Fluorinated biphenyls from aromatic arylations with pentafluorobenzenediazonium and related cations. Competition between arylation and azo coupling

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High yields of the mixed perfluorinated biaryls (C_6F_5–Ar) are obtained by the catalytic dediazoniation of the pentafluorobenzenediazonium salt ($C_6F_5N_2^+BF_4^-$) in acetonitrile solutions containing various aromatic substrates (ArH) together with small amounts of iodide salts. Activated (electron-rich) as well as deactivated (electron-poor) arenes are successfully pentafluorophenylated by this method. The arylation is distinct from the azo coupling of the same substrates, which takes place in the absence of the iodide catalyst and yields the corresponding diazene ($C_6F_5N{=}N$–Ar) as product. The catalytic role of iodide, and the isomeric product distributions obtained with this procedure indicate that the arylation proceeds *via* the pentafluorophenyl radical in a efficient homolytic chain process. Since azo coupling involves electrophilic aromatic substitution of electron-rich ArH by $C_6F_5N_2^+$, the two competing pathways are distinct and do not have reactive intermediates in common.

Introduction

Unsymmetrical fluorinated biaryls (Ar–Ar_F) are promising new materials for nonlinear optics, asymmetric catalysis, and a variety of other physical applications.[1–3] Accordingly, newer methods for their synthesis *via* the direct arylation of aromatic substrates (ArH) under mild conditions are particularly desirable. Fluorinated diazonium cations ($Ar_FN_2^+$) are potentially useful reagents to effect this transformation, since they represent the fluoroaryl synthon (Ar_F) in a highly activated form in which the ready loss of dinitrogen drives the arylation to completion, *i.e.* eqn. (1). The synthetic transformation in eqn. (1) is

$$Ar_FN_2^+ + ArH \longrightarrow Ar\text{–}Ar_F + N_2 + H^+ \qquad (1)$$

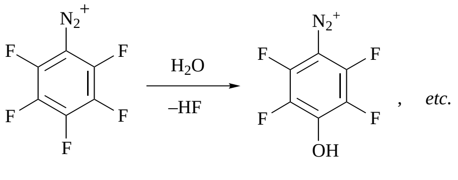
usually realized in aqueous media *via* the classic Gomberg–Bachmann reaction[4,5] and its intramolecular analogue, the Pschorr synthesis.[6,7] These reactions are conventionally carried out in the presence of base, but they are often characterized by low yields and extensive formation of colored side products.[8] Since these drawbacks derive from the wide variety of undesired reactions that diazonium cations undergo in aqueous base,[9] we felt that the new developments in the use of nonaqueous solvents and specific salt catalysis would mitigate these undesirable features and could revive the biaryl coupling in eqn. (1) as a useful synthetic method. In this report, we concentrate on the transfer of the pentafluorophenyl group [$Ar_F = C_6F_5$ in eqn. (1)] to represent a prototype for the introduction of electron-withdrawing substitutents into aromatic systems. Indeed, the product 'push–pull' biaryls that contain donor moieties in conjunction with an electron-withdrawing C_6F_5 substituent are useful in nonlinear laser applications and have been exploited for liquid-crystal displays.[10,11]

Pentafluorophenylation has been carried out under aprotic conditions by the thermal or photochemical activation of a C_6F_5-transfer agent in the presence of the arene ArH.[12] Thus, the thermolysis of perfluorobenzoyl peroxide[13] or the xenon derivative $C_6F_5Xe^+$,[14] the oxidation of pentafluorophenylhydrazine[15] and the photolysis of C_6F_5I[16] have all been exploited to deliver the pentafluorophenyl moiety in nonaqueous media. However, these methods suffer from low yields and many side products, or they require the use of rather exotic starting materials. Although $C_6F_5N_2^+$ represents an alternative reagent for pentafluorophenylation, its synthesis by conventional diazotization methods in aqueous solution has been heretofore unsuccessful (although it can be generated in strongly acidic HF solutions).[17] Accordingly, we will primarily focus on the synthesis of $C_6F_5N_2^+BF_4^-$ and related salts suitable for use in nonaqueous solvents, and the development of methods for efficiently realizing the biaryl synthesis according to eqn. (1).

