

Carboranylhalonium Ions: From Striking Reactivity to a Unified Mechanistic Analysis of Polar Reactions of Diarylhalonium Compounds

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In 1894 Hartmann and Meyer reported the preparation of the first halonium compound, (4-iodophenyl)phenyliodonium hydrogen sulfate.¹ Since that time hundreds of aromatic, aliphatic, and heterocyclic iodonium, bromonium, and chloronium ions have been synthesized and investigated.²⁻⁴ However, neither inorganic nor organometallic halonium ions were known before we started investigations described in the present Account.⁵

Among the variety of halonium ions, diarylhalonium salts are probably the most synthetically useful,⁸ as they are able to arylate nucleophiles effectively under mild conditions. At the same time, mechanisms for polar reactions of diarylhalonium salts with nucleophiles remained unclear, in spite of having been the subject of numerous profound investigations.

Icosahedral *closo*-carboranes(12) are considered to be quasi-aromatic systems.⁹ Chemical properties and reactivities of many functional groups attached to the boron atoms of carboranes(12) are very similar to those of the corresponding benzene derivatives.¹⁰ Synthesis of halonium derivatives of carboranes with a boron-halogen bond seemed to be a challenging problem in accordance with the following considerations.

I. Carboranylhalonium ions would be the first example of inorganic halonium compounds.

II. Like haloarenes, *B*-carboranyl halides (and tosylates) do not undergo nucleophilic substitution even under extremely drastic conditions.^{10,11} At the same time, diarylhalonium compounds are very reactive toward nucleophiles.²⁻⁴ Should *B*-carboranylhalonium ions exist, they might give a unique opportunity by realizing nucleophilic substitution at the boron atom of the carborane cage. This in turn would mean a new approach to the synthesis of previously unknown boron-substituted functionalized derivatives of carboranes. In other words, carboranylhalonium ions could solve the important problem of nucleophilic substitution at a boron atom of icosahedral carboranes.

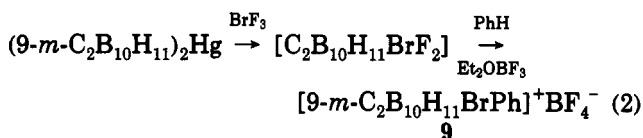
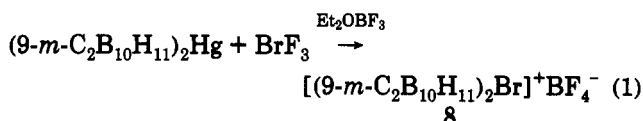
III. Many peculiar and curious features of polar reactions of diarylhalonium salts have not been rationalized in a satisfactory manner. By investigating the reactivity of halonium derivatives of the quasi-aromatic inorganic systems, one might get fresh ideas for

understanding the mechanism of the reaction between aromatic halonium ions and nucleophiles.

Synthesis

The synthesis of aryl(*B*-carboranyl)iodonium cations is based on the oxidation of iodicarboranes to the corresponding iodoso derivatives followed by their condensation with arenes in acidic media (Scheme 1).¹²⁻¹⁴

The carboranylbromonium salts were prepared from bis(*m*-carboran-9-yl)mercury and bromine trifluoride (eqs 1 and 2).¹⁵⁻¹⁷



Heterolytic decomposition of arenediazonium cations in the presence of *m*-carboran-9-yl halides affords

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(5) Some cationic transition metal complexes having bridging halogens⁶ or organic halides⁷ as ligands may be formally regarded as halonium ions with a transition metal-halogen bond. Due to the specific coordination properties of transition metals, most of the authors do not even mention the resemblance between such complexes and organic halonium ions.

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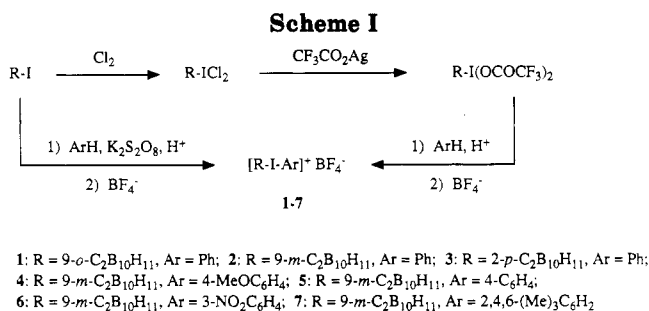
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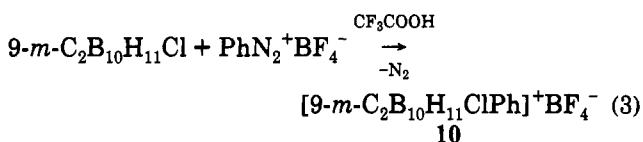
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Table I. Aryl(*B*-carboranyl)halonium Salts

