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THE REACTIONS OF PHENYL(*B*-CARBORANYL)IODONIUM SALTS WITH NUCLEOPHILES *

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Summary

The reactions of phenyl(9-*o*-carboranyl)-, phenyl(9-*m*-carboranyl)- and phenyl(2-*p*-carboranyl)-iodonium salts with the nucleophiles F^-, Cl^-, Br^-, OH^-, C_5H_5N, Hg and CN^-were studied. Depending on the nature of the nucleophile and the carborane ligand in each iodonium compound, these reactions either proceed as nucleophilic substitution or via a radical mechanism. Nucleophilic substitution, which takes place at the boron atom, of the carborane nucleus only, gives "carboranylation" products of nucleophiles. Free-radical processes are characterized by breaking of the $C-I^+$ bonds with the formation of phenyl radicals and their transformation products. The reasons for such an unusual behaviour of phenyl(*B*-carboranyl)iodonium salts in reactions with nucleophilic agents are discussed in the light of the results obtained and previous results.

Recently we have synthesized the first *B*-phenyliodonium derivatives of *o*-, *m*- and *p*-carboranes **, viz. phenyl(9-*o*-carboranyl)- (I), phenyl(9-*m*-carboranyl)- (II) and phenyl(2-*p*-carboranyl)-iodonium (III) salts [1,2]:

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* Dedicated to Prof. O.A. Reutov on the occasion of his 65th birthday.

** *o*-Carborane = 1,2-dicarba-closo-dodecaborane(12); *m*-carborane = 1,7-dicarba-closo-dodecaborane(12); *p*-carborane = 1,12-dicarba-closo-dodecaborane(12).

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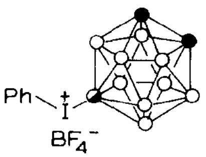
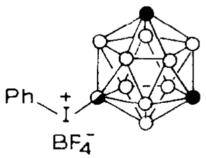
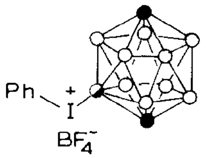


(I)



(II)



(III)

● = CH   ○ = BH   ◑ = B

Like diaryl- and dialkyl-iodonium salts [3,4], these compounds react readily with nucleophiles [2,5–8]. The pathway and the products of these reactions were shown to depend greatly on the nature of both the nucleophilic agent and the carborane fragment of the salt. The reactions can proceed with breaking of either $B–I^+$ (type **A**) or $C–I^+$ (type **B**) bonds which may be accompanied by the destruction of the carborane cage. The latter route is more likely for the salts of the cation of I [5–7]: the ability of carboranes to be destroyed grows in the series (*p*- < *m*- < *o*-), and this trend is enhanced in the presence of electron-acceptor substituents. Therefore the carborane cage of salt I is decomposed by the "classical" splitting agents such as potassium ethylate and piperidine [9], and also by much weaker bases, such as water [5], alcohols [6] and dimethylsulfoxide [6,7], which gives zwitter-ionic 5- or 6-dimethylsulfoxonium-7,8-dicarba-*nido*-undecaborate [7].

This reaction pathway is less typical for II and III, and their chemical behaviour is similar to that of asymmetrical iodonium salts of aromatic series which are known to react with nucleophiles according to the general reaction [3,4]:

$$\mathrm{Ar{-}I^+{-}Ar' + Nu^- \rightarrow ArNu + Ar'I + Ar'Nu + ArI} \qquad (1)$$

The ratio yield of the reaction products depend on the nature of Ar, Ar′ and Nu^-; in most cases mixtures of four compounds are obtained [10–12] *. The presence of two ligands at the iodine atom in I–III which are very different in nature, viz. phenyl and carboranyl, results in striking regiospecificity: depending on the nucleophile the reactions belong either to type **A** (N_3^-, NO_2^-, $PhSO_2^-$, $PhCO_2^-$, SCN^-) or to type **B** (PPh_3, n-BuLi) [2,6,8]. This behaviour is new in onium compounds and requires some explanation.

The present paper describes the reactions of I–III with halide and cyanide ions, reactions of II with pyridine and hydroxide ion, and the interaction between phenyl(9-*m*-carboranyl)iodonium chloride and metallic mercury.

Among the above reagents only halide ions (F^-, Cl^-, Br^-) react with the breaking of the $B–I^+$ bond strictly according to eq. 2, where X = F, Cl, Br

$$\mathrm{C_2H_2B_{10}H_9\overset{+}{I}Ph + X^- \rightarrow \underset{(\sim 100\%)}{C_2H_2B_{10}H_9X} + \underset{(\sim 100\%)}{PhI}} \qquad (2)$$

irrespective of the reaction conditions: treatment with NaX in a two-phase $CHCl_3/H_2O$ system, addition of KF · 18-crown-6 in dry $CHCl_3$, or thermolysis of

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* In addition to these four products, the reaction mixtures often contain arenes and diaryls which are the products of competing radical processes.