Results

Preparation of crystalline pentafluorobenzenediazonium fluoroborate

The diazonium salt $C_6F_5N_2^+BF_4^-$ could not be prepared by the conventional diazotization of pentafluoroaniline with sodium nitrite in aqueous acidic media.[17] Accordingly, the pentafluorobenzenediazonium salt was isolated from a nonaqueous solvent (acetonitrile) by the use of specially prepared nitrosonium tetrafluoroborate as the diazotizing reagent.[18] (See the Experimental section for details of the procedure). The colorless crystalline salt was stable if stored at low temperature, but it rapidly decomposed upon even a short exposure to atmospheric moisture. Since the fluoroborate salts of other diazonium cations are known generally to be stable in moist air, the rapid decomposition of $C_6F_5N_2^+BF_4^-$ indicated that it was especially susceptible to nucleophilic attack by water, *e.g.* eqn. (2). Indeed, the strongly electrophilic nature of this diazonium cation was further exemplified by the facile replacement of the *ortho*- and *para*-fluorine atoms with chlorine to afford the 2,4,6-trichloro analogue merely upon its exposure to a solution of hydrogen chloride in nitromethane at 24 °C (see Experimental section).



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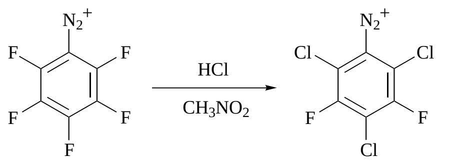

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Table 1 Pentafluorophenylation of benzene induced by sodium iodide in solution[a]

[PhH]/M	NaI consumed/ mmol[b]	Turnover number[c]	Products (%)[d]				
			C_6F_5Ph	C_6F_5I	$(C_6H_4P_2)$[e]	C_6F_5H	I_2
0.17	0.41	2.8	36	31	13	3.7	15
0.34	0.26	6.9	56	14	13	2.6	7.8
0.69	0.12	16	73	5.7	10	1.7	5.6
1.38	0.07	31	83	2.7	6.5	0.9	3.8
2.75	0.03	58	92	2.9	6.5	0.9	3.8
5.52	0.02	74	93	0.6	3.3	0.3	0.6
11.0	0.01	85	94	0.5	1.6	0	0

[a] In acetonitrile at 24 °C with 1.0 mmol of $C_6F_5N_2^+BF_4^-$ (data taken from ref. 19). [b] Added in 0.01–0.05 mmol aliquots until nitrogen evolution ceased. [c] Defined as mmol N_2 evolved per mmol sodium iodide added. [d] Yields based on diazonium salt. [e] $C_6H_4P_2$ = bis(pentafluorophenyl)benzene as a mixture of *o*-, *m*-, *p*-isomers (see Experimental section).

Table 2 Inhibition of pentafluorophenylation by various additives[a]

Additive/(mmol)		NaI consumed/ mmol	Turnover number	Products (%)		
				C_6F_5Ph	C_6F_5I	I_2
None		0.07	14	83	2.7	3.8
O_2	(0.2)	0.24	4.2	74	5.3	12
	(0.4)	0.38	2.6	71	7.9	20
	(0.8)	0.47	2.1	67	9.7	30
I_2	(0.1)	0.22	4.5	76	11	—
	(0.5)	0.33	3.0	61	26	—
	(1.0)	0.44	2.3	55	38	—
CH_2I_2	(8.0)	0.83	1.2	19	70	10
$BrCCl_3$	(8.0)	0.24	4.2	67	5.6 5.0 (C_6F_5Br)	10

[a] See footnotes in Table 1.

Pentafluorophenylation of aromatic hydrocarbons with catalytic amounts of iodide salts

The addition of 1 equiv. of sodium iodide to an acetonitrile solution of $C_6F_5N_2^+BF_4^-$ under an argon atmosphere at 24 °C immediately led to the evolution of 1 equiv. of dinitrogen. Workup of the reaction mixture afforded the iodination product pentafluoroiodobenzene in 85% yield, *i.e.* eqn. (4). In the

