Unified Mechanistic Analysis of Polar Reactions of Diaryliodonium Salts

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Reactions of aryl(*m*-carboran-9-yl)iodonium tetrafluoroborates [aryl = phenyl, (**1**); 4-methoxyphenyl, (**2a**); 4-fluorophenyl, (**2b**); 3-nitrophenyl, (**2c**); mesityl, (**2d**)] with Br^-, NO_2^- (polar reactions) and PPh_3 (radical reactions) have been studied. Polar reactions of **1**, **2a–c** with Br^- and NO_2^- lead regiospecifically to the corresponding iodoarene and substituted *m*-carborane. In contrast to this, reactions of **2d**, containing a bulky aryl ligand, with Br^- and NO_2^- are not regiospecific, since they produce all four possible products: 9-iodo-*m*-carborane, iodomesitylene, substituted *m*-carborane, and substituted mesitylene. These results are rationalized in terms of a new mechanism which includes formation of a 10-I-3 hypervalent intermediate and its subsequent synchronous (cheletropic) decomposition during intramolecular rotation. The mechanism can account for some novel, known chemistry of diaryliodonium ions, including the so-called '*ortho*-effect' and the unusual reactivity of cyclic halonium cations.

Since the first halonium compound, namely 4-iododiphenyliodonium hydrogen sulfate was synthesized by Hartmann and Meyer almost a hundred years ago,[1] the chemistry of many different diaryliodonium ions has been widely investigated.[2–4] High reactivity towards nucleophiles is considered to be the most important and useful[5] property of diaryliodonium compounds. All the reactions of diaryliodonium ions with nucleophiles can be subdivided into two general types, *i.e.* a nucleophilic substitution (S_N reaction), and a one-electron reduction.[4a] One-electron reduction was shown to proceed *via* a 9-I-2 intermediate[6,7] followed by its homolytic decomposition into iodoarene and aryl radical. The latter can abstract hydrogen from a solvent, dimerize, or arylate the nucleophile. The mechanism for nucleophilic substitution in diaryliodonium ions is far less clear.‡ It is generally considered to be of S_NAr character.[3,4a,7,10–15] Indeed, electron-withdrawing groups increase the reactivity of diaryliodonium ions towards nucleophiles, while electron-donating substituents exert the opposite influence [*e.g.* eqns. (1) and (2)[10c]].

Many experimental facts, however, contradict the model of S_NAr type substitution, and cannot be rationalized in its terms. Indeed, 'the polar reactions of diaryliodonium salts with nucleophiles are not without their mechanistic idiosyncrasies',[4b] and our knowledge of S_N reactions of diaryl-iodonium, and also -bromonium and -chloronium cations is very limited. Some examples of these 'inexplicable' observations follow (for detailed considerations see Discussion),.

(a) The so-called '*ortho*-effect'. Nucleophiles unexpectedly prefer to attack an *ortho*-substituted ligand of diaryliodonium ions even if this ligand is less electron-deficient than the alternative. As long as the nature of the *ortho*-effect remains unknown, the dependence of its magnitude on the reacting nucleophile and the 'onium centre (iodonium, bromonium, chloronium) also remains unclear.

(b) Neutral nucleophiles usually effect homolytic reactions of diaryliodonium ions, while charged nucleophiles cause both homolytic and polar transformations.

(c) There is no correlation between ionization potentials of anionic nucleophiles and their ability to react with diaryliodonium ions *via* a radical or polar pathway.

(d) Cyclic iodonium ions possess curious reactivity towards nucleophiles which has not been rationalized in a satisfactory manner.

The main problem with the investigation of the reactivity and the reaction pathways of diaryliodonium salts is the competition between nucleophilic substitution and one-electron reduction.[3–5,14] As a result, it is almost impossible to determine, whether the arylation product was produced *via* the polar mechanism, or *via* the one-electron reduction, or by a combination of both routes. The best model for the investigation of the polar (and radical) reactions could be an unsymmetrical iodonium cation which is able to react with nucleophiles regiospecifically. In other words, a nucleophilic substitution would occur only in one ligand of the cation, whilst a one-electron reduction would lead to the elimination of the other ligand as the radical. In this case the uncertainty would be easily avoided, since each process leads to its own pair of products.

The recently synthesized phenyl(*B*-carboranyl)iodonium cations (Fig. 1) appear to be such unique models,§ since their reactions with nucleophiles are surprisingly regiospecific.[17] For example, phenyl(*m*-carboran-9-yl)iodonium tetrafluoroborate (**1**), reacts with various nucleophiles to give products of either B–I or C–I bond cleavage (Scheme 1).