TABLE 1

BROMIDES AND CHLORIDES OF CATIONS I AND II

Iodonium salt	Yield (%)	Decomposition temperature (°C)	Brutto formula	Analysis (Found (calcd.)(%))	
				C	H
$9\text{-}o\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph\ Br^-$	81	100	$C_8H_{16}B_{10}BrI$	22.67 (22.50)	3.78 (3.78)
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph\ Br^-$	90	120	$C_8H_{16}B_{10}BrI$	22.43 (22.50)	3.73 (3.78)
$9\text{-}o\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph\ Cl^-\cdot H_2O$	68	97	$C_8H_{18}B_{10}ClIO$	23.90 (23.98)	4.48 (4.52)
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph\ Cl^-$	61	117	$C_8H_{16}B_{10}ClI$	25.09 (25.11)	4.32 (4.22)

the corresponding bromides and chlorides. The experimental results are summarized in Table 2, while Table 1 shows the data of phenyl(9-*o*(*m*)-carboranyl)iodonium bromides and chlorides synthesized by us.

The reactions of pyridine, hydroxide ion and metal mercury with cation II belong to type **B**, like those of n-butyllithium and triphenylphosphine [6,8], and only the cyanide ion gives products of both types **A** and **B** with all the three cations of I–III.

All the type **B** reactions studied occurred via a radical mechanism. Thus, the reactions of I–III with PPh_3 which give $Ph_4\overset{+}{P}\ BF_4^-$ and the corresponding iodo-

TABLE 2

REACTIONS OF I–III WITH HALOGEN ANIONS

Reacting cation	Reacting anion	Conditions of reaction	Halogenocarborane		Literature data
			Yield (%)	M.p. (°C)	
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	F^-	[a]	94	267–268	248–250 [13]
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Cl^-	[a]	98	217–218	216–217 [9]
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Br^-	[a]	96	173–174	171–172 [9]
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Cl^-	[b]	94	217	216–217 [9]
$9\text{-}m\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Br^-	[b]	96	171–172	171–172 [9]
$9\text{-}o\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Cl^-	[b]	88	236–237	237–238 [9]
$9\text{-}o\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	Br^-	[b]	93	190–191	192 [9]
$9\text{-}o\text{-}C_2B_{10}H_{11}\overset{+}{I}Ph$	F^-	[c]	97	287–288	284 [13]
$2\text{-}p\text{-}C_2B_{10}H_{11}IPh$[d]	F^-	[a]	100	256	256 [2]

[a] Reaction of II or III with NaX (X = F, Cl, Br) in a two-phase $CHCl_3/H_2O$ system as described in ref. 6. [b] Thermolysis of phenyl(9-*o*(*m*)-carboranyl)iodonium bromides and chlorides. [c] Reaction of I, which is easily decomposed with water or with KF·18-crown-6 in dry $CHCl_3$. [d] The experiment is taken from ref. 2 to present a more complete picture.

carborane, are initiated by light and accompanied by the formation of benzene and diphenyl [2,8].

We show in the present study that an homolysis initiator, such as metallic mercury, vigorously stirred with phenyl(9-*m*-carboranyl)iodonium chloride * in boiling acetone splits only the Ph–I$^+$ bond (eq. 3). This reaction competes with

$$C_2H_2B_{10}H_9\overset{+}{I}Ph\ Cl^- + Hg \xrightarrow[56°C]{acetone} \underset{(28\%)}{C_2H_2B_{10}H_9I} + \underset{(24\%)}{PhHgCl} \quad (3)$$

thermolysis of chloride (eq. 4).

$$C_2H_2B_{10}H_9\overset{+}{I}Ph\ Cl^- \xrightarrow[56°C]{acetone} \underset{(\sim 70\%)}{C_2H_2B_{10}H_9Cl} + \underset{(\sim 70\%)}{PhI} \quad (4)$$

We have further discovered that under slow heating of a pyridine solution of II ** it gradually becomes dark-cherry in colour and a new UV absorption band appears at λ_{max} 470 nm. Boiling the solution under reflux for several hours results in complete decomposition of II, with the dark-cherry colour becoming yellow.

Changes in the reaction conditions (in darkness or under irradiation from a high-intensity incandescent lamp) alter neither the reaction time nor the products, from which 9-iodo-*m*-carborane (68–78%), pyridinium fluoroborate (71–78%), and the mixture of α-, β- and γ-phenylpyridines (11–14%) were preparatively isolated.

Neither phenylpyridinium salts, nor nitrogen- or nucleus-carboranylated pyridines were detected in the reaction mixture, showing that neither intermediate carboranyl-radical, nor phenyl- and carboranyl-cations were produced during the reaction.

The presence of nucleus-phenylated pyridines in the reaction mixture proves unambiguously the radical mechanism of the reaction [15,16].