$$C_6F_5N_2^+ + I^- \longrightarrow C_6F_5I + N_2 \tag{4}$$

presence of an arene such as benzene, the reaction took a different course. For example, the addition of only 7 mol% NaI to a solution of $C_6F_5N_2^+BF_4^-$ in the presence of an eightfold excess of benzene led to complete reaction of the diazonium salt and the evolution of a full equivalent of N_2 within a few minutes.[19] The major product of the reaction was 2,3,4,5,6-pentafluorobiphenyl, which was formed in 83% yield, together with minor amounts of pentafluoroiodobenzene and bis(pentafluorophenyl)benzenes.[20] The reaction was thus designated as an iodide-promoted arylation of benzene, *i.e.* eqn. (5). The minor

$$C_6F_5N_2^+ + PhH \xrightarrow{[I^-]} C_6F_5Ph + N_2 + H^+ \tag{5}$$

product, C_6F_5I, together with a small amount of I_2, accounted for all of the added iodide salt.

The catalytic role of iodide in pentafluorophenylation reactions was also emphasised by the effective promotion of arylation by potassium iodide which was insoluble in the reaction medium. Thus, the addition of solid KI to an acetonitrile solution of $C_6F_5N_2^+BF_4^-$ and benzene at 24 °C immediately led to a vigorous evolution of gas. Dinitrogen (1 equiv.) was evolved within 10 min, and the added KI was largely recovered as an insoluble powder. Workup of the reaction mixture afforded pentafluorobiphenyl in 84% yield.

Since the presence of benzene was sufficient to divert the reaction from iodination to arylation, the effect of added benzene was systematically surveyed with sodium iodide owing to its enhanced solubility in the reaction medium. The results in Table 1 show that progressive increases in the initial concentration of benzene led to increased yields of the arylation product (C_6F_5Ph) and decreased yields of the iodination product (C_6F_5I).[19] Concomitant with these trends, the amount of NaI needed to effect complete reaction decreased. In the presence of a large excess of benzene (entry 7 in Table 1), less than 1 mol% of NaI, was sufficient to promote the complete arylation, and the yield of pentafluorobiphenyl was close to quantitative. The overall trend is presented in column 3 of Table 1 in which the turnover number (*i.e.* the extent of reaction induced by each equivalent of NaI) is tabulated.

The results in Table 2 show that dioxygen drastically reduced the efficiency of the reaction (as reflected in the turnover number in column 3), but had only a minor effect on the distribution of products between C_6F_5Ph and C_6F_5I. Added I_2 had a similar effect on the catalytic efficiency, but was more effective in diverting the course of the reaction from arylation to iodination (compare columns 4 and 5 in Table 2). The polyhalomethanes, CH_2I_2 and $BrCCl_3$ also inhibited the reaction (note the lower turnover number in entries 8 and 9). However, methylene iodide was more effective in changing the reaction pathway, as shown by a comparison of the relatively low yield of C_6F_5Br in entry 9 with the high yield of C_6F_5I in entry 8.

The effect of increasing concentrations of benzene in the heterogeneously catalysed reactions with KI was substantially the same as that for the homogeneously catalysed reaction promoted by NaI (*vide supra*). The comparison is illustrated in Fig. 1 in which the yields of C_6F_5Ph and C_6F_5I are plotted against the initial concentration of benzene. At high concentrations of benzene, the yield of pentafluorobiphenyl was nearly quantitative.

The highest yields of pentafluorophenylated arenes were obtained for those arenes substituted with electron-donating groups (see Table 3). Nitrobenzene and the chlorinated benzenes yielded reduced amounts of the biaryls, and increased amounts of pentafluoroiodobenzene were obtained. Anisole was arylated in high yield, but rather unselectively (entry 12).

Table 3 Pentafluorophenylation of aromatic compounds induced by potassium iodide (solid)[a]

Arene (ArH)	E_i/eV[b]	Products (%)[c] C_6F_5I	Products (%)[c] ArC_6F_5	Isomer distribution of ArC_6F_5
Benzene	9.23	4.1	84	—
Toluene	8.82	4.8	80	*o*:*m*:*p* 48:30:22
Isopropylbenzene	8.71	3.6	66	*o*:*m*:*p* 34:38:28
tert-Butylbenzene	8.65	5.0	74	*o*:*m*:*p* 31:36:33
o-Xylene	8.56	3.9	76	3:4 54:46
p-Xylene	8.44	4.1	75	—
Mesitylene	8.42	1.2	62	—
Chlorobenzene	9.10	11	74	*o*:*m*:*p* 41:29:30
p-Dichlorobenzene	8.94	46	45	
1,3.5-Trichlorobenzene	9.30	44	12	
Nitrobenzene	9.92	44	25	*o*:*m*:*p* 21:60:19
Anisole[d]	8.39	8.0	81	*o*:*m*:*p* 37:13:39
o-Dimethoxybenzene[e]	—	5.0	69	
p-Dimethoxybenzene[e]	7.90	2.2	74	
Naphthalene	8.12	4	81	α:β 62:38