Such regiospecificity is novel and unexpected in the chemistry of halonium ions, including unsymmetrical diaryliodonium cations. The C–I bond cleavage reactions were shown to

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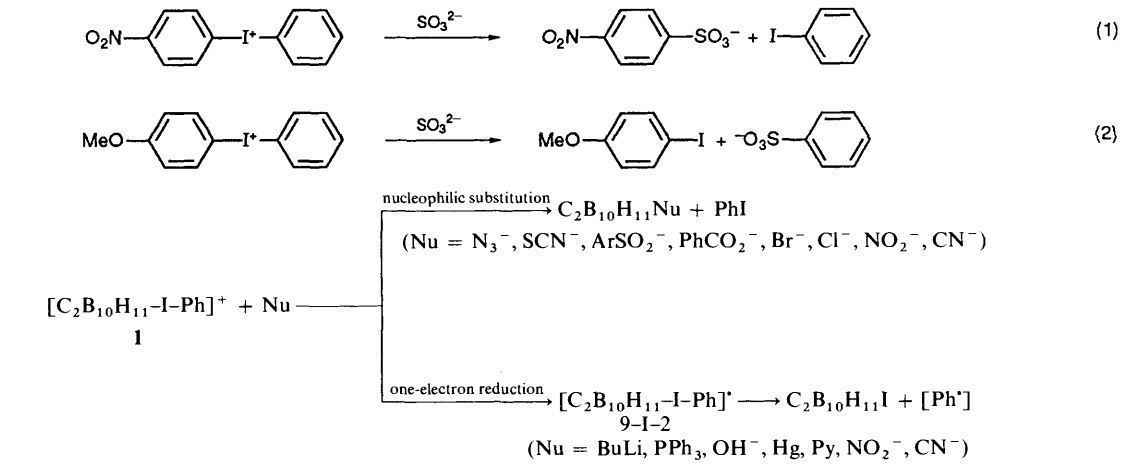
‡ In a few cases it was demonstrated that some reactions of diaryliodonium ions proceed *via* an $S_{RN}1$ mechanism,[8] or *via* the formation of a dehydroarene.[9]

§ Icosahedral *closo*-carboranes(12) are considered to be quasi-aromatic systems.[16] Chemical properties and reactivities of many functional and non-functional groups attached to a boron atom of carboranes(12) were found to be very similar to those of the corresponding benzene derivatives.[17] Smooth nucleophilic substitution at the boron atom of an icosahedral *closo*-carborane under mild conditions is very rare. It is known that nucleophilic substitution reactions of *B*-carboranyl halides and toluene-*p*-sulfonates do not take place even under extremely drastic conditions.[17,18] There are at least two reasons for this. Steric shielding of σ*-antibonding orbitals (boron–element terminal bond) together with the absence of low energy unoccupied orbitals in icosahedral *closo*-carboranes make a mechanism of S_N2-type impossible. In addition, S_N1 type mechanism is also unfavorable. A *B*-carbonyl cation should be highly energy rich since it cannot reach a planar geometry at the cationic centre because of the rigid icosahedral structure of the whole cage.



Scheme 1

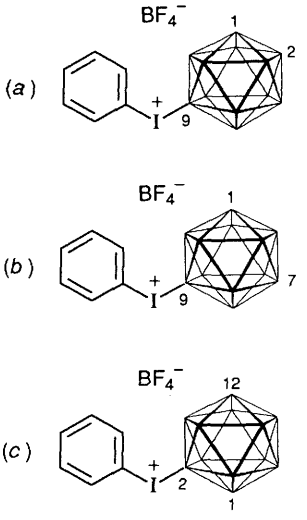


Fig. 1 Phenyl(*B*-carboranyl)iodonium tetrafluoroborates: (*a*) Phenyl(*o*-carboran-9-yl)iodonium tetrafluoroborate [*o*-carborane = 1,2-dicarba-*closo*-dodecaborane(12)]; (*b*) Phenyl(*m*-carboran-9-yl)iodonium tetrafluoroborate, **1** [*m*-carborane = 1,7-dicarba-*closo*-dodecaborane(12)]; (*c*) Phenyl(*p*-carboran-2-yl)iodonium tetrafluoroborate, **3** [*p*-carborane = 1,12-dicarba-*closo*-dodecaborane(12)]

proceed *via* a radical pathway.[19,20] They probably include formation of an unstable 9-I-2 intermediate as the result of a one-electron reduction of the initial iodonium cation and decomposition of these 9-I-2 species to produce iodocarborane and phenyl radicals. The regiospecificity of the decomposition of the 9-I-2 intermediate can be easily accounted for in terms of differing ability of aryl and *B*-carboranyl ligands to delocalise negative charge.[21] The B–I bond cleavage reactions involve *formal* nucleophilic substitution at the boron atom of the carborane cage.[20–22] Usually these S_N reactions occur very smoothly, and lead to substitution products in almost quantitative yields. Only *ipso*-substitution was found to take place. It is noteworthy that some nucleophiles (*e.g.* CN^- [20] and NO_2^- [23]) can cause simultaneous one-electron reduction and S_N reaction of **1**. However, even in these cases nucleophilic substitution occurs only at the carborane boron, while a one-electron reduction results in elimination of phenyl radicals.

In recent publications,[20,21,24] we proposed that the regiospecificity of nucleophilic substitution in phenyl(*B*-carboranyl)iodonium ions and the *ortho*-effect in diaryliodonium salts are related phenomena controlled by steric factors, and result from the same reasons. In the present paper we report the first definitive evidence for this hypothesis, which provides a rationale for the previously 'inexplicable' results (see above) in the chemistry of diarylhalonium ions.

Results

The main goal of the present research was to find any parameter which is able to influence the regiospecificity of the polar reactions of phenyl(*B*-carboranyl)iodonium cations. Electron-withdrawing groups are known to increase the reactivity of diaryliodonium ions towards nucleophiles, while electron-donating substituents exert the opposite effect.[4,10c,25] On the other hand, *ortho*-substituents, including electron-donating methyl groups, facilitate nucleophilic substitution in the ring (the so-called *ortho*-effect).[4,15,25–27] Consequently, aryl(*m*-carboran-9-yl)iodonium compounds **2a–d** containing different substituents in the aryl ring, were chosen for the present investigation of reactivity of such systems towards nucleophiles.

