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Reactions of the Phenyl(*m*-carboran-9-yl)chloronium Cation with Nucleophiles. Influence of the Nature of the Onium Halogen Atom on the Reactivity and the Reaction Pathways of Phenyl(*m*-carboran-9-yl)halonium Compounds

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Reactions of phenyl(*m*-carboran-9-yl)chloronium tetrafluoroborate (**1**) with nucleophiles N_3^-, NO_2^-, OH^-, F^-, C_5H_5N, and PPh_3 occur by several pathways, i.e. nucleophilic substitution, one-electron reduction, and degradation of the carborane icosahedron. Comparing reactions of **1** with analogous reactions of phenyl(*m*-carboran-9-yl)bromonium and phenyl(*m*-carboran-9-yl)iodonium cations revealed the following pattern. For the sequence $[C_2B_{10}H_{11}\text{–I–Ph}]^+$, $[C_2B_{10}H_{11}\text{–Br–Ph}]^+$, $[C_2B_{10}H_{11}\text{–Cl–Ph}]^+$, degradation of the carborane ligand occurs with increasing ease, one-electron reduction reactions lead to only halogen–phenyl bond cleavage regardless of the halogen atom of the halonium cation, and the regioselectivity of S_N reactions decreases dramatically. Nucleophilic substitution in the iodonium cation occurs only at the carborane boron atom. For the bromonium and the chloronium cations, it takes place both at the carborane boron and at the phenyl carbon; however, the regioselectivity of the bromonium cation reaction is significantly higher.

Introduction

In the last decade it was shown that reactions of phenyl(*B*-carboranyl)iodonium cations with nucleophiles occur with surprising regiospecificity. For example, depending on the nature of the nucleophile, the phenyl(*m*-carboran-9-yl)iodonium cation (Figure 1) undergoes either cleavage of only the B–I bond (nucleophilic substitution) or cleavage of only the C–I bond (one-electron reduction and homolytic decomposition of the 9-I-2 intermediate formed).[1-5] Even in rare cases when competition between these two routes takes place (nucleophiles CN^- [1,5] and NO_2^- [6]), nucleophilic substitution occurs only at the boron of the carborane cage, and one-electron reduction results in elimination of only phenyl radicals (Scheme I).

Such regiospecificity is novel in the chemistry of halonium ions. In order to better understand this rather unusual regiospecificity, an investigation was initiated. For this purpose a study was made of the influence of different carboranyl[1,3,5,7] and aryl[6,8] ligands of aryl(*m*-carboran-9-yl)iodonium cations on the selectivity of their reactions with nucleophiles. We have also investigated how the nature of the onium halogen can influence the reactivity of phenyl(*m*-carboran-9-yl)halonium ions. It has been shown that radical reactions of phenyl(*m*-carboran-9-yl)bromonium cations are also regiospecific; i.e., homolysis of only the C–Br bond takes place. At the same time, nucleophilic substitution of the bromonium cation occurs not only at the boron attached to bromine but also at the carbon of the benzene ring.[9] In continuation of this study, we report here some reactions of phenyl(*m*-carboran-9-yl)chloronium tetrafluoroborate (**1**) with nucleophiles and compare them with similar reactions of isostructural bromonium and iodonium salts. It should be noted that aryl(*m*-carboran-9-yl)chloronium tetrafluoroborates, recently synthesized,[10] appear to be the first chloronium ions bearing an organometallic or inorganic ligand. Therefore, an investigation of their reactivity is of particular interest.

Results

Hydrolysis of 1. The reaction of **1** with water was first investigated. Aqueous solutions of **1** were found to be relatively stable. That is, a 0.2 M solution is completely decomposed in approximately 200 h at room temperature. The hydrolysis products consisted mainly of 9-hydroxy-*m*-carborane (56%), 9-chloro-*m*-carborane (8%), and H_3BO_3 (33%). Reactions of **1** with charged nucleophiles in a H_2O–CH_2Cl_2 biphasic system were usually complete in several hours at 20–40 °C (see below). Hence, there was no reason to consider a competition of hydrolysis reactions with other main-course reactions.

Scheme I

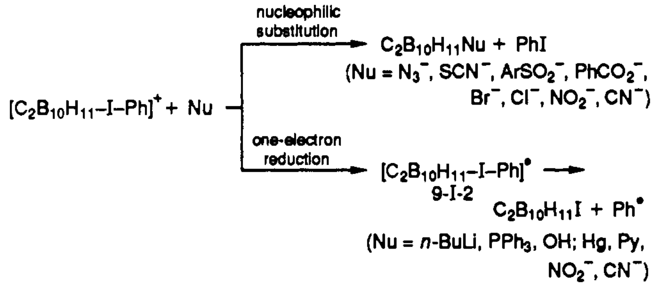
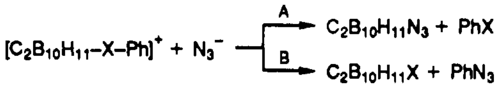


Table I. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with Sodium Azide (Dichloromethane–Water Biphasic System, 20 °C)



X	ratio of the paths A and B, %	
	path A	path B
I[a]	99	0
Br[b]	95	5
Cl	65	35

[a] Data from ref 2. [b] Data from ref 9.