[a] In acetonitrile at 24 °C, with 1.0 mmol $C_6F_5N_2^+BF_4^-$, 8.0 mmol arene and 0.2 mmol solid potassium iodide, unless otherwise noted. [b] Ionization potentials from ref. 44. [c] Yields based on diazonium salt. [d] At −40 °C. [e] At −48 °C.

Table 4 Iodide-promoted arylations with related diazonium cations[a]

Diazonium cation $Ar'N_2^+$	Arene (ArH)	Catalyst (mmol)	Products (%) Ar–Ar′	Products (%) Ar′–I	Products (%) Ar′H
3,5-Difluoro-2,4,6-trichlorobenzenediazonium	Benzene	NaI (0.94)	0.2	86	12
3,5-Difluoro-2,4,6-trichlorobenzenediazonium	Naphthalene	NaI (0.56)	12	45	2.1
3,5-Difluoro-2,4,6-trichlorobenzenediazonium	Naphthalene	KI[b]	66	45	8.3
4-Nitrobenzenediazonium	Benzene	KI[b]	18	79	0.5
3,5-Dinitrobenzenediazonium	Benzene	KI[b]	64	20	0.1

[a] In acetonitrile at 24 °C, using 1.0 mmol diazonium hexafluorophosphate salt and 3.0 mmol arene. [b] Not quantified (insoluble).

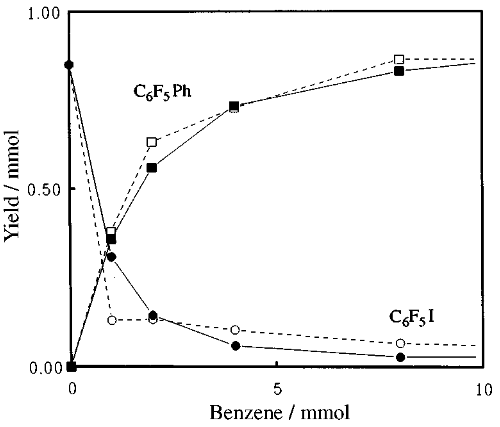


Fig. 1 Catalytic efficiency of iodide in the pentafluorophenylation of benzene with $C_6F_5N_2^+BF_4^-$ in acetonitrile by either added KI (heterogeneous) or NaI (homogeneous), showing the increasing yield of C_6F_5Ph (squares) at the expense of C_6F_5I (circles). (Filled data points are for NaI and open data points are for KI).

Moreover, *ortho*- and *para*-dimethoxybenzenes afforded the products of pentafluorophenylation in reasonable yields. The isomer distributions of the pentafluorophenylated arenes in Table 3 indicated that substitution was quite unselective. For example, toluene was arylated at all three positions (*ortho*, *meta* and *para*) with only a slight preference being shown for reaction at the *ortho* and *para* positions. Moreover, the arylation was only slightly sensitive to steric effects, as shown by the slightly lower yields of the *ortho*-arylated products of the reactions of cumene and *tert*-butylbenzene (entries 3 and 4). Nitrobenzene yielded a preponderance of the *meta*-pentafluorophenylated nitrobenzene, but, again, the preference was not strong. Naphthalene reacted preferentially at the α-position. The lower yields were accompanied by increased yields of pentafluoroiodobenzene, to indicate competition from the iodination reaction [eqn. (4)].