Reactions of **2a–d** *with Bromide Ion.*—The reaction of **1** with NaBr was found to be regiospecific, affording 9-bromo-*m*-carborane and iodobenzene in quantitative yields.[20] Compounds **2a–c** react similarly with Br^- to give only bromocarborane and the corresponding iodoarene, also in quantitative yields [eqn. (3)]. Neither products of nucleophilic

$$[Ar\text{-}I\text{-}C_2B_{10}H_{11}]^+BF_4^- + NaBr \xrightarrow[\text{reflux}]{H_2O\text{-}CHCl_3} \underset{\mathbf{1,2a\text{–}c}}{} C_2B_{10}H_{11}Br + ArI \quad (3)$$

Ar = Ph, **1**; 4-$CH_3OC_6H_4$, **2a**; 4-FC_6H_4, **2b**; 3-$NO_2C_6H_4$,**2c**.

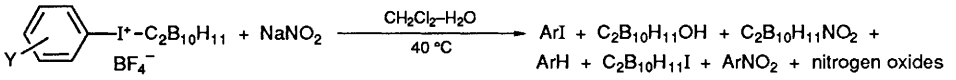
substitution at the carbon atom, nor arenes arising from a one-electron reduction of the starting cations **2a–c**, were found amongst the reaction products. This indicates that both electron-donating and electron-withdrawing substituents in the benzene ring do not affect the regiospecificity of nucleophilic substitution. However, such is not the case of mesityl(*m*-carboran-9-yl)iodonium salt **2d** which gave all four possible products of nucleophilic substitution [eqn. (4)]. Traces of

$$[Ar\text{-}I\text{-}C_2B_{10}H_{11}]^+BF_4^- + NaBr \xrightarrow[\text{reflux}]{H_2O\text{-}CHCl_3} \underset{\mathbf{2d}}{} \underbrace{C_2B_{10}H_{11}Br + ArI}_{85\%} + \underbrace{C_2B_{10}H_{11}I + ArBr}_{15\%} \quad (4)$$

Ar = 2,4,6-$(CH_3)_3C_6H_2$

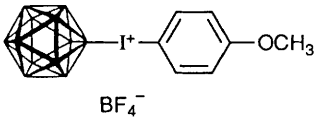
mesitylene (<0.5% yield) were formed in this reaction,

Table 1 Reactions of aryl(*m*-carboran-9-yl)iodonium tetrafluoroborates **1,2a–d** with $NaNO_2$

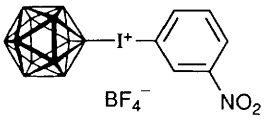


		Yield (%)					
Y	t/h	ArI	$C_2B_{10}H_{11}OH$[a]	$C_2B_{10}H_{11}NO_2$[a]	$C_2B_{10}H_{11}I$[a]	ArH[b]	$ArNO_2$
H, **1**	3	93[b]	79	6	7	4	0.5[b]
4-OCH_3, **2a**	3	88[a]	87	8.5	1.5	1	traces[c]
4-F, **2b**	2.5	90[d]	75	8	8	5[d]	traces[c]
3-NO_2, **2c**	1.5	74[a]	75	4	15	4	2[a]
2,4,6-$(CH_3)_3$, **2d**	7	58[a]	57	*e*	36	3	35[a]

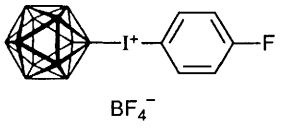
[a] Isolated quantitatively by preparative column chromatography. [b] Yield was determined by GLC using internal standard. [c] Less than 1%; identified by GC–MS. [d] Yield was determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard. [e] 9-nitro-*m*-carborane was not found among the reaction products.



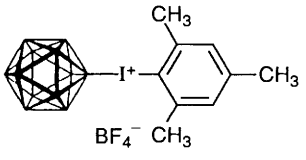
2a



2c



2b



2d

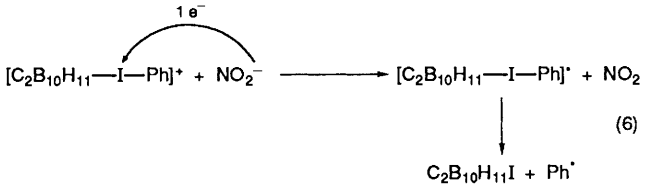
suggesting the minor occurrence of a one-electron reduction of **2d**. Nevertheless, such a dramatic change in the regiospecificity of the S_N reaction cannot be connected with this very modest contribution of a radical reaction pathway.

Reactions of **2a–d** *with Nitrite Ion.*—Competition between nucleophilic substitution and a one-electron reduction was found to take place in the reaction of **1** with $NaNO_2$.[23] The nucleophilic pathway generates 9-hydroxy-*m*-carborane and 9-nitro-*m*-carborane[28] due to the ambidentate nature of the nitrite anion,[23] eqn. (5). At the same time a one-electron

$$[C_2B_{10}H_{11}\text{–I–Ph}]^+ + NO_2^- \longrightarrow [C_2B_{10}H_{11}ONO] + C_2B_{10}H_{11}NO_2 + PhI \quad (5)$$

$$[C_2B_{10}H_{11}ONO] \xrightarrow{H_2O} C_2B_{10}H_{11}OH + \text{nitrogen oxides}$$

reduction of the iodonium ion occurred independently of the S_N reaction, eqn. (6).