Hal	carboranyl group	Ar	A	yield, %	ref
I	9- <i>o</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	BF ₄	75-93	12
I	9- <i>o</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	I	100	12
I	9- <i>o</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	Br	81	19
I	9- <i>o</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	Cl	68	19
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	BF ₄	78-95	12
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	I	100	12
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	Br	90	19
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	Cl	61	19
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	4-FC ₆ H ₄	BF ₄	83	14
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	3-FC ₆ H ₄	BF ₄	8	14
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	4-CH ₃ OC ₆ H ₄	BF ₄	84	14
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	3-NO ₂ C ₆ H ₄	BF ₄	10	14
I	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	2,4,6-(CH ₃) ₃ C ₆ H ₂	BF ₄	84	14
I	2- <i>p</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	BF ₄	80	13
Br	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	BF ₄	25-47	15-17
Br	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	4-FC ₆ H ₄	BF ₄	16	17
Br	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	3-FC ₆ H ₄	BF ₄	5	14
Br	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	BF ₄	40-55	15, 16
Br	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	Br	100	15
Cl	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	C ₆ H ₅	BF ₄	7-10	14, 18
Cl	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	4-FC ₆ H ₄	BF ₄	1.5	14
Cl	9- <i>m</i> -C ₂ B ₁₀ H ₁₁	3-FC ₆ H ₄	BF ₄	5	14

various aryl(*m*-carboran-9-yl)halonium compounds including chloronium salts (e.g., eq 3).^{14,18}



Selected data for all the carboranylhalonium compounds synthesized in the present work are summarized in Table I. Molecular and crystal structures of phenyl(*o*-carboran-9-yl)iodonium iodide²⁰ and bis(*m*-carboran-9-yl)bromonium tetrafluoroborate²¹ were determined by X-ray diffraction. The carboranyliodonium salts

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and carboranyliodoso dichlorides were studied by ¹²⁷I NQR spectroscopy.²²

Reactions of Phenyl(carboranyl)iodonium Ions with Nucleophiles

In contrast with *B*-carboranyl halides,⁹⁻¹¹ iodonium derivatives of carboranes are highly reactive toward nucleophiles. Phenyl(*B*-carboranyl)iodonium cations are capable of reacting regioselectively and regiospecifically with nucleophilic reagents by three main pathways: (i) carbon-halogen bond cleavage; (ii) boron-halogen bond cleavage; (iii) degradation of the carborane polyhedron. Our attention was predominantly focused on the reactions not accompanied by structural changes of carboranyl ligands. The degradation processes were also investigated, however mostly in order to develop methods to avoid them.

Icosahedral *closo*-carboranes(12) are known²³ to undergo degradation to dicarba-*nido*-undecaborate anions upon interaction with strong bases; the ortho isomer is the most susceptible to the degradation. The strongly electron-accepting phenyliodonio group,¹⁷ attached to the *o*-carborane cage, substantially destabilizes the polyhedron toward the degradation. Thus, the carborane cage in phenyl(*o*-carboran-9-yl)iodonium cation is broken up easily by weak bases such as water,²⁴ ethanol,²⁵ and even dimethyl sulfoxide.²⁶ The reaction with dimethyl sulfoxide leads to the zwitterionic 5(6)-dimethylsulfoxonium 7,8-dicarba-*nido*-undecaborate,²⁶ whose structure was established by X-ray diffraction²⁶ and confirmed by IR and Raman spectral data.²⁷ Water completely destroys the carborane skeleton of phenyl(*o*-carboran-9-yl)iodonium cation 1 to give boric acid. Therefore, to obviate the destruction of the carborane nucleus, reactions of 1 with charged nucleophiles should be conducted in dry chloroform or methylene chloride using phase-transfer conditions or an ionic pair extraction technique.

The carborane fragments in iodonium derivatives of *m*- and *p*-carboranes 2 and 3 are much more stable toward alcohols, water, and dimethyl sulfoxide.^{25,26} Reactions of 2 and 3 with charged nucleophiles can be carried out successfully in the biphasic systems H₂O-CHCl₃ and H₂O-CH₂Cl₂. As we have shown,²⁸ such systems possess a number of important advantages (higher yields, lower reaction temperatures, shorter reaction times) over traditional homogeneous media, when used for arylation of anionic nucleophiles with diarylhalonium salts.

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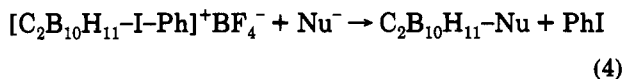
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Table II. Boron-Substituted Carboranes Obtained via Carboranylhalonium Ions

compound	yield, %	ref	compound	yield, %	ref
Previously Unknown					
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ N ₃	99	25	9- <i>m</i> -C ₂ B ₁₀ H ₁₁ N=PPh ₃	93	25
9- <i>o</i> -C ₂ B ₁₀ H ₁₁ N ₃	54	24	9- <i>o</i> -C ₂ B ₁₀ H ₁₁ N=PPh ₃	79	24
2- <i>p</i> -C ₂ B ₁₀ H ₁₁ N ₃	91	13	2- <i>p</i> -C ₂ B ₁₀ H ₁₁ NCS	53	31
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ OS(O)Ph	90	25	(9- <i>m</i> -C ₂ B ₁₀ H ₁₁) ₂ O	25	33, 34
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ OS(O)C ₆ H ₄ CH ₃	86	25	2- <i>p</i> -C ₂ B ₁₀ H ₁₁ CN	98	19
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ OCOPh	95	25	9- <i>m</i> -C ₂ B ₁₀ H ₁₁ CN	58	19
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ NCS	43	25	9- <i>m</i> -C ₂ B ₁₀ H ₁₁ NO ₂	8.5	30
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ NHCH ₃	79	25	[9- <i>m</i> -C ₂ B ₁₀ H ₁₁ PPh ₃] ⁺ BF ₄ ⁻	71	35
2- <i>p</i> -C ₂ B ₁₀ H ₁₁ F	100	13			
Previously Difficult To Obtain					
9- <i>o</i> -C ₂ B ₁₀ H ₁₁ F	98	19, 29	9- <i>m</i> -C ₂ B ₁₀ H ₁₁ NH ₂	91	25
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ F	89	19, 29	9- <i>m</i> -C ₂ B ₁₀ H ₁₁ OH	79	25, 30
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ OCOCH ₃	62	25	9- <i>o</i> -C ₂ B ₁₀ H ₁₁ CN	11	19
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ COOH	94	19	2- <i>p</i> -C ₂ B ₁₀ H ₁₁ OH	77	13
9- <i>m</i> -C ₂ B ₁₀ H ₁₁ SCN	56	25			