Reaction of 1 with NaN_3. Diphenyliodonium,[11,12] -bromonium,[13] and -chloronium[14] salts react smoothly with the azide ion to give

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Table II. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with Sodium Nitrite (Dichloromethane–Water Biphasic System, 40 °C)

$$[C_2B_{10}H_{11}\text{–X–Ph}]^+ + NO_2^- \longrightarrow C_2B_{10}H_{11}OH + C_2B_{10}H_{11}NO_2 + PhX + PhH + PhNO_2 + C_2B_{10}H_{11}X + \text{nitrogen oxides}$$

X	reacn time, h	yield, %					
		$C_2B_{10}H_{11}OH$	$C_2B_{10}H_{11}NO_2$	PhX	PhH	$PhNO_2$	$C_2B_{10}H_{11}X$
I[a]	3	79	6	93	4	0.5	7
Br	2.5	92	*b*	95	1	1	2.5
Cl	1.5	83	*b*	90	1	3	4.5

[a] Data from ref 6. [b] 9-Nitro-*m*-carborane was not found among the reaction products.

Table III. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with Aqueous NaOH at 20 °C

$$[C_2B_{10}H_{11}\text{–X–Ph}]^+ + OH^- \longrightarrow \underset{A}{PhH} + \underset{B}{Ph_2} + \underset{C}{PhX} + \underset{D}{C_2B_{10}H_{11}X} + \underset{E}{PhOH} + \underset{F}{C_2B_{10}H_{11}OH} + \underset{G}{C_2B_{10}H_{11}OPh} + \underset{H}{(C_2B_{10}H_{11})_2O} + \underset{I}{PhOPh} + \underset{J}{C_2B_{10}H_{12}}$$

X	reacn time, h	yield, %									
		A	B	C	D	E[a]	F	G	H	I	J
I[b]	0.7	40	3	10	78	1					
Br[c]	8	40	*d*	41	50	2	8	*d*	25	*d*	*d*
Cl	8.5	*e*	*d*	36	63	27	10	*f*	*f*	*d*	*d*

[a] Isolated and identified as 2,4,6-tribromophenol. [b] Data from ref 1. [c] Data from ref 22. [d] Traces were found among the reaction products by GC-MS analysis. [e] Yield was not determined exactly; it is about 15%. [f] We failed to separate G from H by preparative column chromatography; yield of almost equimolar (GC, GC-MS) mixture is about 10%.

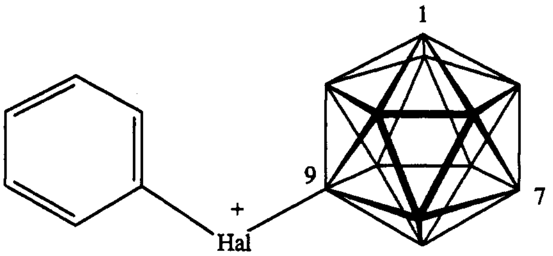

Figure 1. Phenyl(*m*-carboran-9-yl)halonium cations (Hal = I, Br, Cl). Cage positions: 1 and 7, CH; 9, B; others, BH. *m*-carborane = 1,7-dicarba-*closo*-dodecaborane(12).

phenyl azide and the corresponding halobenzene in almost quantitative yields. Data for reactions of phenyl(*m*-carboran-9-yl)halonium cations with NaN_3 in a $H_2O–CH_2Cl_2$ biphasic system are summarized in Table I. These data show clearly that the regioselectivity decreases dramatically over the series iodonium, bromonium, chloronium. It is noteworthy that reactions with the azide ion are not accompanied by radical processes, and they display how the nature of the onium halogen atom can influence the direction of nucleophilic substitution in phenyl(*m*-carboran-9-yl)halonium cations.

Reaction of 1 with $NaNO_2$. Reactions of various diarylhalonium compounds with the nitrite ion have been studied by several groups.[11,12,14–17] The majority of investigators have come to the conclusion that a competition exists between a S_N reaction and a one-electron reduction reaction. Such a competition was clearly observed by us in the reactions of aryl(*m*-carboran-9-yl)iodonium ions with $NaNO_2$.[6] For example, nucleophilic substitution of the phenyl(*m*-carboran-9-yl)iodonium cation by NO_2^- leads to iodobenzene and two carboranylation products (9-hydroxy-*m*-carborane and 9-nitro-*m*-carborane) due to the ambident character of the nitrite ion:

$$[C_2B_{10}H_{11}\text{–I–Ph}]^+ + NO_2^- \longrightarrow$$
$$PhI + C_2B_{10}H_{11}NO_2 + [C_2B_{10}H_{11}ONO] \xrightarrow{H_2O} C_2B_{10}H_{11}OH + \text{nitrogen oxides}$$

Simultaneously and independently of the S_N reaction, a one-electron reduction of the iodonium cation takes place:

$$\begin{tikzcd}
{[C_2B_{10}H_{11}\text{–I–Ph}]^+ + NO_2^-} \arrow[r] & {[C_2B_{10}H_{11}\text{–I–Ph}]^\bullet + NO_2} \arrow[d] \\
& C_2B_{10}H_{11}I + Ph^\bullet
\end{tikzcd}$$

Phenyl radicals produced are transformed mostly to benzene and some small amounts of nitrobenzene.[6] Reactions of **1** and phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate with $NaNO_2$ appear to display a similar competition between nucleophilic substitution and one-electron reduction (Table II).