(6)

The same is true for reactions of salts **2a–c** with $NaNO_2$ (Table 1). The formation of arenes (1–5% yield) indicates that the participation of radical processes is relatively insignificant in all cases. The origin of the nitroarenes formed can be debated. From our point of view, the known[29] reactions of aryl radicals with NO_2 or NO_2^- to give nitroarenes, are more probable than direct nucleophilic substitution at the aryl carbon of the iodonium cations **1,2a–c**. However, this is not very important at the moment, since the result of the reaction of mesityl(*m*-carboran-9-yl)iodonium salt **2d** with $NaNO_2$ was again found to be qualitatively different. This reaction also leads to arene (mesitylene) formation. The yield of mesitylene (3%) is similar to the yields of arenes in the reactions of **2a–c** with $NaNO_2$ (Table 1). At the same time, the yield of nitromesitylene is at least 17–350 times higher than the yields of nitroarenes in the reactions of **2a–c**. It is obvious that here, as in the reactions with Br^-, a significant competition between nucleophilic substitution at the carborane boron and mesityl carbon is taking place. Therefore, neither electron-withdrawing, nor electron-donating, but only *ortho*-substituted aryl ligands are able to change the reactivity of aryl(*m*-carboran-9-yl)iodonium cations towards nucleophiles.

Reaction of **2d** *with Triphenylphosphine.*—Phenyl(*B*-carboranyl)iodonium compounds react with PPh_3 (acetone, 56 °C, visible light irradiation) *via* a radical pathway.[19,30] These reactions are regiospecific, since they lead to only C–I bond cleavage, and the formation of tetraphenylphosphonium tetrafluoroborate, iodocarborane and small amounts of benzene. Mesityl(*m*-carboran-9-yl)iodonium salt **2d** was found to be much less reactive towards triphenylphosphine. The interaction between **2d** and PPh_3 (twofold excess) requires drastic conditions (UV) and prolonged reaction time, eqn. (7). Although this reaction produces neither mesityltriphenylphosphonium, nor carboranyl(triphenyl)phosphonium salt[19]

(^{31}P NMR spectroscopy), it still remains regiospecific. The formation of 9-iodo-*m*-carborane (82% yield) and mesitylene (50% yield) is indicative of a homolytic mechanism for the reaction. No products resulting from the cleavage of the B–I bond of **2d** were detected.

$$[Ar\text{–}I\text{–}C_2B_{10}H_{11}]^+BF_4^- \; PPh_3 \xrightarrow[56\,^\circ C,\ 110\ h.]{UV,\ acetone} \quad (7)$$

2d

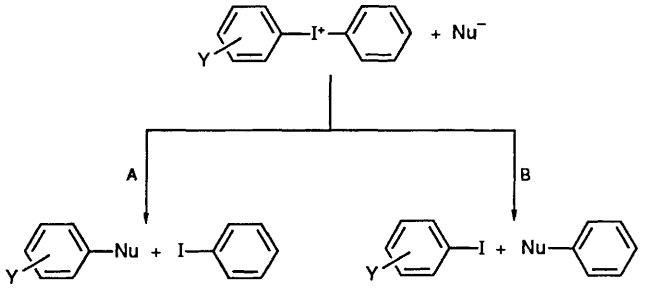
$$C_2B_{10}H_{11}I \; (82\%) \; + \; ArH \; (50\%)$$

Ar = 2,4,6-$(CH_3)_3C_6H_2$

Discussion

All the data obtained show that neither electron-withdrawing, nor electron-donating groups at the *para*- or *meta*-position of an aryl(*m*-carboran-9-yl)iodonium cation influence the regiospecificity of nucleophilic substitution. The situation changes significantly when one considers mesityl(*m*-carboran-9-yl)-iodonium salt **2d**, which contains two methyl groups in the *ortho*-positions. At the same time the *ortho*-methyl substituents, as anticipated,[7,21] do not disturb the regiospecificity of the radical processes (reactions of **1** and **2d** with PPh_3).

Nucleophilic substitution in **2d** by Br^- and NO_2^- resembles the so-called '*ortho*-effect' in the polar reactions of *ortho*-substituted unsymmetrical diaryliodonium ions.[3,4] Scheme 2 illustrates the *ortho*-effect. Usually the more electron-deficient ring of an unsymmetrical diaryliodonium cation is attacked by a nucleophile, while similar reactions of isomeric *ortho*-substituted cations lead to the products in opposite ratio.[14,26] Introduction of two methyl groups in the *ortho*-positions increases this tendency.[15,25–27]

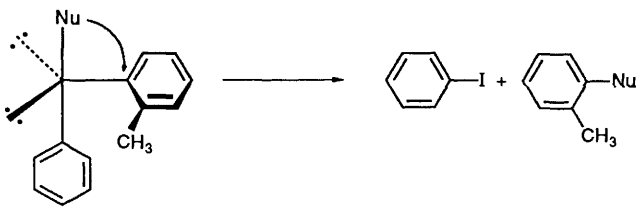


Y	Nu^-	A:B
4-CH_3	NO_2^-	1.0:2.7
	Br^-	1.0:1.9
2-CH_3	NO_2^-	9.6:1.0
	Br^-	6.7:1.0
2,4,6-$(CH_3)_3$	NO_2^-	>100:1
	Br^-	24.0:1.0

Scheme 2

An explanation of the *ortho*-effect in diaryliodonium salts has been based on the following assumptions.[4,15,26,31] A nucleophile attacks the onium iodine to give a tricovalent iodine(III) complex (10–I–3 intermediate; see Scheme 3). This intermediate is believed to be T-shaped, as are diaryliodonium compounds in the crystal state (according to the X-ray data).[4] The bulkier of the two aryl ligands together with 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.