The major peculiarity of reactions between phenyl(*B*-carboranyl)iodonium salts and nucleophiles occurring without destroying the *closo* structure of the carborane ligand is their regioselectivity. Depending on the nature of the nucleophile, either rupture of the boron-iodine bond takes place or the carbon-iodine bond is cleaved. This reactivity is novel and unique, since no analogy exists in the chemistry of other onium compounds.

Boron-Iodine Bond Cleavage. Iodonium salts 1-3 smoothly react with a number of anions to give iodobenzene and the corresponding *B*-substituted carboranes in good to quantitative yields (eq 4).^{13,24,25,29-31}



Nu⁻ =



The reaction of 2 with NaNO₂ in a CH₂Cl₂-H₂O biphasic system leads to two products of carboranylation, i.e., 9-hydroxy-*m*-carborane (79%) and 9-nitro-*m*-carborane (6%).^{25,30,31} The products of O- and N-carboranylation of the nitrite anion form simultaneously and independently of each other.³⁰ The reaction between phenyl(*m*-carboran-9-yl)iodonium cation 2 and NaSCN gives rise to a mixture (1.3:1) of *m*-carboran-9-yl thiocyanate and the corresponding isothiocyanate with a total yield of 99%.²⁵ At the same time, the phenyliodonium derivative of the less electron-donating *p*-carborane, 3, reacts with NaSCN under the same conditions to give isomeric thiocyanate and isothiocyanate in a 1:2.65 ratio.³¹ Evidently, electronic properties of carboranyl ligands can control reactions of phenyl(carboranyl)iodonium cations with ambiden-

tate nucleophiles. This is consistent with the general perturbation theory of a donor-acceptor interaction.³²

As seen, the carboranylation of nucleophiles with phenyl(*B*-carboranyl)iodonium salts results in good to quantitative yields of new *B*-substituted carborane derivatives along with iodobenzene. The substituent always occurs on the boron atom of the icosahedron which previously carried the phenyliodonio group (*ipso* substitution). The boron-iodine bond cleavage reactions are not inhibited by radical traps, e.g., 1,1-diphenylethylene.¹⁹ Neither unsubstituted carboranes nor any other byproduct of a free boron-centered carboranyl radical transformation was found in the reaction mixtures. Rather, the reactivity of phenyl(*B*-carboranyl)iodonium cations appeared to be dependent on electronic effects of the carboranyl ligands and on the solvent polarity. Among salts 1-3, the fastest carboranylation reactions were observed for cation 3, containing the least electron-donating *p*-carboran-2-yl group, in organic media of low polarity. Therefore, a radical mechanism for the carboranylation reactions can be ruled out.

Representing the unique example of nucleophilic substitution at a boron atom of icosahedral *closo*-carboranes, the above described carboranylation reactions afford some *B*-carboranyl derivatives which either are accessible with difficulty or cannot be obtained by any other means (Table II). Some of the new *B*-substituted functional derivatives of carboranes appeared to be interesting subjects for physical investigations. For instance, the first experimental data on electron density distribution in carboranes were obtained by a low-temperature X-ray diffraction study of 9-azido-*m*-carborane.³⁶

Carbon-Iodine Bond Cleavage. Reactions of phenyl(*B*-carboranyl)iodonium salts with nucleophiles lead-

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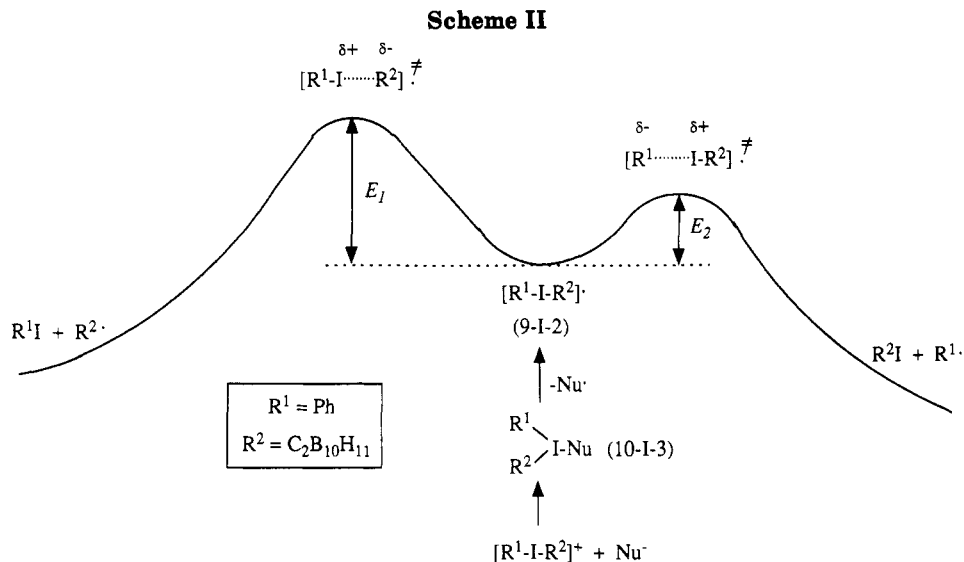
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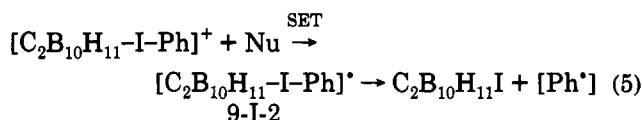
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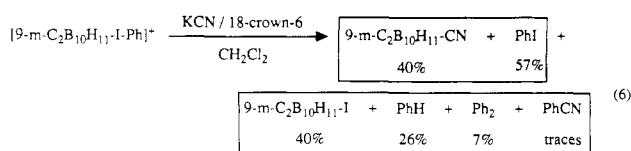