As anticipated,[14–20] the impact of a one-electron reduction and, therefore, the yield of benzene decrease in the order iodonium > bromonium > chloronium. The yield of nitrobenzene increases in the same direction, and the regioselectivity of nucleophilic substitution decreases (as was observed in the reactions with sodium azide). The influence of both effects leads to changes in yields of halocarboranes and carboranylation products depending on the nature of the onium halogen atom. The yield of carboranylation products increases from iodonium to bromonium but decreases from bromonium to chloronium. In contrast, the yield of halocarborane follows the opposite trend.

It is interesting to note that the reactions of bromonium and chloronium cations with NO_2^- do not lead to 9-nitro-*m*-carborane. This product could result from the carboranylation of the softer nucleophilic center (N) of the anion. Since the bromonium and

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Table IV. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with Pyridine at 115 °C

$$[C_2B_{10}H_{11}\text{–Hal–Ph}]^+ + Py \longrightarrow PyH^+ + C_2B_{10}H_{11}Hal + PhHal + {}^-C_2B_9H_9\text{–}Py^+ + Ph\text{–}C_5H_4N + H_3BO_3$$

Hal	reacn time, h	yield, %					
		$PyH^+BF_4^-$	$C_2B_{10}H_{11}Hal$	PhHal	${}^-C_2B_9H_9Py^+$	PhC_5H_4N	H_3BO_3
I[a]	12	71–78	68–78			11–14	
Br[b]	4	69	30	*c*	50	7.5	
Cl	9	68	25	55–60	53	2	9.5[d]

[a] Data from ref 1. [b] Data from ref 9. [c] The yield was not determined. [d] Calculated on the basis of the total boron in the chloronium cation.

chloronium cations have a harder electrophilic character than the iodonium cation,[12,14] reaction with the soft nucleophilic center is unfavorable. A similar situation was observed for the reactions of diphenyliodonium, -bromonium, and -chloronium tetrafluoroborates with $NaNO_2$[14] and $PhSO_2Na$.[12]

Reaction of 1 with Aqueous NaOH. Alkaline hydrolysis of diphenylhalonium cations results in not only phenol and phenyl ether as the double-phenylation product but also some amounts of benzene[14] and biphenyl.[21] Therefore, some competition is occurring between nucleophilic substitution and one-electron reductions. Phenyl(*m*-carboran-9-yl)iodonium tetrafluoroborate reacts with aqueous NaOH via a radical pathway exclusively. Benzene and 9-iodo-*m*-carborane are the main products of this reaction.[1,5] Alkaline hydrolysis of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate under the same conditions is not as selective because of the competition between nucleophilic substitution and one-electron reductions[22] (Table III). Nucleophilic substitution occurs to an insignificant extent at the phenyl carbon, whereas this occurs readily at the boron atom of the carborane cage to give 9-hydroxy-*m*-carborane and bis(*m*-carboran-9-yl) oxide as the main products.[22]

Radical processes are less important for the reaction of chloronium salt **1** with NaOH. At the same time, the selectivity of the nucleophilic substitution is lowered, occurring mainly at the phenyl carbon. This is confirmed by comparison of the yields of phenol, bis(*m*-carboran-9-yl) oxide, and phenyl *m*-carboran-9-yl ether (Table III). The formation of all the products can be rationalized by the scheme suggested for the alkaline hydrolysis of the isostructural bromonium salt.[22]

Reaction of 1 with NaF. Diphenyliodonium tetrafluoroborate reacts smoothly with fluoride ions to give mixtures of fluorobenzene and iodobenzene.[12,23] Recently we showed that phenyl(*o*-carboran-9-yl)iodonium, phenyl(*m*-carboran-9-yl)iodonium,[1,5] and phenyl(*p*-carboran-2-yl)iodonium[1,5,7] cations also easily react with F^- to form iodobenzene and the corresponding fluorocarborane in high yields. In the present paper, the interactions of phenyl(*m*-carboran-9-yl)bromonium and -chloronium tetrafluoroborates with NaF in a CH_2Cl_2–H_2O biphasic system were found to give rise to 9-fluoro-*m*-carborane and the corresponding phenyl and *m*-carboran-9-yl halides:

$$[C_2B_{10}H_{11}\text{–X–Ph}]^+BF_4^- + NaF \xrightarrow[40\ ^\circ C,\ 5\ h]{CH_2Cl_2\text{–}H_2O} \underset{}{PhX} + \underset{45–50\%}{C_2B_{10}H_{11}F} + \underset{8–10\%}{C_2B_{10}H_{11}X}$$

$$X = Br, Cl$$

However, the yield of fluorocarborane (45–50%) and the total yield of halocarboranes (no more than 60%) are rather low. This seems to be connected with a process involving degradation of the carborane icosahedron under the action of base.[24] The fluoride ion is acting as a base under these conditions. The base-induced degradation of icosahedral *closo*-carboranes is known to proceed much more easily when an electron-withdrawing substituent is present in the carborane nucleus,[5,9,25] and phenylbromonium and phenylchloronium groups are known to be the strongest inductive electron acceptors,[26] much more powerful than phenyliodonium groups.

Table V. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with PPh_3 at 56 °C

Hal	irradiation	reacn time, h	yield, %	
			$C_2B_{10}H_{11}Hal$	$Ph_4P^+BF_4^-$
I[a]	visible light	7.5	78	82
Br[b]	visible light	10	67	95
Cl	UV	38	82	95

[a] Data from ref 3. [b] Data from ref 9.