The first step of the reaction results evidently in the formation of a coloured iodonium cation complex *** with pyridine. This complex is homolytically decomposed to form a separated solvated radical pair, viz. phenyl(9-*m*-carboranyl)iodine radical and the cation radical of pyridine. The former is in its turn decomposed into 9-iodo-*m*-carborane and phenyl radical, while the latter abstracts hydrogen from the pyridine nucleus, thus turning into a pyridinium ion and generating $\alpha(\beta,\gamma)$-pyridyl radical. Recombination of this radical with phenyl radical results in nucleus-phenylated pyridine, which can also be formed upon direct interaction between pyridine and phenyl radicals (Scheme 1).

Both phenyl and pyridyl radicals seem to undergo other kinds of transformations (for instance those giving benzene, diphenyl and bipyridyls), and this accounts for low yields of phenylpyridines compared to the pyridinium salt yields obtained in amounts almost equivalent to that of the iodocarborane.

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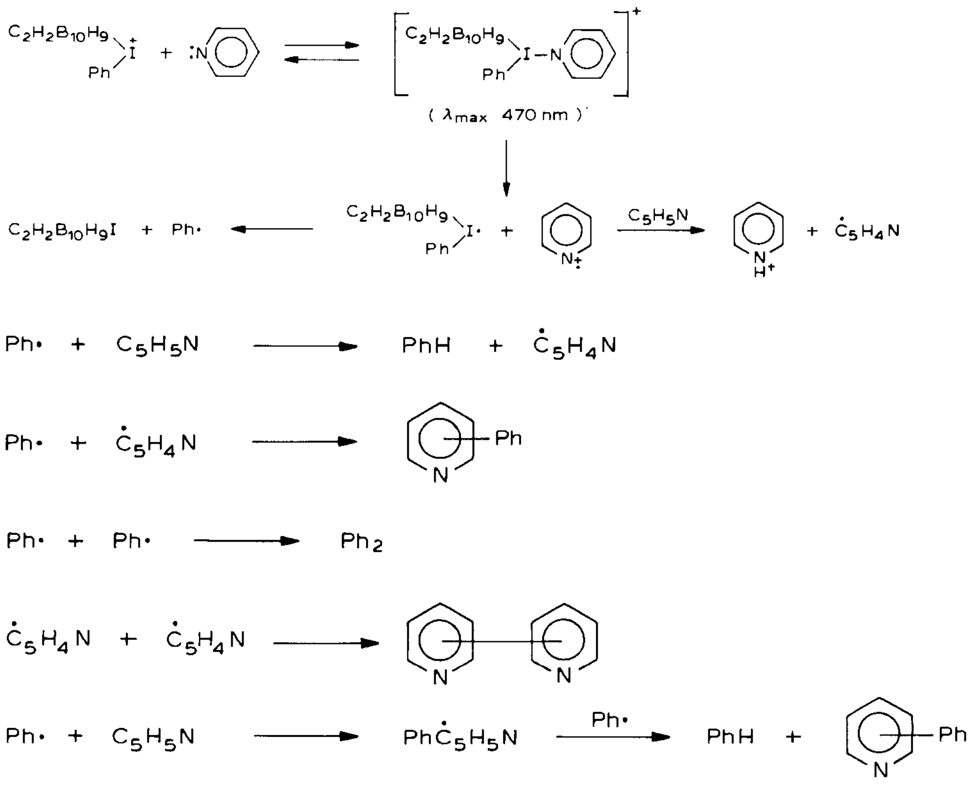
* Like diphenyliodonium fluoroborate [14], II does not react with metallic mercury in a boiling solution and can be quantitatively recovered from the reaction mixture after 5 h.

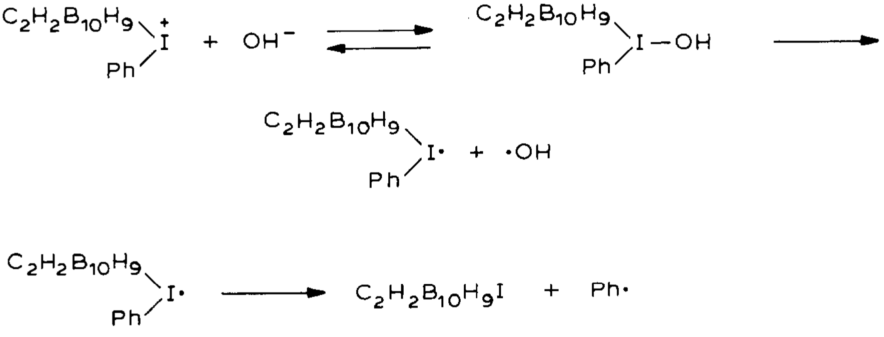
** I is decomposed by pyridine at a temperature as low as 20°C with liberation of hydrogen which indicates degrataion of the carborane cage.

*** Such diaryliodonium salt complexes are well-known, and some of them (e.g., aniline complexes [17]) have been individually isolated. The I–N bond in the diphenyliodonium fluoroborate-aniline complex was shown [17] to be readily homolyzed under heating or UV exposure.