ing to carbon-iodine bond cleavage reveal an obvious homolytic mechanism (eq 5). They selectively lead to the corresponding iodocarboranes and compounds arising from phenyl radical transformations, i.e., benzene, biphenyl, and radical phenylation products (e.g., Ph_4P^+ , α -, β -, and γ -phenylpyridines, and $PhHgCl$ in cases of PPh_3 , pyridine, and metallic mercury, respectively).^{13,19,25,35,37} Similar to radical reactions of diaryliodonium salts,^{2-4,38} the reactions of phenyl(*B*-carboranyl)iodonium ions with carbon-iodine bond cleavage proceed apparently via 9-I-2 intermediates, $[R-I-R']\cdot$, which are formed by a one-electron reduction of the initial iodonium cation.



$Nu = Ph_3P, C_5H_5N, OH^-, Hg, n-BuLi, e^-/Hg \text{ cathode}$

A few nucleophiles react with phenyl(*B*-carboranyl)iodonium salts via two pathways simultaneously, causing the cleavage of both the boron-iodine and the carbon-iodine bonds. The most pronounced example is the reaction of the *m*-carboranyliodonium derivative 2 with the cyanide anion.¹⁹ The distribution of the products clearly indicates that the two directions are equally possible (eq 6).



The reaction pattern does not change in the presence of the radical trap 1,1-diphenylethylene, altering only the $PhH:Ph_2$ ratio.³⁹ Yields of all other products remain unchanged, supporting a nonchain mechanism for the

radical route. Trace amounts of benzene and iodocarborane were also formed in the above described reactions of phenyl(*B*-carboranyl)iodonium cations with NO_2^- ³⁰ and F^- ,²⁹ indicating a very modest contribution of a radical reaction pathway.

Mechanistic Studies

Phenyl(*B*-carboranyl)iodonium cations, as we have seen, possess a unique reactivity toward nucleophiles resulting in two vastly differing mechanisms. Like diaryliodonium salts,²⁻⁴ they readily react with nucleophiles via either a polar or radical pathway; on the other hand, upon reacting with nucleophiles, unsymmetrical diaryliodonium ions undergo cleavage of both carbon-iodine bonds, regardless of which mechanism (polar or radical) operates the reaction. Some such reactions are known to be quite selective. However, there are no examples in the chemistry of organic halonium ions where nucleophilic substitution occurs only on one ligand of an unsymmetrical halonium compound, while a radical reaction (a one-electron reduction) of the same salt leads to the elimination of only the opposite ligand as the radical. The only exception is phenyl(*B*-carboranyl)iodonium salts, which deserve to be called extremists among halonium compounds. Their transformations with either boron-iodine bond cleavage or carbon-iodine bond cleavage are perfect and pure models of the two very extreme cases, which are known in the chemistry of halonium (and other onium) compounds as *polar* and *radical* reactions, respectively.

The regiospecificity of the radical reactions of phenyl(*B*-carboranyl)iodonium cations with nucleophiles can be easily rationalized¹⁷ in light of Tanner's paper on 9-I-2 intermediates³⁸ (Scheme II). The first step of the radical reaction is a single electron transfer (SET) from a nucleophile to an iodonium cation. The resulting 9-I-2 intermediate has two decomposition paths. The energy of the transition states strongly depends on electronic effects of the substituents attached to the iodine; that is, the more capable the substituent of delocalizing a negative charge, the lower the energy. *o*-Carboran-9-yl and *m*-carboran-9-yl groups are strong electron donors,¹⁰ whereas a phenyl group is an electron acceptor. Moreover, unlike carboranyl groups (their σ_R° constants are close to 0), the phenyl substituent is

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(38) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* 1982, 104, 3917 and references cited therein.

(39) Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *J. Org. Chem.* 1978, 43, 2432.

able to delocalize a negative charge by resonance. As a result, the difference between activation energies E_1 and E_2 (Scheme II) appears to be sufficient to make the radical reactions of phenyl(*B*-carboranyl)iodonium salts regiospecific.