However this model cannot explain why the magnitude of the *ortho*-effect depends on the nature of the nucleophile[26] and

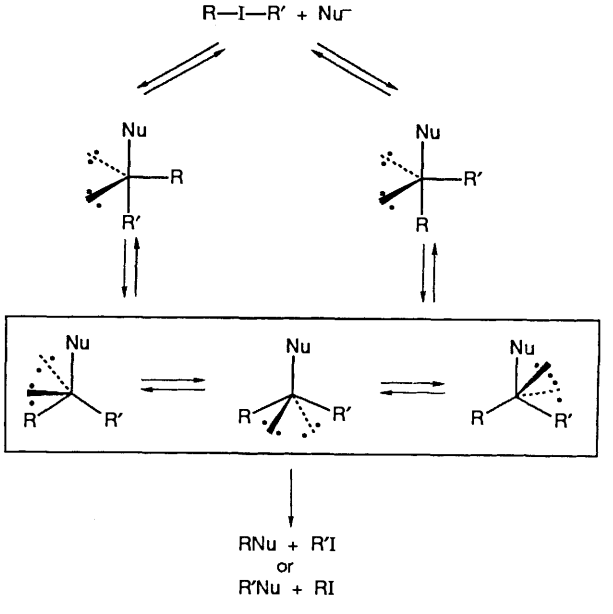


Scheme 3

'onium halogen.[15,24] Then, nucleophilic substitution in indol-3-ylphenyliodonium trifluoroacetate leads to iodobenzene and the corresponding indolyl derivative,[32] although in the solid state the indolyl ligand was found to occupy the apical, not equatorial position of the starting iodonium molecule.[33] Finally, a nucleophilic attack on icosahedral *closo*-carborane-(12) boron bearing any substituent except hydrogen was shown to be unlikely.[21,34,35]

In 1981 Budylin *et al.* proposed for the first time that 10–I–3 intermediates can undergo synchronous (cheletropic) extrusion of an iodoarene.[32] This concept of reductive elimination from tricovalent iodine(III) complexes was widely used by Moriarty and Vaid.[5a] Let us consider this model in detail, and develop it.

Assuming lone electron pairs (phantom ligands) of iodine play a role as substituents, 10–I–3 complexes exhibit a trigonal bipyramidal structure in the crystalline state.[4] Apical–equatorial interactions in a trigonal bipyramidal structure were shown to be symmetry forbidden.[36] In solution trigonal bipyramidal complexes can undergo permutational transformations such as Berry pseudorotation or turnstile rotation. In fact, triaryliodine(III) compounds were found to be stereochemically non-rigid in solution.[37] Permutational processes possibly occur *via* tetragonal pyramidal intermediates in which the iodine atom, nucleophile, and both substituents lie in one plane so as to minimize steric interactions (Scheme 4). According to calculations[36] 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. 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



Scheme 4

will eliminate in order to decrease the positive charge on the iodine atom.

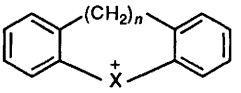
Nucleophilic substitution in **1** is regiospecific because the carboranyl ligand is significantly larger than the phenyl substituent. Introduction of a substituent into the *meta*- or *para*-position of the phenyl ligand does not affect the regiospecificity. Obviously *meta* and *para* substituted aryl ligands cause almost the same steric strain (as a non-substituted phenyl ligand) in the tetragonal pyramid. The situation changes when going to cation **2d**, as the mesityl ligand is bulky enough to compete with the carboranyl group to bind the nucleophile.

Electronic factors can also be important for the polar reactions, and not only when both ligands possess equal dimensions. For instance, iodonium salt **3** (Fig. 1) bearing the less electron-donating *p*-carboran-2-yl substituent (*cf.* the *m*-carboran-9-yl group of **1**)[17] reacts with anions F^-, N_3^-, NO_2^- faster than **1**.[30] This is in good agreement with the concept of reductive elimination. Also **3** exhibits a stronger tendency than **1** to co-ordinate with the harder nucleophilic centre of ambident anions. Reaction of **1** with NaSCN leads to a mixture of *m*-carboran-9-yl thiocyanate and isothiocyanate in a 1.3:1 ratio.[22] As shown in the present work, **3** reacts with NaSCN under the same conditions to give thiocyanate and isothiocyanate in 1:2.65 ratio (see the Experimental section). It is noteworthy that **2d** arylates only at the nitrogen atom, but carboranylates only at an oxygen atom of NO_2^-. Therefore, the type of co-ordination which depends on electronic properties of polydentate donors and acceptors influences the stability of the transition state for reductive elimination.