SCHEME 1

We isolated 9-iodo-*m*-carborane (78%) and phenol (1%) from the reaction mixture of II with an aqueous solution of NaOH. GLC showed the presence of benzene (40%), iodobenzene (10%) and diphenyl (3%) and the absence of *m*-carborane and its 9-hydroxy derivative. The presence of benzene and diphenyl points to a radical mechanism for this reaction. Here, as in the case of pyridine, the hydroxide ion apparently attacks the iodine atom, and the resulting covalent form of iodonium hydroxide is immediately homolytically decomposed, as is described by Sandin and Brown for diphenyliodonium hydroxide [15] (Scheme 2).



SCHEME 2

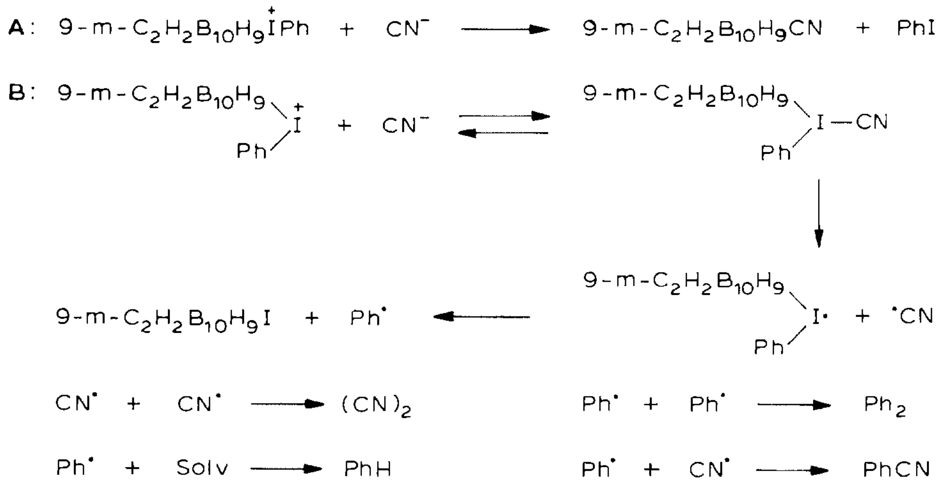
A small amount of phenol detected among the products could result from recombination of Ph$^{\cdot}$ and OH$^{\cdot}$ radicals according to Scheme 2. The iodobenzene may be formed by alkaline destruction of the carborane nucleus (similar to the reaction of I with water [5] which gives iodobenzene) since the reaction mixture contains neither carborane nor hydroxycarborane which are the products of B–I$^+$ bond splitting. The fragments of the carborane isocahedron resulting from the destruction are most likely to serve as a source of hydrogen in the transformation of the phenyl radical to benzene. They can also reduce the hydroxide radical to an anion. On the other hand, a certain amount of iodonium salt (although not very high, since the yield of iodocarborane in the reaction is 78%) can first react with alkali with destruction of the carborane cage to some *nido*-structures. The latter are known [9] to be much less stable to oxidizing agents as compared to *closo*-carboranes(12), and can therefore reduce the phenyl(9-*m*-carboranyl)iodonium cation to the radical which is then decomposed into the phenyl radical and iodocarborane both stable to an aqueous alkaline solution. It is still difficult to decide which of the two proposed mechanisms is occurring; the reactions can proceed according to both schemes, each of them equally contributing to the formation of the products observed.

The cyanide ion is the only one of all the nucleophiles studied which is able to react with I–III via both reaction pathways (types **A** and **B**). This trend is more pronounced for II, for which the two pathways are equally possible (Scheme 3).

The results of the reactions between II and KCN · 18-crown-6 in CH_2Cl_2 are summarized in Table 3. The reaction pattern does not seem to change in the presence of a radical trap, 1,1-diphenylethylene, which alters only the PhH/Ph_2 ratio, as described in ref. 12.

The relative amounts of other products remain unchanged, which supports the non-chain radical process.

As could be expected from decrease in the electron-donor effect for carboranyl groups in the series 9-*o*-> 9-*m*-> 2-*p*- [18–20], III reacts with cyanide ions almost entirely via route **A**, yielding 98% of previously unknown 2-*p*-carboranylcyanide (eq. 5) and only trace amounts of radical reaction products.



