrophenyldicarbaundecaborane, which, on oxidation with chromic mixture, gave *p*-nitrobenzoic acid:

$$p\text{-}NO_2C_6H_4C{-}CH\begin{pmatrix}\text{barene cage}\\ B_{10}H_{10}\end{pmatrix}+KOH \xrightarrow{C_2H_5OH} p\text{-}NO_2C_6H_4C_2B_9H_{11} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} p\text{-}NO_2C_6H_4COOH$$

The mixture of mononitrophenylbarenes obtained by nitration was subjected to a similar transformation. In this case a mixture of *p*-nitrobenzoic and *m*-nitrobenzoic acids was isolated. The nitro acids were identified through their methyl esters by thin-layer chromatography on alumina. *o*-Nitrobenzoic and benzoic acids were not detected. On reduction of the mixture of nitrophenylbarenes with tin and–

* Neobarene (neocarborane) is an isomer of barene. In it the carbon atoms are apparently located in the meta position of the icosahedral structure (there is no C–C bond) (4).

** Mixtures of phenylbarene with concentrated nitric acid have strong explosive properties. In a number of cases these mixtures exploded spontaneously.

with hydrochloric acid in ethyl alcohol, a mixture of the corresponding amines was obtained in high yield; it was possible to separate it and isolate in pure form *p*-aminophenylbarene (m.p. 104.5–105°)

Found, %:	C 41.43; H 7.42; B 45.52; N 5.95
$C_8H_{17}B_{10}N$. Calculated, %:	C 40.81; H 7.28; B 45.96; N 5.95

and *m*-aminophenylbarene (m.p. 83–84°)

Found, %: C 40.67; H 7.51; B 45.54; N 6.16

$$NO_2C_6H_4C{-}CHB_{10}H_{10}+Sn+HCl \xrightarrow{C_2H_5OH} H_2NC_6H_4C{-}CHB_{10}H_{10}+H_2NC_6H_4C{-}CHB_{10}H_{10}.$$

Both these amines proved to be different from 1-amino-2-phenylbarene (m.p. 97–98°)

Found, %:	N 6.19
$C_8H_{17}B_{10}N$. Calculated, %:	N 5.95

obtained in the rearrangement of phenylbarenecarboxylic acid azide (m.p. 92–93°) under the action of conc. H_2SO_4. In an attempt to obtain 1-amino-2-phenylbarene by reducing 1-nitroso-2-phenylbarene with tin and hydrochloric acid in alcohol, only 1-hydroxylamino-2-phenylbarene was isolated (m.p. 98–99°)

Found, %:	C 38.60; H 6.89; B 43.63; N 6.04
$C_8H_{17}B_{10}NO$. Calculated, %:	C 38.25; H 6.78; B 43.05; N 5.58

$$C_6H_5C{-}CLiB_{10}H_{10}{+}ClNO \xrightarrow[-75^\circ]{} C_6H_5C{-}CNOB_{10}H_{10} \xrightarrow[C_2H_5OH]{Sn+HCl} C_6H_5C{-}CNHOHB_{10}H_{10}$$

1-Nitroso-2-phenylbarene (m.p. 54–55°)

Found, %:	C 37.83; H 6.10; B 43.52; N 5.59
$C_8H_{15}B_{10}NO$. Calculated, %:	C 38.55; H 6.03; B 43.37; N 5.62

is formed from phenyllithiumbarene and nitrosyl chloride at −75° in a yield of about 60%. When nitrosyl chloride was passed into a benzene solution of phenyllithiumbarene at 10–15°, bis(phenylbarene)amine was isolated (m.p. 239–241°)

Found, %:	C 42.70; H 6.88; B 47.61; N 3.44
$C_{16}H_{31}B_{20}N$. Calculated, %:	C 42.35; H 6.84; B 47.60; N 3.09

$$C_6H_5C{-}CLiB_{10}H_{10} + ClNO \xrightarrow[15^\circ]{} C_6H_5C{-}CB_{10}H_{10}{-}NH{-}CB_{10}H_{10}{-}CC_6H_5$$

From *m*-aminophenylbarene, by oxidation with 90% H_2O_2 in trifluoroacetic acid, *m*-nitrophenylbarene was obtained (m.p. 144–145°)