Reaction of 1 with Pyridine. The diphenyliodonium cation can phenylate either at the pyridine nucleus (radical reaction)[27] or at the pyridine nitrogen atom (ionic reaction),[28] depending on the reaction conditions. The latter is more typical for reactions of pyridine with diphenylbromonium and diphenylchloronium tetrafluoroborates.[14] Phenyl(*m*-carboran-9-yl)iodonium tetrafluoroborate reacts with boiling pyridine via a radical pathway only, independent of the reaction conditions, including either absence of light or powerful incandescent lamp irradiation. The products are 9-iodo-*m*-carborane, pyridinium tetrafluoroborate, and a mixture of α-, β-, and γ-phenylpyridines.[1] The radical mechanism is typical for the reaction of the isostructural phenyl(*m*-carboran-9-yl)bromonium salt under similar conditions. However, parallel to this is the degradation of the carborane cage to give a zwitterionic B–N-bonded pyridinium 7,9-dicarbo-*nido*-undecaborate.[9,29]

The reaction of **1** with pyridine was found to be very similar to the bromonium salt reaction (Table IV); however, some differences should be noted. First, the carborane ligand of the chloronium cation undergoes more extensive degradation, since H_3BO_3 (9.5%) was found among the reaction products. Second, pyridinium tetrafluoroborate is isolated in a crystalline form from the reactions of iodonium and bromonium cations but as an oil from the reaction of the chloronium cation. This leads to the obvious conclusion that in the latter case a small amount of *N*-phenylpyridinium salt may be formed as a result of the minor process of *N*-phenylation of pyridine with **1**. Unfortunately, attempts to isolate pure *N*-phenylpyridinium tetrafluoroborate were unsuccessful.

Reaction of 1 with Triphenylphosphine. Previous literature has confirmed that the interactions of diphenyliodonium, -bromonium, and -chloronium salts with PPh_3 proceed via a radical path, resulting in the formation of the tetraphenylphosphonium cation, halobenzene, and small amounts of benzene.[30] Initiated by

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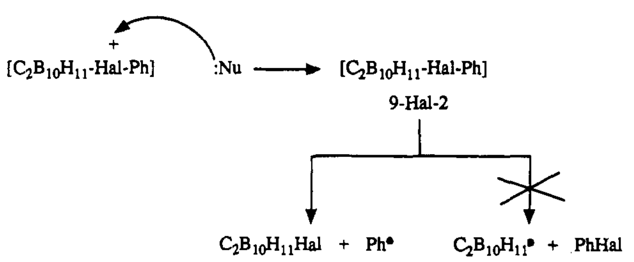
Scheme II



irradiation, radical reactions of PPh_3 with phenyl(*B*-carboranyl)iodonium,[3,5,7] phenyl(*m*-carboran-9-yl)bromonium,[5,9] tetrafluoroborates, and **1** lead to cleavage of only the C–Hal bond and formation of the corresponding 9-halo-*m*-carborane, tetraphenylphosphonium tetrafluoroborate, and small amounts of benzene (see Table V; the exact yield of benzene in the reaction of **1** was not determined).

$$[C_2B_{10}H_{11}\text{-X-Ph}]^+BF_4^- + PPh_3 \rightarrow C_2B_{10}H_{11}X + [Ph_4P]^+BF_4^- + PhH$$

$$X = I, Br, Cl$$

The formation of benzene in these reactions is indicative of a radical mechanism, as well as the fact that under the same conditions iodonium salts react faster than bromonium salts with PPh_3, while even more rigid conditions (UV irradiation) and prolonged reaction times are necessary for the reaction of the chloronium salt **1**.

Cleavage of the B–Cl bond in **1** does not take place in the reaction with PPh_3. *m*-Carborane (GLC) and triphenyl(*m*-carboran-9-yl)phosphonium tetrafluoroborate[3] (^{31}P NMR) are absent in the reaction products.

Discussion

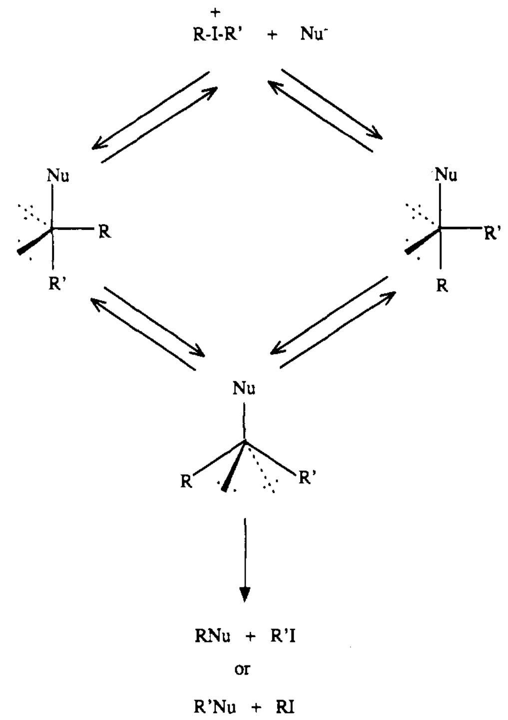
The results obtained show that the nature of the halogen atom exerts significant influence on both reactivity and reaction pathways of halonium ions. Let us consider the series $[R\text{–I–Ph}]^+$, $[R\text{–Br–Ph}]^+$, $[R\text{–Cl–Ph}]^+$ ($R = 9\text{-}m\text{-}C_2B_{10}H_{11}$) and point out some regularities.