SCHEME 3

TABLE 3

REACTION OF II WITH KCN·18-crown-6 IN CH_2Cl_2

Reaction conditions	Yield of reaction products (%)					
	9-m-$C_2B_{10}H_{11}I$	9-m-$C_2B_{10}H_{11}CN$	PhI	PhH	Ph_2	PhCN
Without Ph_2C=CH_2	40	40	57	26	7	0.3
In the presence of Ph_2C=CH_2 (5 mol per 1 mol of II)	40	45	55	4	20	0.5

In contrast to this, I reacts with KCN · 18-crown-6 predominantly via route **B**, which is evident by the 1/2 ratio between yields of 9-*o*-carboranylcyanide (11%) and 9-iodo-*o*-carborane (21%). However, low absolute yields of both carboranyl derivatives and a relatively high yield of iodobenzene (40–60%) point to the fact that this reaction mainly involves destruction of the carborane cage.

$$\text{III} + \text{KCN} \cdot \text{18-Crown-6} \xrightarrow{CH_2Cl_2} \underset{(98\%)}{2\text{-}p\text{-}C_2H_2B_{10}H_9CN} + \text{PhI} \qquad (5)$$

The structure of carboranyl cyanides was found by the transformation of the *m*-isomer into the known 9-*m*-carboranecarboxylic acid.

Discussion

The results obtained in studying the reactions between phenyl(*B*-carboranyl)iodonium salts and nucleophiles give rise to certain speculations about the reaction mechanism.

Type **B** reactions seem to proceed through intermediate phenyl(*B*-carboranyl)iodine radicals, the products of one-electron reduction of the initial iodonium cations. The reduction process can be seen as either a direct one-electron transfer from the nucleophile to the iodonium cation, or as intermediate formation of a complex of tricoordinated iodine which is then homolytically decomposed. This results in labile iodine-centered radicals, which are selectively decomposed to iodocarborane and phenyl radicals. The reasons for such selectivity of decomposition of phenyl(*B*-carboranyl)iodine radicals are not yet clear; it is possible, however, that a product of alternative decomposition, *B*-carboranyl radical, has higher energy than the phenyl radical and so its formation is unlikely. On the other hand, the unpaired electron in these iodine-centered radicals is apparently delocalized only over the phenyl but not over the carboranyl ligand, which can also lead to the products observed. The existence of intermediate phenyl(*B*-carboranyl)iodine radicals in the reactions of type **B** is also confirmed by data on electrochemical reduction of II described in detail elsewhere [ref. 38].

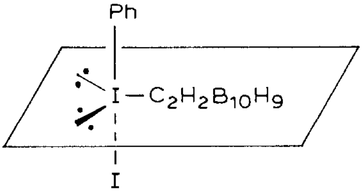
The reaction of type **A** is initiated only by anions and gives new B-substituted carboranes and iodobenzene with high yields without side processes. These reactions proceed readily in low-polar organic media but are difficult to observe in high-polar solvating solvents. Finally, the rate of these reactions largely depends on the electronic effect of the carboranyl group attached to the iodine onium atom [2].

The information presented suggests that we are dealing with nucleophilic substitution reactions at a boron atom * which are exceptional for icosahedral *closo*-carboranes.

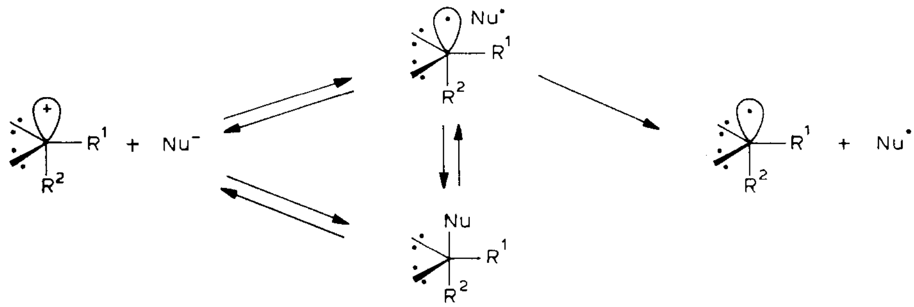
Special experiments are needed to elucidate the mechanisms of this substitution reaction; however, the mechanism similar to S_N1 can be ruled out since we did not find products of free carboranyl cations side transformations in any of the reactions.

The results obtained can be easily explained in terms of the mechanism recently suggested for reactions of iodonium salts with nucleophiles [25] which involve nucleophilic attack at the iodine onium atom.

Iodonium salts in crystal state are trigonal bipyramids with lone electron pairs of iodine (phantom ligands) and with the most bulky substituent in an equatorial position. The second substituent and the counterion are in apical positions. This is also true for the structure of phenyl(9-*o*-carboranyl)iodonium iodide as shown by X-ray data [26]:



In the solution when salts are dissociated, the iodonium cation can form a complex with a nucleophile, but one-electron transfer giving rise to a radical pair is also possible. Depending on the nature of the reacting species, this is followed by either dissociation of this radical pair or transfer of the second electron with the formation of the covalent bond (Scheme 4). The free radicals thus formed undergo the usual transformations, like those observed in the **B** type reactions. If a trigonal-bipyramidal intermediate has been formed, it can be either homolytically decomposed (giving again an iodine-centered radical) or can undergo synchronously, the