The size of the nucleophile should play a significant role in the contribution to the general steric tension in tetragonal pyramid. Clearly, the larger the nucleophile, the greater the steric factor, and therefore, the lower the regioselectivity. Lancer and Wiegand[26] have clearly shown that the magnitude of the *ortho*-effect depends on the nucleophile. The same was observed for reactions of **2d**. Thus, in the case of NO_2^- the product ratio of carboranylation/arylation is *ca.* 1.6:1. This ratio is equal to 5.7:1 when **2d** reacts with Br^-, while polar reactions with Cl^-, F^-,[38] and N_3^- (see Experimental section) were found to be regiospecific. The dramatic difference between N_3^- and NO_2^- 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 co-ordinate through the terminal atoms.

The mechanism (Scheme 4) does not involve any *ipso*-nucleophilic attack on a ligand attached to the iodonium centre. Such an attack is conceivable only for bromonium and chloronium cations, or if an aryl ligand contains strong electron-withdrawing substituent(s), (*e.g.* nitro or cyano groups) in the *ortho*- and/or *para*-positions. In such cases the S_NAr process, involving the formation of Meisenheimer-type complex,[39] might compete with synchronous reductive elimination (cheletropic reaction). Indeed, competition between these two routes was observed in the polar reactions of bromonium and chloronium cations, $[Ph–X–R]^+$ (X = Br, Cl; R = *o*-tolyl[15] and *m*-carboran-9-yl[24]). Reductive elimination gives the product of substitution at the bulkier ligand, while in the course of the S_NAr reaction the nucleophile preferentially attacks the phenyl rather than the *o*-tolyl carbon, or the carboranyl boron. As the result, the *ortho*-effect decreases in the order $[Ph–I–R]^+ > [Ph–Br–R]^+ > [Ph–Cl–R]^+$, in accordance with electron-withdrawing properties of the groups RCl^+ (R = Ph, $\sigma_I = +1.72$; R = 9-*m*-$C_2B_{10}H_{11}$, $\sigma_I = +1.65$), RBr^+ (R = Ph, $\sigma_I = +1.63$; R = 9-*m*-$C_2B_{10}H_{11}$, $\sigma_I = +1.60$), and RI^+ (R = Ph, $\sigma_I = +1.35$; R = $C_2B_{10}H_{11}$, $\sigma_I = +1.39$).[21]

The new mechanistic model also explains the reactivity of cyclic aromatic halonium compounds. Obviously, structural non-rigidity of iodonium ions is critical for the permutational processes and the cheletropic decomposition (Scheme 4). For example, diphenyliodonium cation reacts smoothly with a variety of charged nucleophiles (*e.g.*, Cl^-, Br^-, NO_2^-, N_3^-, $R_2NCS_2^-$) to give iodobenzene and the corresponding substituted benzene in high yields.[2–4,10a,14a,25,39] Reactions of the highly flexible 11,12-dihydro-10*H*-dibenz[*b*,*g*]iodocinium cation, **4**, with anions NO_2^-, Br^- and N_3^- also lead to the corresponding products of a non-radical 'polar' reaction in almost quantitative yields.[40] Being able to change its geometry easily, the iodonium ion **4** exhibits the same reactivity and reaction pathways as the non-cyclic diphenyliodonium ion. The



4; *n* = 3, X = I
5; *n* = 1, X = I
6; *n* = 0, X = I
7; *n* = 0, X = Br
8; *n* = 0, X = Cl

reactivity of the less flexible 10*H*-dibenz[*b*,*e*]iodinium cation, **5**, is noticeably different. The thermolysis of its chloride leads not only to 2-chloro-2′-iododiphenylmethane (93% yield), but also to some amounts of radical decomposition products.[41a] Finally, reactions of the most rigid dibenz[*b*,*d*]iodolium cation, **6**, containing iodine in the five-membered ring, with the same nucleophiles require more severe conditions, and implies a homolytic mechanism.[41,42] 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 that 'This change in reactivity could not be accounted for'.[42] However the new mechanistic model readily accounts for this behaviour. Rigidity of the five-membered ring in **6** makes the rearrangement of the trigonal bipyramidal stucture into a tetragonal pyramid impossible, and thus the 10–I–3 complex reacts by homolysis of the iodine–nucleophile bond. Bromonium and chloronium ions **7** and **8** are isostructural and isoelectronic with **6**. However, in contrast with **6**, they react smoothly with I^- to give the corresponding 2-halogeno-2′-iodobiphenyl in quantitative yield,[41a,43] since bromonium and chloronium salts can undergo nucleophilic substitution *via* S_NAr-type mechanism (*vide supra*).

Aryl(*B*-carboranyl)iodonium salts react with neutral nucleophiles only *via* a radical pathway,[17] and the same is true for diaryliodonium cations, although it seems unlikely on initial considerations.* A 10–I–3 intermediate can, in principle, decompose *via* two general routes. The first possibility includes intramolecular rotation followed by reductive elimination. Another possibility is a homolysis of the I–Nu bond affording a 9–I–2 radical. A 10–I–3 intermediate is neutral when the nucleophile is negatively charged, or can bear a positive charge if the nucleophile is neutral. In the latter case a major part of the positive charge is concentrated on the atom which has donated its lone electron pair to iodine. The electrostatic interaction between this positive charge and phantom ligands of iodine increases the barrier to rotation, and makes the reductive elimination unlikely. This is why diaryliodonium and aryl-

* There are two exceptions. Some high temperature reactions proceed *via* elimination of the aryl cation from the iodonium ion (S_N1 mechanism).[44] These cases are rare. Diaryliodonium cations containing strong electron-withdrawing groups (*e.g.* NO_2, CN) in the *ortho* and/or *para* positions are able to react with anions and neutral nucleophiles *via* a S_NAr pathway,[7] *i.e. via* formation and decomposition of a Meisenheimer-type complex. All the mechanistic considerations described above do not apply to the exceptions, but address all other cases.