1. Base-induced degradation of the carborane icosahedron (reactions with NaF and pyridine) proceeds more readily in the order I < Br < Cl. This is not surprising, as strong electron-withdrawing groups are well-known to assist in reactions of this kind.[5,9,25] The σ_I value grows regularly in the series $RI^+ < RBr^+ < RCl^+$.[26]

2. Radical reactions, which seem to begin with a one-electron reduction of the halonium cation,[1,3–6,26] require more severe conditions and extended reaction times in order to reach completion when passing from iodonium to bromonium and further to chloronium cation. This is most obvious in the reactions with PPh_3. It is known that the proclivity of diphenylhalonium ions for the one-electron reduction decreases in the order $Ph_2I^+ > Ph_2Br^+ > Ph_2Cl^+$ [19] and is related to a decrease of the positive charge on the halogen atom.[26] The same regularity is likely to take place in the case of phenyl(*m*-carboran-9-yl)halonium cations.[26] It should be pointed out that all radical reactions of phenyl(*m*-carboran-9-yl)halonium cations proceed regiospecifically (Scheme II). Only in one of the two possible pathways of 9-Hal-2 intermediate did decomposition take place to give the phenyl radical and the corresponding carboranyl halide.

Earlier we have attributed this regiospecificity to the different capabilities of phenyl and *m*-carboran-9-yl ligands to delocalize the negative charge in 9-Hal-2 intermediates.[26] Traces of *m*-carborane have been detected among the reaction products of alkaline hydrolysis of phenyl(*m*-carboran-9-yl)bromonium and -chloronium cations. This indicates that the contribution of the second route for the decomposition of 9-Hal-2 intermediates is negligible.

Scheme III



Phenyl radicals formed can phenylate the nucleophile (e.g. pyridine and triphenylphosphine; for mechanisms see refs 1 and 30, respectively), abstract hydrogen from the solvent to produce benzene, or dimerize to give biphenyl. The formed pyridine and triphenylphosphine radical cations can undergo hydrogen abstraction, giving stable pyridinium and unstable (because of the low basicity of triphenylphosphine) triphenylphosphonium cations. The latter eliminates a proton to give PPh_3, which is then phenylated with the phenyl radical. The tetraphenylphosphorus radical formed reduces another halonium ion to give a stable and unreactive tetraphenylphosphonium cation as the final product. Note that this mechanism is very similar to the $S_{RN}1$ reaction.

3. The regiospecificity of nucleophilic substitutions that is typical for the phenyl(*m*-carboran-9-yl)iodonium cation changes for the case of the isostructural bromonium ion and even more so for that of the chloronium ion. The ratio of phenylation and carboranylation product yields depends on the nature of the nucleophile. For example, this ratio is larger for the reaction of **1** or the phenyl(*m*-carboran-9-yl)bromonium salt with N_3^- than with for the reaction with NO_2^- (see Tables I and II). Also, the reaction of this bromonium ion with Cl^- occurs regiospecifically, leading to bromobenzene and 9-chloro-*m*-carborane in quantitative yields:

$$[C_2B_{10}H_{11}\text{-Br-Ph}]^+BF_4^- + NaCl \xrightarrow{CH_2Cl_2\text{-}H_2O} \underset{100\%}{C_2B_{10}H_{11}Cl} + \underset{100\%}{PhBr}$$

This interesting problem is discussed below.

The regiospecificity of nucleophilic substitution in phenyl(*B*-carboranyl)iodonium cations has been shown to result largely from steric factors.[1,5,6,26] Nucleophilic attack at the iodonium atom leads to a hypervalent 10-I-3 intermediate of trigonal-bypiramidal structure (Scheme III). Such a structure is typical for covalent forms of diaryliodonium salts in the solid state.[15,16] In solution, some permutational processes like Berry pseudorotation or turnstile rotation take place, possibly via a tetragonal-pyramidal intermediate that can undergo synchronous reductive elimination from the iodine atom to give products. This seems to be impossible for the trigonal bipyramid because the apical–equatorial cheletropic interaction is symmetry forbidden, as shown for pentacoordinated phosphorus compounds.[31] The nucleophile binds with

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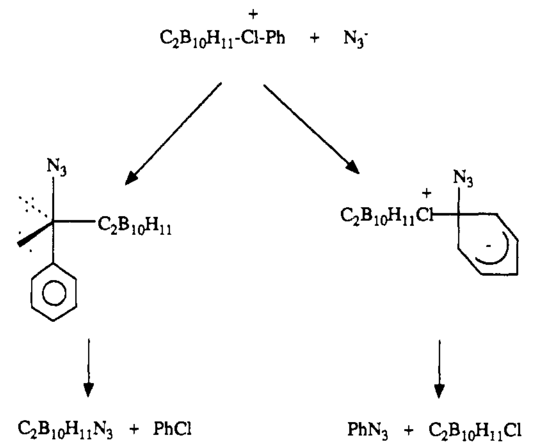
Scheme IV



the most electron-deficient ligand of the two (it decreases the positive charge on central iodine atom), or, more importantly, with the more bulky ligand, because it leads to a decrease in steric tension on the base of tetragonal pyramid.