SCHEME 4

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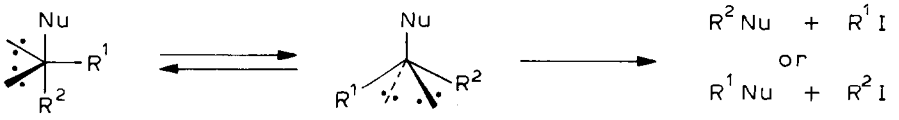
* Along with numerous electrophilic and radical substitution reactions at boron atoms of carboranes(12), there are only two nucleophilic substitution reactions viz. the interaction of 3-*o*-carboranyldiazonium salts with water and HF, resulting in 3-hydroxy- and 3-fluoro-*o*-carboranes, respectively [21]. *B*-Carboranyl halides and tosylates are exclusively passive in nucleophilic substitution reactions [18,22–24].

so-called heletropic decomposition. However, it was shown, for five-coordinated phosphorus, that apical–equatorial interaction in a trigonal bipyramid is symmetrically forbidden [27]; therefore a trigonal bipyramid with a low activation energy should first be rearranged into a tetragonal pyramid [25] in which heletropic decomposition can take place [27]:

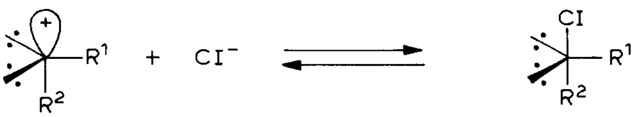


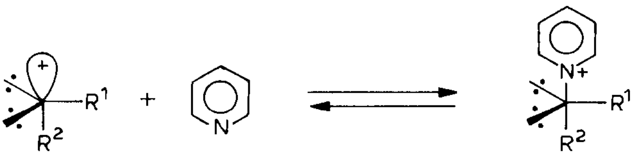
In this situation the nucleophile binds the ligand which is most able to decrease the energy of the transition state. It can be either the most electron-deficient ligand, or the most bulky one. The latter feature is more important, since the removal of the bulky ligand decreases the steric strain at the base of the tetragonal pyramid.

Evidently, along the lines of this model heletropic reactions of phenyl(*B*-carboranyl)iodonium salts should result in nucleophilic binding with a carboranyl radical, since it is much bulkier than the phenyl group. Similarly, bulkier (*ortho*-substituted) radicals often bind nucleophiles in diaryliodonium salts, even if they are less electron-deficient (the so-called "*ortho*-effect") [28,29]. Heletropic removal of iodobenzene is easier in III than in II, other conditions being equal, since the 2-*p*-carboranyl radical is more electron-deficient than the 9-*m*-carboranyl [19,20].

Nucleophilic substitution in I–III (type **A** reactions) occurs only with charged nucleophiles, whereas uncharged nucleophiles favour only type **B** radical reactions. It should be stressed that in the latter case no correlation exists between an ionization potential of a nucleophile and its ability to act as a one-electron reducing agent for iodonium cations. The ability of uncharged nucleophiles to cause radical reactions of iodonium compounds specifically, irrespective of their ionization potential, seems to be a general trend which is true not only for I–III, but also for many diaryliodonium salts. The reactions of S_N1, such as high-temperature phenylation of pyridine by its nitrogen atom with diphenyliodonium fluoroborate [16] represent the only exception.

In terms of the above mechanism this can be explained as follows. A charged nucleophile forms a neutral trigonal-bipyramidal intermediate with the iodonium cation, whereas with an uncharged nucleophile the intermediate bears an integral positive charge, the greatest portion of which is accumulated at the nucleophilic atom bonded to iodine e.g.:





Electrostatic interaction between this positive charge and the phantom ligands of the iodine atom hinders the rearrangement of the trigonal bipyramid into a tetragonal pyramid, and homolytic decomposition of the tricoordinate iodine complex becomes more preferable than heletropic decomposition.

Certain charged nucleophiles exhibiting strong reducing properties, such as cyanide [12] and ethylate ions [11] often cause homolysis of diaryliodonium salts. These reactions are usually characterized by competition between nucleophilic substitution and radical reactions. This also occurs when the salts I–III interact with cyanide anion.

Experimental

I, II and III are prepared as described in refs. 1 and 2 and are purified by filtration of the solutions in CH_2Cl_2 through an Al_2O_3 layer (*m*- and *p*-isomers) or silica gel (*o*-isomer).

GLC analysis was performed using a "Chrom-4" chromatograph with a flame-ionization detector and a "Kent Chromalog-2" type electron integrator. Glass columns were filled with Chromosorb W 100/120 mesh. Two stationary phases, polyethylene glycol adipinate (0.65%) and Dexil-200 (2%) were used for the analysis. The velocity of the carrier gas (He) was 30 ml/min and the temperature program was 20–300°C, velocity 6°/min.

Specially prepared solutions of known concentrations containing the analyzed substances and inner standards were used to find the product yields by GLC. The standards were usually reaction products for which yields were previously determined by preparative isolation from the reaction mixture.