Factors determining the regiospecificity of the polar reactions of phenyl(*B*-carboranyl)iodonium cations (boron–iodine bond cleavage) were far less clear. The classical S_N1 mechanism was ruled out by kinetic measurements showing that the reaction between **2** and NaN_3 is second order (first order on each reagent).¹⁷ In addition, hydroxycarboranes would have been formed as byproducts in any biphasic reaction, if the latter proceeded via formation of *B*-carboranyl cations. The classical S_N2 mechanism, involving a nucleophilic attack on the carborane boron attached to the onium iodine, is also unlikely. Nucleophiles never attack an icosahedron *closo*-carborane boron if it bears any substituent except hydrogen.⁴⁰ However, even if such an attack took place, a conversion of the *closo*-carborane cluster to a nido framework would have occurred.⁴¹ The nido compound 7-phenyl-12-(1-phenyl-1,2-dicarba-*closo*-dodecaboran-2-yl)-7,8-dicarba-*nido*-dodecaborate anion, synthesized and structurally characterized by Zakharkin et al.,⁴² represents an excellent and unique model of the intermediate in the carborane(12) degradation reaction. All attempts to convert this nido structure back to the *closo*-carborane icosahedron were unsuccessful.⁴² The polar reactions of phenyl(*B*-carboranyl)iodonium cations never led to either formation of nido structures or skeletal rearrangements of the cage which should have taken place if the process followed the path *closo*–*nido*–*closo*.⁴¹ Thus, special studies were necessary to clarify the mechanism of the polar reactions of phenyl(*B*-carboranyl)iodonium salts, and the reasons for their regiospecificity.

Electronic Effects of Phenylhalonio and *m*-Carboranylhalonio Groups. The reactivity of phenyl(*m*-carboran-9-yl)iodonium ions toward many nucleophiles including N_3^- , NO_2^- , and PhSO_2^- is quite similar to that of the diphenyliodonium ion. The mechanism for polar reactions of diaryliodonium ions is usually considered to be of $S_N\text{Ar}$ character, involving a nucleophilic attack on the α -carbon atom.^{38,39,43,44} If so, why do nucleophiles not attack the α -carbon atom of the phenyl(*B*-carboranyl)iodonium cations? Do strong electron-donating effects of *o*(*m*)-carboran-9-yl groups, which are transmitted through the onium halogen atom, make the α -carbon atom indifferent toward nucleophiles? In order to examine this hypothesis, we obtained the

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(43) (a) Beringer, F. M.; Brierley, A.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, *75*, 2708. (b) Beringer, F. M.; Gindler, E. M. *J. Am. Chem. Soc.* **1955**, *77*, 3203. (c) Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* **1964**, 4442. (d) Growder, I. R.; Glover, E. E.; Grundon, M. F.; Kaempfen, H. X. *J. Chem. Soc.* **1963**, 4578. (e) Yamada, Y.; Kashima, K.; Okawara, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3179. (f) Gronowitz, S.; Holm, B. *Tetrahedron* **1977**, *33*, 557. (g) Lubinkowski, J. J.; Arrieche, C. G.; McEwen, W. E. *J. Org. Chem.* **1980**, *45*, 2076.

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Table III. Electronic Effects of Phenylhalonio and *m*-Carboran-9-ylhalonio Groups (in CHCl_3)

group	σ_I	σ_R°	group	σ_I	σ_R°
PhCl^+	+1.72	+0.03	$\text{C}_2\text{B}_{10}\text{H}_{11}\text{Br}^+$	+1.60	-0.02
$\text{C}_2\text{B}_{10}\text{H}_{11}\text{Cl}^+$	+1.65	0	PhI^+	+1.35	+0.02
PhBr^+	+1.63	0	$\text{C}_2\text{B}_{10}\text{H}_{11}\text{I}^+$	+1.39	0

Table IV. Reactions of Phenyl(*m*-carboran-9-yl)halonium Tetrafluoroborates with Sodium Azide (Dichloromethane–Water Biphasic System, 20 °C)¹⁸

X	ratio of pathways A and B, %	
	A	B
I	99	0
Br	95	5
Cl	65	35

corresponding σ -constants of all phenylhalonio and *m*-carboran-9-ylhalonio groups,¹⁷ using the Taft method.⁴⁵ The results presented in Table III show onium halogen atoms as incapable of transmitting electronic effects. Evidently, the phenyl ring carbon attached to a halonio group is equally activated toward nucleophilic attack (in terms of electronic factors), regardless of the second ligand (phenyl or strongly electron-donating *m*-carboran-9-yl) of the halonio cation. Nevertheless, nucleophilic substitution at the α -carbon of phenyl(*B*-carboranyl)iodonium cations does not take place, in contrast to the case of diphenyliodonium ions. These results are of significant importance, since they make the concept of $S_N\text{Ar}$ -type substitution in diaryliodonium ions questionable.

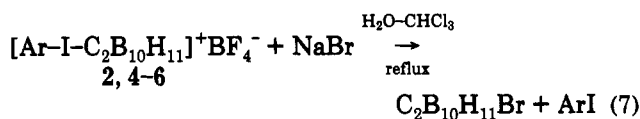
Reactions of Phenyl(*m*-carboran-9-yl)bromonium and -chloronium Ions. The study of reactions of phenyl(*m*-carboranyl)bromonium, **9**,^{16,18} and phenyl(*m*-carboran-9-yl)chloronium, **10**,¹⁸ tetrafluoroborates with a number of nucleophiles showed the dramatic decrease of the regioselectivity of S_N reactions over the series iodonium, bromonium, chloronium.¹⁸ The reactions with sodium azide (Table IV) represent the most pronounced and clear example; similar results were obtained for nucleophilic substitution in cations of **2**, **9**, and **10** by NO_2^- and OH^- .