This mechanism, suggested for the first time by Budylin,[32] explains the regiospecificity of nucleophilic substitution in phenyl(*B*-carboranyl)iodonium cations as well as the so-called "ortho effect". The latter takes place in nucleophilic substitution reactions of unsymmetrical diaryliodonium ions[16] and seems to arise from the same circumstances resulting in the regiospecificity noted above.[1,6,26] The ortho effect arises when the nucleophile completely or at least preferably binds with the more bulky ligand attached to the iodine onium atom, even if this ligand bears electron-donating methyl groups in the ortho positions of benzene ring.[12,15-17,33] The ortho effect depends on the nature of both the nucleophile[33] and onium halogen atom.[17] Other things being equal, the magnitude of the ortho effect noticeably decreases in the series $[Ar-I-Ar']^+ > [Ar-Br-Ar']^+ > [Ar-Cl-Ar']^+$.[17] Such a regularity has been clearly observed in the reactions of phenyl(*m*-carboran-9-yl)halonium ions with the azide ion. It may be associated with the different geometry of the transition state undergoing synchronous reductive elimination, which depends on the nature of the halogen atom. In our opinion, however, an even more important factor is the increase of electron-withdrawing properties of halonium groups in the series $RI^+ < RBr^+ < RCl^+$.[26] The positive charge facilitates nucleophilic ipso attack at the benzene ring. Thus, two mechanisms of nucleophilic substitution compete in reactions of bromonium and chloronium ions, i.e. a synchronous mechanism (onium halogen is attacked) and a S_NAr mechanism (α-carbon is attacked). This competition leads to a decrease of the ortho effect. Considering that nucleophilic ipso attack at the carborane boron atom is unlikely,[26] nucleophilic substitution in phenyl(*m*-carboran-9-yl)bromonium and -chloronium cations occurs via two paths with each one leading to its own pair of products (Scheme IV).

Obviously, the tendency of the nucleophile to attack the halonium atom or α-carbon atom depends on the electronic properties (e.g., orbital electronegativity) of the nucleophile. For this reason, the ratios of carboranylation and phenylation products can be very different for different nucleophiles, other things being equal.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WP-200 SY spectrometer. Infrared spectra were recorded on a UR-20 instrument from Carl Zeiss (Jena, Germany). GLC measurements were performed with a Biokhrom-1 instrument equipped with a 50 m × 0.22 mm XE-60 capillary column. GC-MS analyses were carried out with a Finnigan Ion Trap-700 instrument. TLC was carried out by use of Silufol UV 254 plates from Kavalier (Prague, Czechoslovakia). Phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate was prepared as described in the literature.[26]

1. Phenyl(*m*-carboran-9-yl)chloronium Tetrafluoroborate (1).[10] (a) A solution of aniline (1.82 mL; 20 mmol) in trifluoroacetic acid (8 mL) was diazotized at 0 °C with solid $NaNO_2$ (1.84 g; 26.7 mmol). The resulting solution was mixed with a solution of 9-chloro-*m*-carborane[10] (10.4 g; 58.3 mmol) in hexafluorobenzene (35 mL). Trifluoroacetic anhydride (8.3 mL) was slowly added dropwise, and the mixture was refluxed for 30 min until the diazonium cation disappeared (2-naphthol test). Solvents were removed under vacuum; the residue was treated with pentane–ether (2:3), and the mixture was extracted with water until the water extract portion failed to form a precipitate with aqueous $NaHgBr_3$. Combined aqueous extracts were treated with 40% HBF_4 (20 mL), and the mixture was extracted with nitromethane–chloroform (3:1). Combined organic extracts were evaporated, and the residual oil was treated with ether to give crude **1**, which was purified by filtration of its dichloromethane solution through a short alumina plug followed by recrystallization (acetone–ether): yield of analytically pure **1** 0.50 g (7%); mp 164 °C dec; ^{1}H NMR (acetone-d_6, 25 °C) δ 4.3 (br s, 2 H, carborane CH), 7.8–8.2 (m, 5 H, C_6H_5). Anal. Calcd for $C_8H_{16}B_{11}ClF_4$: C, 28.05; H, 4.71. Found: C, 27.69; H, 4.79.

(b) A solution of phenyldiazonium tetrafluoroborate (4 g; 20.8 mmol) in trifluoroacetic acid (10 mL) was added dropwise to a boiling mixture of 9-chloro-*m*-carborane (8.2 g; 45.9 mmol), hexafluorobenzene (20 mL), and trifluoroacetic acid (5 mL); the mixture was then refluxed for 30 min until the diazonium salt disappeared. The solution was evaporated to dryness, the remaining solid was dissolved in acetone, and the solution was treated with excess ether to give **1**, which was purified as described above: yield 0.73 g (10%); mp 164 °C dec.

2. Hydrolysis of 1. A mixture of **1** (0.30 g; 0.87 mmol) and water (5 mL) was stirred at room temperature until **1** was completely decomposed (ca. 200 h). The aqueous solution was extracted with benzene, and the combined benzene solutions were evaporated to dryness. The resulting solid was chromatographed on silica 40/100 μ (15 × 200 mm column) first with a benzene–hexane (1:1) mixture, to give 9-chloro-*m*-carborane (0.013 g; 8%), mp 221–222 °C (hexane; see ref 10), and then with ether, to give 9-hydroxy-*m*-carborane (0.079 g; 56%), mp 328–329 °C (benzene–heptane; see ref 2). Evaporation of the aqueous solution gave H_3BO_3 (0.18 g; 33%) as identified by IR spectroscopy.