1. Phenyl(9-o-carboranyl)- and phenyl(9-m-carboranyl)iodonium halides

Bromides were prepared by adding saturated solutions of I and II in acetone to an excess of a concentrated aqueous solution of NaBr. Precipitated phenyl(9-*o*-carboranyl)- and phenyl(9-*m*-carboranyl)-iodonium bromides were washed with water and a small quantity of acetone and ether.

Chlorides of phenyl(9-*o*-carboranyl)- and phenyl(9-*m*-carboranyl)iodonium were prepared according to ref. 30 by treatment of suspensions of the corresponding iodides [1] in chloroform with excess dry chlorine under 5–10°C, followed by treatment with acetone. After removal of the solvents under vacuum, the salts were purified by reprecipitation with dry ether from moist acetone solutions.

The yields, decomposition temperatures, and elemental analysis data for phenyl(9-*o*(*m*)-carboranyl)iodonium halides are given in Table 1.

2. Interaction of II with NaX ($X = F$, Cl, Br) in the system $CHCl_3/H_2O$

A mixture of II (0.7 mmol), NaX ($X = F$, Cl, Br) (2.1 mmol), water (3 ml) and $CHCl_3$ (3 ml) was boiled with vigorous stirring to attain complete decomposition of the iodonium salt (1–3 h). GLC analysis of the organic layer showed iodobenzene and the corresponding halogenocarborane in 1/1 molar ratio. Halogencarboranes were isolated by preparative column chromatography of the residue which was obtained by evaporation of chloroform from the organic layer (Al_2O_3, hexane/benzene 2/1), and purified by vacuum sublimation.

3. *Thermolysis of phenyl(9-o(m)-carboranyl)iodonium halides*

Phenyl(9-*o*(*m*)-carboranyl)iodonium halide (0.7 mmol) * was kept in a sealed tube for 10 min at temperatures 10° higher than the decomposition point. GLC analysis of the thermolysis products revealed iodobenzene and the corresponding chloro- and bromo-carboranes isolated as in the previous experiment.

4. *Reaction of I with KF · 18-crown-6 in $CHCl_3$*

I (1.50 g) was added portionwise to the mixture of 1.34 g of 18-crown-6 ether, anhydrous KF (1 g) and dry $CHCl_3$ (10 ml) with vigorous stirring. The exothermic reaction was completed in 1–2 min. GLC analysis of the liquid phase showed iodobenzene and 9-fluoro-*o*-carborane in the 1/1 molar ratio. Preparative column chromatography of the residue after evaporation of chloroform (Al_2O_3, benzene/hexane 1/1) gave 0.54 g (97%) of 9-fluoro-*o*-carborane.

The yields, melting points and literature data for halogenocarboranes obtained in experiments 2–4 are shown in Table 2.

5. *Reaction of II with pyridine*

(a) A boiling solution of II (0.4 g) in dry pyridine (3 ml) was illuminated with a 100 W incandescent lamp against a background of aluminum foil. The resulting dark-cherry colour gradually faded to yellow in 12 h when the reaction was completed. After removal of pyridine under vacuum, the residue was treated with ether giving pyridinium fluoroborate (0.11 g, 71%) as a precipitate with m.p. 200–205°C (from ethanol). (Lit. [31] m.p. 217°C). Found: C, 35.90; H, 3.93; N, 8.42. $C_5H_6BF_4N$ calcd.: C, 35.98; H, 3.62; N, 8.39%. The ethereal solution was concentrated by evaporation and the residue was dissolved in benzene and extracted with 10% acetic acid. The acidic extracts were treated with 10% NaOH to obtain alkaline pH, and then extracted with ether. After removal of ether the residue contained 0.02 g (14%) a mixture of α,β,γ-monophenylpyridines (identified by TLC on authentic samples).

A benzene layer was dried over $CaCl_2$ and vacuum-evaporated to dryness; the resulting 9-iodo-*m*-carborane was sublimed under vacuum. The yield was 0.17 g (68%), m.p. 110–111°C (from hexane). According to ref. 32 the m.p. is 109–110°C.

(b) A solution of II (0.4 g) in dry pyridine (3 ml) was boiled in a light-protected flask. The reaction was also completed in 12 h. Treatment as in experiment 5a gave 0.12 g of pyridinium fluoroborate (78%), 0.015 g of an α,β,γ-monophenylpyridines mixture (11%) and 0.195 g of 9-iodo-*m*-carborane (78%).

6. *Reaction of II with Aqueous NaOH.*

II (0.5 g) was stirred with NaOH (0.23 g) in water (5 ml) at 20°C until complete decomposition of the iodonium salt (40 min) occurred. The reaction mixture was treated with ether. GLC analysis of the ethereal extracts showed the presence of benzene (40%), iodobenzene (10%) and diphenyl (3%). The ethereal extracts were evaporated to dryness and the residue was chromatographed in hexane on Al_2O_3 giving 0.241 g (78%) of 9-iodo-*m*-carborane with m.p. 109–111°C (from hexane).