Found, %:	C 36.07; H 5.88; B 40.67; N 5.25
$C_8H_{15}B_{10}NO_2$. Calculated, %:	C 36.21; H 5.70; B 40.77; N 5.28

$$H_2NC_6H_4C{-}CHB_{10}H_{10} + H_2O_2 \xrightarrow{CF_3COOH} NO_2C_6H_4C{-}CHB_{10}H_{10}$$

It turned out that *p*- and *m*-aminophenylbarenes possess weak basic properties: they dissolve only in conc. H_2SO_4 (the *m*-isomer upon heating), but on dilution of the solution with water they are precipitated in the free state. 1-Amino-2-phenylbarene behaves similarly. Upon heating acetic anhydride with *p*-aminophenylbarene, *p*-acetylaminophenylbarene was obtained.

(m.p. 176–177°)

$C_{10}H_{19}B_{10}NO$.	Found, %: C 43.09; H 6.90
	Calculated, %: C 43.28; H 6.90

Aminophenylbarenes are smoothly diazotized by nitrosylsulfuric acid in acetic acid solution. The sulfuric acid diazonium salt of the *n*-isomer is soluble in water. In its reaction with β-naphthol in alkaline medium, a red azo dye was obtained—*n*-barenylphenylazonaphthol-2 (λ_{max} = 4700 Å, acetone, m.p. 231-232°).

$C_{18}H_{18}B_{10}N_2O$. Found, %: N 6.50
Calculated, %: N 6.89

$$n\text{-}H_2NC_6H_4C{-}CH(B_{10}H_{10}) \xrightarrow[H_2SO_4]{NaNO_2} n\text{-}N_2^+C_6H_4C{-}CH(B_{10}H_{10}) \xrightarrow[KOH]{\beta\text{-naphthol}}$$

n-barenylphenylazonaphthol-2

On reaction with potassium iodide, *n*-iodophenylbarene is formed (m.p. 112.5-113°).

$C_8H_{15}B_{10}J$. Found, %: C 27.97; H 4.54; B 31.67; J 36.40
Calculated, %: C 27.74; H 4.37; B 31.24; J 36.65

On treatment with cuprous chloride and cuprous bromide, the known [6] *n*-chlorophenylbarene (m.p. 142-142.5°) and *n*-bromophenylbarene (m.p. 132-132.5°), respectively, were obtained. The sulfuric acid diazonium salt of the *m*-isomer is poorly soluble in water; from it and β-naphthol in alkaline medium, *m*-barenylphenylazonaphthol-2 was obtained (λ_{max} = 4700 Å), acetone, m.p. 203-203.5°.

$C_{18}H_{18}B_{10}N_2O$. Found, %: N 7.02
Calculated, %: N 6.89

$$m\text{-}H_2NC_6H_4C{-}CH(B_{10}H_{10}) \xrightarrow[H_2SO_4]{NaNO_2} m\text{-}N_2^+C_6H_4C{-}CH(B_{10}H_{10}) \xrightarrow[KOH]{\beta\text{-naphthol}}$$

m-barenylphenylazonaphthol-2

The reaction with cuprous chloride gave *m*-chlorophenylbarene, which by the method indicated above was oxidized to *m*-chlorobenzoic acid; this rigorously proved the structure of the *m*-isomer. Nitration of phenylbarenecarboxylic acid with nitrating mixture at 20° in CCl_4 solution proceeds with formation of a mixture of *n*-nitrophenylbarenecarboxylic and *m*-nitrophenylbarenecarboxylic acids:

$$C_6H_5C{-}CCOOH(B_{10}H_{10}){+}HNO_3 \xrightarrow[20^\circ]{H_2SO_4} O_2NC_6H_4C{-}CCOOH(B_{10}H_{10}){+}O_2NC_6H_4C{-}CCOOH(B_{10}H_{10})$$

To determine the ratio of the acid isomers, they were quantitatively decarboxylated to nitrophenylbarenes by heating their potassium salts in aqueous solution:

$$O_2NC_6H_4C{-}CCOOK(B_{10}H_{10}){+}H_2O \xrightarrow{100^\circ} O_2NC_6H_4C{-}CH(B_{10}H_{10}){+}KHCO_3$$