Reactions of Aryl(*m*-carboran-9-yl)iodonium Ions. Electron-withdrawing groups are known to increase the reactivity of diaryliodonium ions, while electron-donating substituents exert the opposite effect.²⁻⁴ On the other hand, ortho substituents, including electron-donating methyl groups, facilitate nucleophilic substitution on the ring (the so-called *ortho*-effect).^{4,28b,44,46,47} With this in mind, we investigated polar reactions between a number of nucleophiles and aryl(*m*-carboran-9-yl)iodonium compounds **4**–**7**, having different substituents in the aryl ring. Like salt **2**, with no substituents on the phenyl ligand, compounds **4**–**6** react with Br^- to give only bromocarborane and the corresponding iodoarene, in quantitative yields (eq 7).³¹ However, such was not the case for

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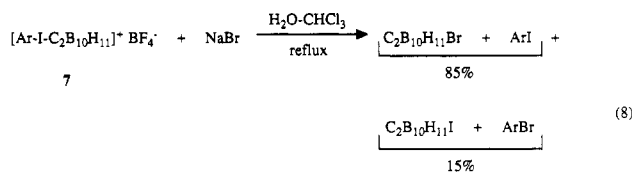
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Ar = Ph, 2; 4-CH₃OC₆H₄, 4; 4-FC₆H₄, 5; 3-NO₂C₆H₄, 6

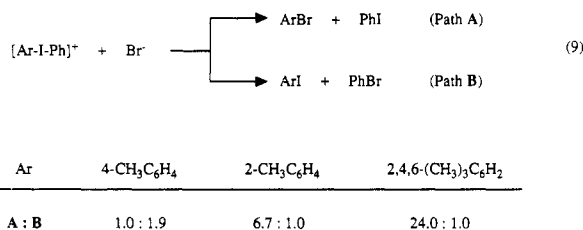
mesityl(*m*-carboran-9-yl)iodonium salt 7, which gave all four possible products of nucleophilic substitution (eq 8).



Ar = 2,4,6-(CH₃)₃C₆H₂

The same reactivity pattern was observed for the reactions of salts 4-7 with NaNO₂. Nucleophilic substitution in cations of 4-6 by NO₂⁻ is as highly selective as that in the cation of 2. At the same time, in the reaction of the mesityliodonium salt 7 with the nitrite ion, a significant competition between nucleophilic substitution at the carborane boron and the mesityl carbon takes place.^{30,31} Hence, it is neither electron-withdrawing nor electron-donating substituents but rather ortho-substituted aryl ligands which are able to influence the regioselectivity of nucleophilic substitution in aryl(*B*-carboranyl)iodonium cations.

The results of nucleophilic substitution in 7 by Br⁻ and NO₂⁻ strongly resemble the "ortho-effect" in the polar reactions of ortho-substituted unsymmetrical diaryliodonium ions.^{4,28b,44,46,47} Equation 9 illustrates the ortho-effect. Usually the more electron-deficient ring of unsymmetrical diaryliodonium cation is attacked by a nucleophile, while similar reactions of isomeric ortho-substituted cations lead to the products in an opposite ratio. This tendency increases with the introduction of two phenyl groups at the ortho positions.^{28b,44,47}



The vaguest part of our knowledge on aromatic halonium compounds is the ortho-effect: "The polar reactions of diaryliodonium salts with nucleophiles are not without their mechanistic idiosyncrasies" (see ref 4, p 1295). An explanation of the ortho-effect in diaryliodonium salts has been based on the following assumptions.^{4,44,47} A nucleophile attacks the onium iodine to give a tricovalent iodine(III) complex (10-I-3 intermediate). This intermediate is believed to be T-shaped, as are diaryliodonium compounds in the solid state.⁴ The bulkier of the two aryl ligands and two lone electron pairs (phantom ligands) usually occupy the less encumbered equatorial positions. The complex undergoes intramolecular aromatic nucleophilic substitution (S_NAr collapse), and being closer to the

nucleophile, the equatorial ligand is subsequently attacked. This model does not explain why the magnitude of the ortho-effect depends on the nature of the nucleophile⁴⁷ and onium halogen.⁴⁴ In addition, nucleophilic substitution on 3-indolylphenyliodonium trifluoroacetate leads to iodobenzene and the corresponding indolyl derivative,⁴⁸ although in the solid state the indolyl ligand was found to occupy the apical, not equatorial, position of the starting iodonium molecule.⁴⁹ Finally, it was shown that a nucleophilic attack on icosahedral *closo*-carborane(12) boron bearing any substituent except hydrogen is unlikely (see above).

In 1981 Budylin proposed for the first time that 10-I-3 intermediates can undergo synchronous (cheletropic) extrusion of an iodoarene.⁴⁸ Later, this concept of reductive elimination from tricovalent iodine(III) complexes was widely used by Moriarty and Vaid.^{8b} Let us now consider and develop this model in detail.

The 10-I-3 complexes exhibit a trigonal bipyramidal structure in the crystalline state, assuming that the lone electron pairs (phantom ligands) of iodine play a role as substituents.⁴ Apical-equatorial interactions in a trigonal bipyramidal structure were shown to be symmetry forbidden.⁵⁰ In solution, trigonal bipyramidal complexes can undergo permutational transformations such as Berry pseudorotation or a turnstile rotation. In fact, triaryliodonium(III) compounds were found to be stereochemically nonrigid in solution.⁵¹ Permutational processes can possibly occur via tetragonal pyramidal intermediates in which the iodine atom, the nucleophile, and both substituents lie in one plane so as to minimize steric interactions (Scheme III). The interaction between any two of the three substituents lying in one plane, together with the central atom of the tetragonal pyramid, will be symmetry allowed, according to calculations by Hoffmann et al.⁵⁰ While it is possible to bind to one of the two ligands, the nucleophile prefers the more bulky one, since it decreases the steric strain in the tetragonal pyramid to a greater extent. When both of the substituents are of similar effective bulk, the nucleophile together with the more electron-deficient ligand will eliminate in order to decrease the positive charge on the iodine atom.