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* Unstable phenyl(9-*o*-carboranyl)iodonium chloride crystallohydrate was immediately dehydrated in vacuum over P_2O_5 just after preparation and then subjected to thermolysis.

The aqueous layer after extraction with ether was filtered, acidified with 15% HCl and then treated with bromine water. The yield of 2,4,6-tribromophenol was 0.005 g (1%), m.p. 93–95°C (Lit. [33] m.p. 96°C).

7. *Reaction of phenyl(9-m-carboranyl)iodonium chloride with metallic mercury in acetone*

A mixture of phenyl(9-*m*-carboranyl)iodonium chloride (0.3 g), mercury (0.45 ml) and acetone (10 ml) was stirred vigorously for 1 h at 20°C and boiled for 0.5 h until complete decomposition of the iodonium salt occurred. GLC analysis of the reaction mixture showed iodobenzene (70%), 9-chloro-*m*-carborane (71%) and 9-iodo-*m*-carborane (28%). The solution was decanted from mercury, evaporated to dryness, and the residue was thoroughly washed with hexane. The yields of hexane-insoluble phenylmercury chloride was 0.061 g (24%), m.p. 248–250°C (Lit. [34] m.p. 258°C).

8. *Reaction of II with KCN · 18-crown-6 in CH_2Cl_2*

(a) II (3 g) was added portionwise to a solution of KCN (0.684 g) and 18-crown-6 ether (2.73 g) in CH_2Cl_2 (12 ml) with vigorous stirring. The reaction was exothermic (CH_2Cl_2 boiled) and was completed in 15 min. The GLC analysis data of the reaction mixture are given in Table 3. After evaporation of CH_2Cl_2 the residue was extracted with ether. Preparative column chromatography of the remaining oil (silica gel, benzene/hexane 1/1) gave 0.752 g (40%) of 9-iodo-*m*-carborane with m.p. 109–110°C (from hexane) and 0.466 g (40%) of 9-*m*-carboranylcyanide with m.p. 211°C (from heptane), $m/z = 169$. Found: C, 21.45; H, 6.59; N, 8.21. $C_3H_{11}B_{10}N$ calcd.: C, 21.29; H, 6.55; N, 8.28%.

(b) Under the reaction conditions of experiment 8a KCN (0.021 g), 18-crown-6 ether (0.084 g) diphenylethylene (0.21 g) (synthesized according to ref. 35) in CH_2Cl_2 (8 ml) were mixed with II (0.11 g). The results of GLC analysis are listed in Table 3.

9. *Hydrolysis of 9-m-carboranylcyanide*

A mixture of 9-*m*-carboranylcyanide (0.1 g), acetic acid (3 ml) and concentrated H_2SO_4 (4 ml) was heated at 105–110°C for 2.5 h, then $NaNO_2$ (0.1 g) was added with vigorous stirring at 0°C. The mixture was slowly heated to 90°C, kept at this temperature for 30 min, cooled to 20°C, poured into ice and extracted with ether. The ethereal solution was extracted with 5% NaOH and the alkaline extracts were treated with 5% HCl to obtain acid pH. The residue was extracted with ether and the ethereal solution was dried over $CaCl_2$ and concentrated by evaporation. The residue contained 0.104 g (94%) 9-*m*-carboranecarboxylic acid with m.p. 215–216.5°C (from water). (Lit. [36] m.p. 214–216°C).

10. *Reaction of III with KCN · 18-crown-6 in CH_2Cl_2*

III (0.7 g) was added portionwise to a solution of KCN (0.140 g) and 18-crown-6 ether (0.590 g) in CH_2Cl_2 (7 ml) and the reaction mixture was stirred vigorously for 15 min. GLC analysis indicated the presence of iodobenzene, 2-*p*-carboranyl cyanide and trace amounts (about 0.1%) of 2-iodo-*p*-carborane. Preparative column chromatography of the residue after CH_2Cl_2 removal (silicagel, hexane) gave 0.266 g (98%) of 2-*p*-carboranyl cyanide with m.p. 196–197°C (from hexane). $m/z = 169$. Found: C, 21.72; H, 6.68; N, 7.86. $C_3H_{11}B_{10}N$ calcd.: C, 21.29; H, 6.55; N, 8.28%.

11. Reaction of I with KCN · 18-crown-6 in CH_2Cl_2

I (1.5 g) was added to a solution of KCN (0.342 g) and 18-crown-6 ether (1.368 g) in CH_2Cl_2 (8 ml) with vigorous stirring. The reaction mixture was stirred for a further 1.5 h and evaporated; the residue was extracted with ether. Preparative column chromatography of the remaining oil after removal of the ether (silica gel, benzene) gave 0.195 g (21%) of 9-iodo-*o*-carborane with m.p. 118–120°C (from heptane) (Lit. [9] m.p. 117–118°C), and 0.066 g (11%) of 9-*o*-carboranyl cyanide with m.p. 236–238°C (from benzene/heptane) (Lit. [37]; m.p. 236–237°C). $m/z = 169$.

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