The ratio of the para-isomer to the meta-isomer in the resulting mixture, determined by thin-layer chromatography on aluminum oxide, is approximately $3:7$. Thus, introduction of an electron-withdrawing substituent at the carbon atom of the barene nucleus increases its $-I$ effect, which leads to an increase in the amount of the *m*-isomer compared with unsubstituted phenylbarene. Nitration of phenylneobarene with nitrating mixture at 20° in CCl_4 solution also occurs only in the benzene ring.

with formation of a mixture of mononitrophenylneobarenes, consisting mainly of *p*-nitrophenylneobarene (m.p. 148–149°).

Found, %: C 36.61; H 6.22; B 40.45; N 5.50
$C_8H_{17}B_{10}NO_2$. Calculated, %: C 36.21; H 5.70; B 40.77; N 5.28

$$neo\text{-}C_6H_5CB_{10}H_{10}CH + HNO_3 \xrightarrow[20^\circ]{H_2SO_4} neo\text{-}O_2NC_6H_4CB_{10}H_{10}CH$$

By means of thin-layer chromatography on aluminum oxide it was not possible to separate the obtained mixture of mononitrophenylneobarenes. To determine the structure of the substituted phenylneobarenes, we developed a method for oxidizing them to substituted benzoic acids. It turned out that, on heating phenylneobarene with hydrazine, cleavage of the neobarene nucleus readily occurs with liberation of one mole of hydrogen per mole of phenylneobarene and formation of a water-soluble salt of the degradation product. This product can be precipitated in the form of the methylpyridinium salt (m.p. 90–92°). In contrast to phenylneobarene, which is stable to the action of chromic mixture, the product of its degradation is readily oxidized by chromic mixture to benzoic acid (under milder oxidation conditions benzaldehyde is formed):

$$neo\text{-}C_6H_5CB_{10}H_{10}CH \xrightarrow{N_2H_4} \text{degradation product} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_6H_5COOH.$$

Benzoic acid was obtained in 85% yield, calculated on phenylneobarene. To determine the structure of *p*-nitrophenylneobarene, it was reduced with tin

and hydrochloric acid to *p*-aminophenylneobarene, which, through the diazonium salt with subsequent reaction with cuprous chloride, was converted into *p*-chlorophenylneobarene. The latter, after cleavage with hydrazine and oxidation by chromic mixture, gave *p*-chlorobenzoic acid in high yield:

$$p\text{-}O_2NC_6H_4CB_{10}H_{10}CH \rightarrow p\text{-}H_2NC_6H_4CB_{10}H_{10}CH \rightarrow p\text{-}ClC_6H_4CB_{10}H_{10}CH \rightarrow$$

$$\rightarrow p\text{-}ClC_6H_4COOH.$$

For comparison of the electron-acceptor effect of the barene nucleus and the neobarene nucleus, competitive nitration at 20° was carried out on an equimolecular mixture of phenylbarene and phenylneobarene with a nitrating mixture containing one equivalent of nitric acid. It turned out that under these conditions only phenylneobarene undergoes nitration. This confirms the conclusion made earlier ([7]) that the neobarene nucleus possesses a weaker electron-acceptor effect than the barene nucleus. In competitive nitration with nitrating mixture at 20° of benzene, chlorobenzene, and nitrobenzene, respectively, with phenylbarene, it was found that in the presence of phenylbarene only benzene and chlorobenzene are nitrated, whereas in the presence of nitrobenzene only phenylbarene is nitrated. Thus, the barene nucleus deactivates the benzene ring considerably more than a chlorine atom, but considerably less than a nitro group. Competitive nitration of benzene and chlorobenzene with phenylneobarene showed that, in the presence of phenylneobarene, only benzene is nitrated, while the rates of nitration of chlorobenzene and phenylneobarene are of the same order.

The results obtained for nitration of phenylbarene, phenylbarenecarboxylic acid, and phenylneobarene confirm the presence of an electron-acceptor effect in the barene and neobarene groupings. The absence of the *ortho* isomer in nitration indicates that the barene nucleus presents greater steric hindrance to the *ortho* positions of the benzene ring.

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