Nucleophilic substitution in 1-6 is regioselective because the carboranyl icosahedron is sufficiently larger than the aryl group. Introduction of a substituent into the meta or para position of the phenyl ligand does not affect the regioselectivity. Meta- and para-substituted aryl ligands cause almost the same steric strain (as a nonsubstituted phenyl ligand) in the tetragonal pyramid. The situation changes when going to cation 7, as the mesityl ligand is bulky enough to compete with the carboranyl group to bind the nucleophile.

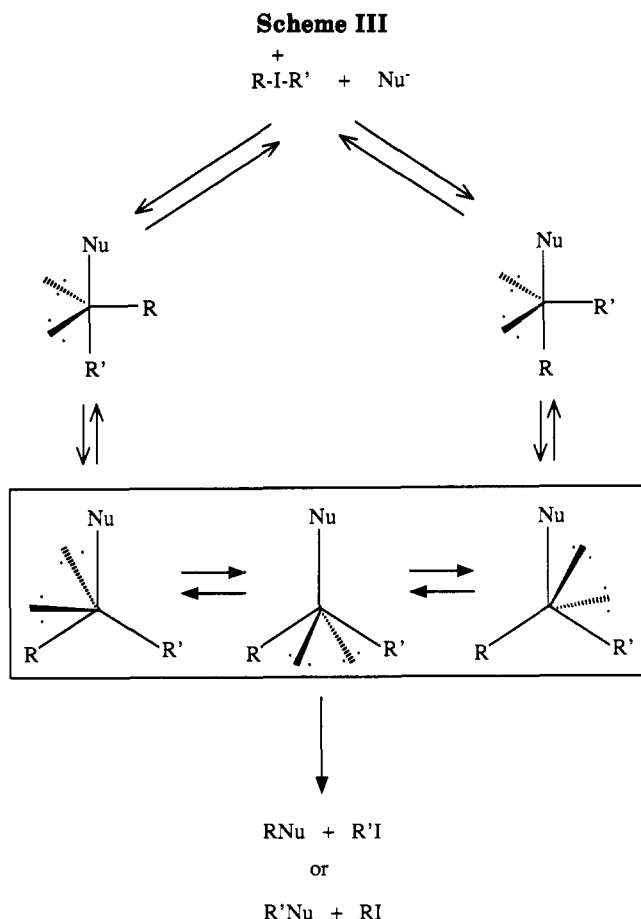
The mechanism (Scheme III) does not involve any ipso nucleophilic attack on a ligand attached to the onium center. Such an attack is conceivable only if an aryl ligand contains strong electron-withdrawing substituent(s), (e.g., nitro or cyano groups) in the ortho and/or para positions. In these cases the S_NAr process,

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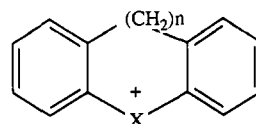


including the formation of a Meisenheimer-type complex,⁵² might compete with synchronous reductive elimination (cheletropic reaction).

As seen, the suggested mechanism easily explains the ortho-effect and related results previously rationalized in terms of classical aromatic nucleophilic substitution. There are some other key questions of diarylhalonium chemistry which have not been answered before. Successful rationalization of those "anomalous" facts with the help of the new mechanistic model is given below.

Why Do Some Cyclic Aromatic Iodonium Cations Prefer To React with Nucleophiles via a Radical Pathway Rather Than by a Polar Mechanism? Evidently, structural nonrigidity of iodonium ions should be crucial for the permutational processes and the cheletropic decomposition (Scheme III). For example, the diphenyliodonium cation reacts smoothly with a variety of charged nucleophiles to give iodobenzene and the corresponding substituted benzene in high yields.²⁻⁴ Reactions of the highly flexible cation 11 with anions NO₂⁻, Br⁻, and N₃⁻ also lead to the corresponding products of a nonradical "polar" reaction in quantitative yields.⁵³ The iodonium ion 11 exhibits the same reactivity and reaction pathways as the noncyclic diphenyliodonium ion, as 11 is able to change its geometry easily.

The reactivity of the less flexible 10*H*-dibenz[*b,e*]iodinium cation, 12, is noticeably different. Thermolysis of its chloride salt leads not only to (2-chlorophenyl)(2-



- 11, *n* = 3; X = I;
12, *n* = 1; X = I;
13, *n* = 0; X = I;
14, *n* = 0; X = Br;
15, *n* = 0; X = Cl;

iodophenyl)methane (93% yield) but also to some amounts of radical decomposition products.^{54a} Finally, reactions of the most rigid dibenz[*b,d*]iodolium cation, 13, containing iodine in the five-membered ring, with the same nucleophiles require more severe conditions, and this implies a homolytic mechanism.^{54,55} The products of a formal substitution reaction usually form in very low yields or not at all. In one of the recent publications on this subject it was noted, "This change in reactivity could not be accounted for."⁵⁵ However, the new mechanistic model readily accounts for this behavior. Rigidity of the five-membered ring in 13 makes the rearrangement of the trigonal bipyramidal structure into a tetragonal pyramid impossible, and thus the 10-I-3 complex reacts by homolysis of the iodine-nucleophile bond.