(*B*-carboranyl)iodonium ions prefer to react with neutral nucleophiles *via* a radical pathway.

Conclusions

Electronic factors were shown to determine regioselectivity of radical reactions of diaryliodonium[7] and aryl(*B*-carboranyl)-iodonium[21] ions proceeding *via* 9–I–2 intermediates. In contrast, steric factors play a major role in the polar reactions of diaryliodonium and aryl(*m*-carboran-9-yl)iodonium ions. A difference in size between the two ligands attached to iodine determines the selectivity of polar reactions. The suggested mechanism easily explains the *ortho*-effect and other results which were previously rationalized poorly in terms of classical aromatic nucleophilic substitution. In conclusion, this paper can explain the most salient features of the chemistry of diarylhalonium ions.

Experimental

^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY spectrometer. IR spectra were recorded on a Carl Zeiss, Jena, UR-20 instrument. 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. A PRK-2 mercury lamp was used as a source of UV irradiation. Iodonium compounds **1**,[45] **2a–d**[46] and **3**[30] were synthesized as described in the literature.

Reactions of **2a–d** *with* NaBr.—A mixture of aryl(*m*-carboran-9-yl)iodonium tetrafluoroborate (0.23 mmol), NaBr (0.07 g; 0.68 mmol), water (1 cm^3), and chloroform (1 cm^3) was vigorously stirred under reflux for 3.5 h. An internal standard (chlorobenzene) was added, and the organic layer was analysed by GLC.

Reaction of **2a** *with* $NaNO_2$.—A mixture of **2a** (1.00 g, 2.15 mmol), $NaNO_2$ (0.74 g, 10.73 mmol), water (5 cm^3), and dichloromethane (5 cm^3) was vigorously stirred under reflux (evolution of nitrogen oxides) for 3 h. Internal standard (chlorobenzene) was added, and the organic phase was analysed by GLC and GC–MS. The organic layer was separated, and evaporated. The residue was chromatographed on silica gel (5/40 mesh) first with hexane, to give consecutively 4-iodoanisole (0.44 g; 88%), m.p. 50–52 °C (hexane), and 9-iodo-*m*-carborane (0.009 g, 7%), m.p. 105–107 °C (hexane, see ref. 16); then with benzene–hexane (1:1) mixture, to give 9-nitro-*m*-carborane (0.035 g, 8.5%), m.p. 234–235 °C (hexane, see ref. 23); then with diethyl ether, to give 9-hydroxy-*m*-carborane (0.30 g, 87%), m.p. 326–327 °C (benzene–heptane, see ref. 47). All the compounds obtained were found to be identical with authentic samples.

Reaction of **2b** *with* $NaNO_2$.—A mixture of **2b** (1.50 g, 3.32 mmol), $NaNO_2$ (1.2 g, 17.4 mmol), water (7 cm^3), and dichloromethane (7 cm^3) was vigorously stirred under reflux for 2.5 h. Internal standards (chlorobenzene and benzotrifluoride) were added, and the organic phase was analysed by GLC, GC–MS and ^{19}F NMR spectroscopy. The organic layer was separated, and evaporated. The residue was chromatographed on silica gel (5/40 mesh) first with hexane, to give 9-iodo-*m*-carborane (0.071 g, 8%), m.p. 107–109 °C (hexane), then with benzene–hexane (1:1) mixture, to give 9-nitro-*m*-carborane (0.05 g, 8%), m.p. 234–235 °C (hexane), then with diethyl ether, to give 9-hydroxy-*m*-carborane (0.40 g, 75%), m.p. 329–331 °C. All the compounds obtained were found to be identical with authentic samples.

Reaction of **2c** *with* $NaNO_2$.—A mixture of **2c** (0.60 g, 1.25 mmol), $NaNO_2$ (0.44 g, 6.4 mmol), water (2 cm^3), and dichloromethane (2 cm^3) was vigorously stirred under reflux for 1.5 h. Internal standard (chlorobenzene) was added, and the organic layer was analysed by GLC and GC–MS. The organic phase was separated, and evaporated. The remaining solid was chromatographed on silica gel (5/40 mesh) first with hexane, to give consecutively 9-iodo-*m*-carborane (0.05 g, 15%), m.p. 107–109 °C, and 3-iodonitrobenzene (0.23 g, 74%), m.p. 34–35 °C (ethanol), then with benzene–hexane (1:1) mixture, to give consecutively 1,3-dinitrobenzene (0.005 g, 2%), m.p. 84–85 °C (ethanol) and 9-nitro-*m*-carborane (0.01 g, 4%), m.p. 234–235 °C (hexane), then with ether, to give 9-hydroxy-*m*-carborane (0.15 g, 75%), m.p. 326–328 °C (benzene–heptane). All the compounds obtained were found to be identical with authentic samples.