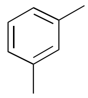
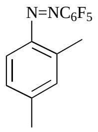
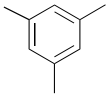
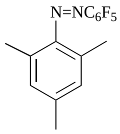
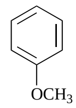
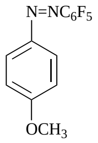
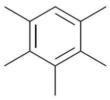
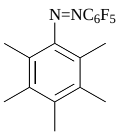
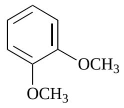
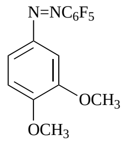
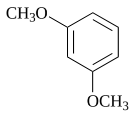
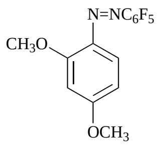
Iodide promotion of aromatic arylations with related diazonium salts

The applicability of iodide catalysis in aromatic arylation was also examined with other electrophilic benzenediazonium $Ar'N_2^+$ salts, including those with electron-withdrawing substituents such as the 3,5-difluoro-2,4,6-trichloro, 3,5-dinitro and 4-nitro derivatives. The results in Table 4 show that the yields of the biaryl (Ar′-Ph) products were generally lower than those obtained with the highly electrophilic pentafluoro analogue (Table 3). In each case, the deficit in the aryl moiety (Ar′) derived from the diazonium cation was primarily accounted for as the corresponding aryl iodide (Ar′I in column 5) together with smaller amounts of reduced arene (Ar′H in column 6).

Spontaneous (unpromoted) reactions of $C_6F_5N_2^+$ with aromatic donors leading to azo coupling

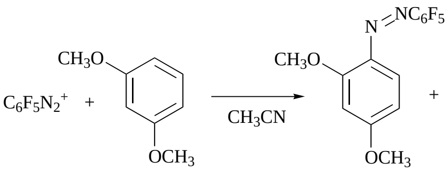
In the absence of added iodide salts, the mixture of pentafluorobenzenediazonium ($C_6F_5N_2^+$) salt and benzene (ArH) in acetonitrile was unchanged for prolonged periods (in the dark), and no nitrogen was evolved. Although similar solutions of $C_6F_5N_2^+$ with a more reactive arene (ArH) such as toluene also remained quiescent, those that contained *m*-xylene slowly turned red upon standing (14 d). Analysis of the residual reaction mixture indicated a 54% conversion of $C_6F_5N_2^+$, and the azo-coupling product,[21,22] $C_6F_5N{=}NC_6H_3(CH_3)_2$ was isolated in essentially quantitative yield (see Experimental section). The electron-rich mesitylene and pentamethylbenzene reacted progressively faster (1 h and <30 s, respectively), and the corresponding azo coupling products were similarly isolated in high yields, as listed in Table 5. Neither the arylated products C_6F_5-Ar nor reduced arene (C_6F_5H) could be observed.

Table 5 Azo coupling of arenes with pentafluorobenzenediazonium tetrafluoroborate[a]

Arene (ArH)	E_a/eV[b]	Reaction time	Product	Yield (%)[c]
	8.71	14 d		100[d]
	8.88	1 h		95
	8.88	1 h		92
	9.07	<30 s		98
		60 s		94
		<30 s[e]		91

[a] In acetonitrile at 24 °C with 1.01 mmol $C_6F_5N_2^+BF_4^+$ and 8.00 mmol arene, unless otherwise noted. [b] Proton affinity from ref. 45. [c] Based on diazonium salt. [d] 54% conversion of $C_6F_5N_2^+BF_4^-$. [e] at −40 °C.

The methoxylated arenes anisole, *o*- and *m*-dimethoxybenzenes reacted rapidly with $C_6F_5N_2^+$ in acetonitrile even at rather low temperatures (see Table 5) to afford the azo-coupling products in high (isolated) yields. In contrast to the iodide-promoted arylation of anisole in Table 3 (entry 12), only a single (*para*) isomer was formed in the azo-coupling (Table 5, entry 3). Similarly *o*- and *m*-dimethoxybenzene afforded only one diazene isomer, *e.g.* eqn. (6). It is particularly noteworthy that the isomeric *p*-dimethoxybenzene under the same (dark) conditions afforded high yields of the corresponding biaryl, *i.e.* eqn. (7). Moreover, the isomeric 1,4-/1,3-dimethoxybenzenes showed the same dichotomy between arylation–azo-coupling with 3,5-dinitrobenzenediazonium (Table 6, entries 2/3). Interestingly, 3-methylanisole afforded a mixture of biaryl–azo-coupling products with 3,5-dinitrobenzenediazonium (Table 6, entry 4). A similar mixture of arylated and azo-coupling products was obtained with mesitylene and 3,5-difluoro-2,4,6-trichlorobenzenediazonium (Table 6, entry 9). In the absence of iodide, naphthalene was unreactive to both pentafluoro- and difluorotrichloro-benzenediazonium in arylation as well as azo-coupling.