3. Reaction of 1 with NaN_3. A mixture of **1** (0.498 g; 1.45 mmol), sodium azide (0.30 g; 4.62 mmol), dichloromethane (5 mL), and water (5 mL) was vigorously stirred at 20 °C for 30 min. GLC analysis of the organic phase (with iodobenzene as internal standard) showed the formation of chlorobenzene (65% yield) and phenyl azide (35% yield). The organic layer was separated out and evaporated, and the remaining oil was chromatographed on silica 40/100 μ (15 × 200 mm column) with a hexane–benzene (15:1) mixture, to give 9-chloro-*m*-carborane (0.092 g; 35% yield), mp 221–222 °C (heptane), and 9-azido-*m*-carborane (0.161 g; 60% yield), mp 93–95 °C (hexane; see ref 2).

4. Reaction of Phenyl(*m*-carboran-9-yl)bromonium Tetrafluoroborate with $NaNO_2$. A mixture of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate (0.724 g; 1.87 mmol), sodium nitrite (0.39 g; 5.65 mmol), dichloromethane (5 mL), and water (5 mL) was vigorously stirred under reflux for 2.5 h (nitrogen oxides evolved). GLC analysis of the organic phase (with chlorobenzene as internal standard) showed the formation of bromobenzene (95% yield), nitrobenzene (1% yield), and benzene (1% yield). The organic layer was separated out and evaporated. The residue was chromatographed on silica 40/100 μ (15 × 200 mm column) first with hexane, to give 9-bromo-*m*-carborane (0.010 g; 2.5% yield), mp 182–184 °C (pentane; see ref 9), and then with ether, to give 9-hydroxy-*m*-carborane (0.277 g; 92%), mp 327–329 °C (benzene–hexane).

5. Reaction of 1 with $NaNO_2$. A mixture of **1** (0.503 g; 1.46 mmol), sodium nitrite (0.30 g; 4.35 mmol), dichloromethane (5 mL), and water (5 mL) was vigorously stirred under reflux for 1.5 h (nitrogen oxides evolved). GLC analysis of the organic layer (with iodobenzene as internal standard) showed the formation of chlorobenzene (90% yield), nitrobenzene (3% yield), and benzene (1% yield). The mixture was separated as described in the previous experiment, to give 9-chloro-*m*-carborane (0.012 g; 4.5% yield), mp 217–219 °C (hexane), and 9-hydroxy-*m*-carborane (0.196 g; 83% yield), mp 329–331 °C (benzene–hexane).

6. Reaction of 1 with NaOH. A mixture of **1** (0.500 g; 1.46 mmol), sodium hydroxide (0.29 g; 7.25 mmol), water (6 mL), and ether (6 mL) was stirred at 20 °C for 8.5 h. The organic layer was separated out, and the aqueous solution was washed with ether (2 × 2 mL). GLC and GC-MS analyses of combined organic solutions (with iodobenzene as internal standard) showed the formation of benzene (exact yield was not determined; ca. 15%), biphenyl (traces), chlorobenzene (36% yield), phenyl ether (traces), *m*-carborane (traces), 9-chloro-*m*-carborane, bis-

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(*m*-carborane-9-yl) ether, phenyl *m*-carboran-9-yl ether, and 9-hydroxy-*m*-carborane. Ether was removed under vacuum, and the residual oil was chromatographed on silica 40/100 μ (15 × 200 mm column) first with hexane, to give 9-chloro-*m*-carborane (0.164 g; 63% yield), mp 220–222 °C (hexane), and then with a benzene–hexane (1:1) mixture, to give 0.036 g (ca. 10%) of a mixture of phenyl *m*-carboran-9-yl ether (for the mass spectrum see ref 22) and bis(*m*-carboran-9-yl) ether.[22] The ratio of the two components of this mixture was determined by GC-MS analysis. Finally, elution with ether gave 9-hydroxy-*m*-carborane (0.024 g; 10%), mp 326–328 °C (benzene–heptane).

The aqueous solution was acidified with 15% HCl, and the mixture was treated with aqueous bromine, to give 2,4,6-tribromophenol, which was filtered out, dried, and sublimed under vacuum: yield 0.130 g (27%); mp 92–94 °C.

7. Reaction of Phenyl(*m*-carboran-9-yl)bromonium Tetrafluoroborate with NaF. A mixture of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate (0.05 g; 0.13 mmol), sodium fluoride (0.013 g; 0.38 mmol), dichloromethane (1 mL), and water (1 mL) was vigorously stirred under reflux for 5 h. GLC and GC-MS analyses of the organic layer (9-iodo-*m*-carborane as internal standard) showed the formation of benzene, bromobenzene (exact yields were not determined; ca. 10% and 70%, respectively), 9-fluoro-*m*-carborane (45% yield), and 9-bromo-*m*-carborane (8% yield). No fluorobenzene was found among the reaction products (GC-MS).

8. Reaction of 1 with NaF. A mixture of **1** (0.05 g; 0.15 mmol), sodium fluoride (0.018 g; 0.43 mmol), dichloromethane (1 mL), and water (1 mL) was vigorously stirred under reflux for 5 h. GLC and GC-MS analyses of the organic layer (9-iodo-*m*-carborane as internal standard) showed the formation of benzene, chlorobenzene (exact yields were not determined; ca. 10% and 70%, respectively), 9-fluoro-*m*-carborane (50%), and 9-chloro-*m*-carborane (10%). Again, formation of fluorobenzene (GC-MS) did not occur.