Reaction of **2d** *with* $NaNO_2$.—A mixture of **2d** (1.00 g, 2.1 mmol), $NaNO_2$ (0.72 g, 10.5 mmol), water (5 cm^3), and dichloromethane (5 cm^3) was vigorously stirred under reflux for 7 h. Internal standard (chlorobenzene) was added, and the organic layer was analysed by GLC and GC–MS. The organic phase was separated and evaporated. The residue was chromatographed on silica gel (5/40 mesh) first with hexane, to give consecutively iodomesitylene (0.30 g, 58%), m.p. 26–28 °C (hexane), and 9-iodo-*m*-carborane (0.21 g, 36%), m.p. 106–108 °C; then with benzene–hexane (1:1) mixture, to give nitromesitylene (0.12 g, 35%), m.p. 41–42 °C (methanol), then with ether, to give 9-hydroxy-*m*-carborane (0.19 g, 57%), 326–327 °C (benzene–heptane). All the compounds isolated were found to be identical with authentic samples.

Reaction of **2d** *with* NaN_3.—A mixture of **2d** (0.27 g, 0.57 mmol), NaN_3 (0.10 g, 1.54 mmol), water (5 cm^3), and dichloromethane (5 cm^3) was vigorously stirred at 20 °C for 1.5 h. The organic layer was analysed by GLC and GC–MS, and then evaporated to dryness. The remaining solid was chromatographed on silica (40/100 mesh) with hexane–benzene (15:1 mixture), to give consecutively iodomesitylene (0.13 g, 93%), m.p. 29–30 °C (hexane); 9-iodo-*m*-carborane (0.005 g, 3%), m.p. 105–107 °C (hexane); 9-azido-*m*-carborane (0.094 g, 89%), m.p. 94–95 °C (hexane, see ref. 22). All the compounds were found to be identical with authentic samples.

Reaction of **2d** *with* PPh_3.—A solution of **2d** (0.03 g, 0.06 mmol) and PPh_3 (0.03 g, 0.12 mmol) in acetone (1.5 cm^3) was refluxed under UV irradiation (quartz flask) for 110 h. The resulting solution was analysed by GLC (with chlorobenzene as an internal standard), and by ^{31}P NMR spectroscopy. The solution was evaporated, and the residue was extracted with hexane. Evaporation of hexane solution gave 0.014 g (82%) of 9-iodo-*m*-carborane, m.p. 105–107 °C (hexane).

Dimesityliodonium Tetrafluoroborate.—A quarter of the dimesityliodonium salt solution obtained according to the procedure of ref. 48 was treated with 40% HBF_4 (60 cm^3). The mixture was extracted with a nitromethane–chloroform (3:1) mixture. Organic solvents were removed under reduced pressure and the remaining solid was recrystallized by addition of diethyl ether to a clear acetone solution; yield 34.6 g (42.5%), m.p. 200 °C. (Calc. for $C_{18}H_{22}BF_4I$: C, 47.82; H, 4.91. Found: C, 47.7; H, 4.9%).

Mesityl(triphenyl)phosphonium Tetrafluoroborate.—A solution of dimesityliodonium tetrafluoroborate (1.5 g, 3.3 mmol) and PPh_3 (1.74 g, 6.6 mmol) in acetone (10 cm^3) was refluxed under UV irradiation (quartz flask) for *ca.* 160 h. The resulting solution was treated with ether, to give a mixture of triphenylphosphine oxide and mesityltriphenylphosphonium

tetrafluoroborate. The latter was isolated by chromatography on silica gel (5/40 mesh, dichloromethane–acetone (3:1) mixture). Yield 0.35 g (23%), m.p. 253–256 °C. (Calc. for $C_{27}H_{26}BF_4P$: C, 69.25; H, 5.60; P, 6.61. Found: C, 69.4; H, 5.6; P, 6.6%). δ_H ([$^2H_6$]acetone) 1.88 (s, 6 H, 2,6-CH_3), 2.45 (s, 3 H, 4-CH_3) and 7.13–8.05 (m, 17 H, aromatic).

Reaction of **3** *with* NaSCN.—A mixture of **3** (0.35 g, 0.81 mmol), NaSCN (0.20 g, 2.47 mmol), water (5 cm^3) and chloroform (5 cm^3) was vigorously stirred at 20 °C for 2.5 h. The organic phase was separated and evaporated. The residue was chromatographed on silica (40/100 mesh) first with benzene–hexane (3:1) mixture, to give a mixture of iodobenzene and *p*-carboran-9-yl isothiocyanate; then with benzene, to give *p*-carboran-9-yl thiocyanate (0.033 g, 20%): m.p. 42–43 °C (pentane, see ref. 49); ν/cm^{-1} 2170 (CN).

p-Carboran-2-yl isothiocyanate was separated from iodobenzene by crystallization from pentane at −78 °C (the procedure was repeated three times), and then sublimed *in vacuo*; yield 0.085 g (53%), m.p. 130–133 °C. (Calc. for $C_3H_{11}B_{10}NS$: C, 17.90; H, 5.51; N, 6.96; S, 15.93. Found: C, 18.2; H, 5.1; N, 7.2; S, 15.9%); ν(Nujol)/cm^{-1} 2120 (N=C=S).

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