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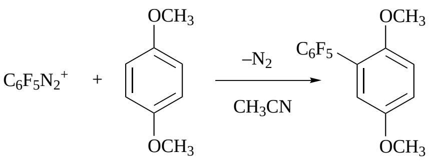

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Discussion

Pentafluorobenzenediazonium tetrafluoroborate is an effective reagent for the introduction of the C_6F_5 moiety into aromatic systems, and it represents a new and attractive alternative to previously developed perfluoroarylation procedures. Earlier attempts to obtain $C_6F_5N_2^+$ by the diazotization of pentafluoroaniline in aqueous media yielded only the triazene, decafluorodiazoaminobenzene $C_6F_5N{=}NNHC_6F_5$ (presumably from the rapid addition of $C_6F_5N_2^+$ onto the unreacted pentafluoroaniline).[17] On the other hand, we find that the gradual addition of pentafluoroaniline to a cooled (−30 °C) suspension of finely divided nitrosonium tetrafluoroborate in acetonitrile affords $C_6F_5N_2^+BF_4^-$ which can be isolated in 81% yield. The white crystalline salt is rapidly hydrolysed by water and must be stored under strictly anhydrous conditions.

The diazonium salt $C_6F_5N_2^+BF_4^-$ reacts readily with 1 equiv. of sodium iodide in acetonitrile to yield the iodination product, a reaction that is general for many types of diazonium cations,[23,24] irrespective of the medium. In the presence of aromatic substrates, however, less than 1 equiv. of added iodide initiates the pentafluorophenylation of the arene, *i.e.* eqn. (8).

Table 6 Competition between arylation and azo coupling of $Ar'N_2^+$ with electron-rich aromatic donors[a]

Aromatic donor	Substituted benzenediazonium	t/h	Conv (%)	Products (%)		
				Ar–Ar′	Ar′–H	Ar–N=N Ar′
1,4-Dimethoxybenzene	Pentafluoro	0.2	100	72	[b]	0
1,4-Dimethoxybenzene	3,5-Dinitro	8	88	71	8	0
1,3-Dimethoxybenzene	3,5-Dinitro	8	100	0	0	100
3-Methylanisole	3,5-Dinitro	8	100	18	[b]	78
m-Xylene	3,5-Dinitro	8	2	0	0	0
Naphthalene	Pentafluoro	8	3	0	0	0
p-Xylene	Pentafluoro	8	78	43	0	0
Naphthalene	3,5-Difluoro-2,4,6-trichloro	8	8	4	[b]	0
Mesitylene	3,5-Difluoro-2,4,6-trichloro	8	100	5	1	93

[a] In acetonitrile solutions containing 1.0 mmol diazonium salt ($Ar'N_2^+$) and 3.0 mmol arene (ArH) in the dark at 24 °C (without added iodide). [b] Not determined.

$$ArH + C_6F_5N_2^+ \xrightarrow[CH_3CN]{[I^-]} ArC_6F_5 + N_2 + H^+ \qquad (8)$$

The same transformation can be induced with the insoluble KI salt (heterogeneously), and the yields and isomer distributions of the products of the two reactions are essentially identical. Unlike the stoichiometrically equivalent Gomberg–Bachmann reactions,[4,5] the yields of the biaryls are high, and there are no significant side products. The primary difference can be attributed to the use of a nonaqueous solvent (which obviates the hydrolysis of the diazonium starting material[25]) and to the use of iodide as a promoter.

The iodide-catalysed pentafluorophenylation of arenes is particularly suitable for the synthesis of biphenyls in Table 3 and 4 with electron-donating groups on one ring and electron-withdrawing fluorine substituents on the other. ‘Push-pull’ π-conjugated systems of this type are promising materials for nonlinear optical (NLO) studies, owing to their large molecular hyperpolarizabilities.[26,27] Moreover, the synthetic system, $C_6F_5N_2^+$ plus arene, can also be utilized (in the absence of iodide catalysis) to synthesize ‘push-pull’ diazenes, in Table 5 and 6 which have been previously identified[28] as potentially powerful NLO materials.