How Does the Nature of the Nucleophile Influence the Magnitude of the Ortho Effect? Lancer and Wiegand⁴⁷ have clearly shown that the magnitude of the ortho effect depends on the nucleophile. The same was observed for the reactions of 7.³¹ Thus, in the case of NO₂⁻ the product ratio of carboranylation/arylation is 1.6:1. This ratio increases to 5.7:1 when 7 reacts with Br⁻, while polar reactions with Cl⁻, F⁻,²⁹ and N₃⁻ were found to be regioselective in favor of substitution at the boron atom. The size of the nucleophile obviously contributes to the general steric strain in the tetragonal pyramid. Clearly, the larger the nucleophile, the greater the steric factor and, therefore, the lower the regioselectivity. The dramatic difference between N₃⁻ and NO₂⁻ relates to the ability of the latter to attack iodonium ions not only through the terminal oxygen but also through the central nitrogen atom, creating significant steric tensions. In contrast, the azide ion can only coordinate through terminal atoms.

How Does the Nature of Onium Halogen Influence the Magnitude of the Ortho Effect? The ortho effect decreases in the order [Ph-I-R]⁺ > [Ph-Br-R]⁺ > [Ph-Cl-R]⁺ (R = *o*-tolyl⁴⁴ and *m*-carboran-9-yl¹⁸). This is probably due to the ability of bromonium and chloronium cations to undergo nucleophilic substitution not only via the reductive elimination mechanism but also through a classical S_NAr pathway. Competition between the two routes leads to the observed products. Reductive elimination gives rise to the product of substitution at the bulkier ligand, while in the case of the S_NAr reaction the nucleophile preferentially attacks the phenyl rather than the *o*-tolyl carbon, or the carboranyl boron. Comparison of electron-withdrawing properties of the groups RCl⁺, RBr⁺, and RI⁺ (R = Ph, 9-*m*-C₂B₁₀H₁₁; see Table III) is supportive of the proposal of S_NAr reactions for bromonium and chloronium salts. The most concrete evidence for the ability of aromatic bromonium and chloronium cations to react with nucleophiles via an S_NAr mechanism is found in

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the reactions of dibenz[*b,d*]bromolium,⁵⁶ 14, and -chlorolium,^{54a} 15, ions with I⁻. Both reactions were observed to produce the corresponding 2-halo-2'-iodobiphenyl in quantitative yield. Similar reactions of the isostructural iodonium cation 13 proceeded via a radical pathway,⁵⁶ since neither an S_NAr pathway nor a reductive elimination pathway is possible.

Why Do Neutral Nucleophiles Usually Cause Homolytic Reactions of Diaryliodonium and Aryl(*m*-carboran-9-yl)iodonium Ions, While Charged Nucleophiles Effect Both Homolytic and Polar Transformations? There is no correlation between the ionization potential of a nucleophile and its ability to play a role as a one-electron reductant toward diaryliodonium ions. Interestingly, aryl(*B*-carboranyl)iodonium salts always react with neutral nucleophiles via a radical pathway. The same is true for diaryliodonium cations, although it seems unlikely on initial considerations.⁵⁷ A 10-I-3 intermediate can, in principle, decompose via two general routes. The first possibility includes intramolecular rotation followed by reductive elimination (Scheme III). Another possibility is a homolysis of the I-Nu bond affording a 9-I-2 radical (Scheme II). Competition between reductive elimination and radical decomposition depends on the difference in activation energies. A 10-I-3 intermediate either is neutral, when the nucleophile is negatively charged, or is positive, when the nucleophile

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(57) There are two exceptions. Some high-temperature reactions proceed via elimination of the phenyl cation from the diphenyliodonium ion (S_N1 mechanism).²⁻⁴ These cases are rare. Diaryliodonium cations containing strong electron-withdrawing groups (e.g., NO₂, CN) in the ortho and/or para positions are able to react with anions and neutral nucleophiles via an S_NAr path.³⁸

is neutral. In the latter case a major part of the positive charge is concentrated on the atom which has donated its lone pair to iodine. The electrostatic interactions between this positive charge and phantom ligands of iodine increase the barrier to rotation and make the reductive elimination unlikely.

Conclusions

Synthesis of carboranylhalonium ions is remarkable not simply because they represent a new class of compounds, i.e., inorganic halonium salts, but also because they can be regarded as unique synthons of carboranyl cations, opening new possibilities for inorganic synthesis. Smooth and regiospecific nucleophilic ipso substitution at the boron atom of phenyl(*B*-carboranyl)iodonium cations afforded a number of previously unknown functional derivatives of icosahedral *closo*-carboranes. Detailed investigations of these reactions revealed their striking similarity to the corresponding transformations of diaryliodonium compounds. The regioselectivity of polar reactions of carboranylhalonium ions and the ortho effect in the chemistry of diarylhalonium compounds were proved to be related phenomena controlled by steric factors. In contrast, electronic factors largely determine the regioselectivity of radical reactions of diaryliodonium and aryl(*B*-carboranyl)iodonium ions proceeding via 9-I-2 intermediates. The mechanism for nucleophilic substitution in carboranylhalonium cations successfully applies to the chemistry of diarylhalonium compounds, explaining and unifying its most salient features which had never before been rationalized in a satisfactory manner.