9. Reaction of 1 with Pyridine. A solution of **1** (1.00 g; 2.9 mmol) in pyridine (10 mL) was refluxed for 9 h. Pyridine was removed under vacuum, and the residue was treated with ether, giving an oil that solidified only after a minimum of five reprecipitations with ether from acetone. The yield of pyridinium tetrafluoroborate was 0.083 g (68%); mp 210–225 °C (ethanol; see ref 1). Combined ether and ether–acetone solutions were evaporated to dryness. The remaining residue was washed with benzene, to give boric acid (0.174 g; 9.5% yield), which was identified by IR spectroscopy. The benzene solution was extracted with 10% acetic acid. Combined acidic solutions were treated with 10% NaOH, and the mixture was extracted with ether. Evaporation of ether gave a mixture of α-, β-, and γ-phenylpyridines (0.008 g; 2% yield; identified by TLC comparison, with authentic samples). The remaining benzene solution (after extraction of phenylpyridines) was filtered through alumina and reduced to dryness. The solid residue was washed with hexane, to give crystalline zwitterionic B–N-bonded pyridinium 7,9-dicarba-*nido*-undecaborate, which was purified by vacuum sublimation: yield 0.326 g (53%); mp 163–165 °C (see refs 9 and 29). Evaporation of the hexane solution and vacuum sublimation of the residue gave 9-chloro-*m*-carborane (0.133 g; 25% yield), mp 220–222 °C.

10. Reaction of 1 with PPh_3. An acetone solution (3 mL) of **1** (0.20 g; 0.58 mmol) and triphenylphosphine (0.31 g; 1.18 mmol) in a quartz tube was irradiated with UV light (Soviet-made PRK-2 mercury lamp) for 38 h. GLC analysis of the reaction mixture showed the presence of benzene (ca. 1% yield) and the absence of *m*-carborane among the reaction products. The ^{31}P NMR spectrum of the reaction mixture showed no formation of triphenyl(*m*-carboran-9-yl)phosphonium tetrafluoroborate (for the spectrum see ref 3). Treatment of the mixture with ether led to the precipitation of tetraphenylphosphonium tetrafluoroborate (0.232 g; 95% yield), mp 348–351 °C (acetone–ether; see ref 30). The ether solution was reduced to ca. 5 mL and treated with methyl iodide (0.5 mL), and the resulting mixture was refluxed for 1.5 h, to remove excess PPh_3. The methyltriphenylphosphonium iodide formed was filtered out, the mother liquor evaporated, and the remaining solid extracted with hexane. The hexane solution was filtered through alumina and evaporated, to give 9-chloro-*m*-carborane (0.086 g; 82% yield), mp 220–222 °C (hexane).

11. Reaction of Phenyl(*m*-carboran-9-yl)bromonium Tetrafluoroborate with NaCl. A mixture of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate (0.049 g; 0.13 mmol), sodium chloride (0.02 g; 0.34 mmol), chloroform (1 mL), and water (1 mL) was vigorously stirred under reflux for 1 h. GLC analysis of the organic phase (iodobenzene as internal standard) showed the formation of only bromobenzene and 9-chloro-*m*-carborane in quantitative yields.

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Organotransition-Metal Metallacarboranes. 18.[1] η^6,η^5-Benzyltetramethylcyclopentadienide(1−) as a Bridging Ligand in Multilevel Iron–Cobalt Sandwich Complexes

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Benzyltetramethylcyclopentadiene ($Me_4C_5CH_2Ph$) was prepared in high yield from commercial reagents and deprotonated with butyllithium to give the red title anion, which was converted to the orange sandwich complex $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)$ (**1**) via reaction with $CoCl_2$ and $Na^+Et_2C_2B_4H_5^-$ in THF. Decapitation (apex BH removal) of **1** with wet TMEDA gave yellow $(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (**2**), which in turn was bridge-deprotonated and reacted with $CoCl_2$ and the title anion to give a burgundy-colored triple-decker complex, $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (**3**). The thermal cyclooctatriene-displacement reaction of **1** with $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ produced an orange bimetallic species, $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**4**). Similar treatment of **3** with the same cyclooctatriene–ferracarborane reagent gave the iron–dicobalt complex $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (**5**) and the diiron–dicobalt species $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (**6**), both isolated as red oils. Complex **2** was benzylated at the B(5) location on the open face by bridge deprotonation to give the anion **2**$^-$, followed by reaction with benzyl bromide to form the yellow solid derivative $(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**7**). Mono- and bis(ferracarboranyl) derivatives of **7** were prepared by thermal displacement of cyclooctatriene from $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ by **7** to give primarily $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**8**) and a small amount of $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**9**). The monoiron species **8** consisted almost entirely of one isomer (**8a**), having the iron coordinated to the *B*-benzyl unit; the alternative isomer (**8b**), in which the iron is bonded to the cyclopentadienyl benzyl group, was detected in only trace amounts in NMR spectra. The much higher reactivity in **7** of the *B*-benzyl vs the cyclopentadienyl benzyl group toward iron coordination suggests deactivation of the latter by the adjacent cobalt atom.

Introduction

Bimetallic[2] and polymetallic[3] linked sandwich complexes are attracting increasing attention, in part because they provide a bridge between molecular chemistry and materials science and also because they have potential for utilization in novel electronic devices. In our research, a current focus of interest is the design

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