Radical-chain mechanism for iodide catalysis of pentafluorophenylation

The role of iodide as the catalytic promoter of the pentafluorophenylation with $C_6F_5N_2^+$ points to the involvement of a chain reaction,[29] the free-radical character of which is supported by the effect of inhibitors[30,31] such as oxygen, iodine and the halomethanes in Table 2. The intermediacy of a relatively unselective, and thus highly reactive aryl radical ($C_6F_5\cdot$) is further suggested by the nearly statistical isomer distribution obtained from the reaction of substituted benzenoid substrates in Table 3. The pentafluorophenylation of aromatic substitutes (ArH) is a homolytic substitution,[32] as judged by the similarity of the isomer ratios obtained in related homolytic processes such as the photolysis of pentafluorophenyl iodide[16] and the oxidation of pentafluorophenylhydrazine,[15] which are known to generate free pentafluorophenyl radicals. On this basis, the radical-chain mechanism shown in Scheme 1 can be proposed.[19]

$$C_6F_5\cdot + ArH \longrightarrow C_6F_5\text{–}ArH\cdot \qquad (9)$$

$$C_6F_5\text{–}ArH\cdot + C_6F_5N_2^+ \xrightarrow[-N_2]{-H^+} C_6F_5\text{–}Ar + C_6F_5\cdot, \textit{etc.} \qquad (10)$$

Scheme 1

According to this formulation the well-known homolytic addition of $C_6F_5\cdot$ onto ArH [eqn. (9)][32] is followed by the rapid oxidation of the cyclohexadienylic (radical) adduct by the diazonium cation to regenerate the chain-carrying species ($C_6F_5\cdot$) in eqn. (10).[33] In addition, the initiation step derives from the known mechanism for iodination of diazonium cations with iodide.[34–36] Thus the redox initiation of $C_6F_5N_2^+$ with iodide proceeds *via* a two-step process involving the rate-limiting electron transfer (k_{ET})[37] followed by the rapid dediazoniation of the aryldiazenyl radical,[38] *i.e.* eqn. (11).

$$C_6F_5N_2^+ + I^- \xrightarrow{k_{ET}} C_6F_5N_2\cdot + I\cdot \xrightarrow{\text{fast}} C_6F_5\cdot + N_2 + I\cdot \qquad (11)$$

Electrophilic aromatic substitution with $C_6F_5N_2^+$

The direct (azo-coupling) reaction of $C_6F_5N_2^+$ with the various arenes to afford the push–pull diazenes, *i.e.* eqn. (12), in the

$$Ar_FN_2^+ + ArH \xrightarrow[CH_3CN]{} Ar_FN{=}NAr + H^+ \qquad (12)$$

absence of added iodide (Table 5) is tantamount to other well-known electrophilic aromatic substitutions that have been identified with cationic electrophiles.[39] As such, the reactivity trend in Table 5 (column 2) generally follows the electron-donor ability of the aromatic substitute, as measured by the ionization potential.[40,41] Although $C_6F_5N_2^+$ is among the best diazonium electrophiles, it still requires a relatively electron-rich aromatic donor such as mesitylene for efficient azo-coupling. In this regard, the mechanism of azo coupling with $C_6F_5N_2^+$ in Scheme 2 is somewhat comparable to electrophilic nitrosation with NO^+, as presented recently,[42] in which the multistep

$$Ar_FN_2^+ + ArH \overset{k_A}{\rightleftharpoons} Ar_FN{=}N\text{–}ArH^+ \qquad (13)$$

$$Ar_FN{=}N\text{–}ArH^+ \longrightarrow Ar_FN{=}NAr + H^+ \qquad (14)$$

Scheme 2

substitution occurs *via* the reversible formation of the Wheland intermediate.[22]

Comments on the competition between arylation and azo coupling

The ambivalent behavior of the electrophilic pentafluorobenzenediazonium cation toward aromatic donors (ArH) is manifested by the efficient dediazoniative arylations in Table 3 on one hand and the exclusive azo couplings in Table 5 on the other. The question thus arises as to how these are mechanistically related. Let us consider the reactivity of three aromatic donors, *viz.* mesitylene, anisole and dimethoxybenzene, which are subject to both dediazoniative arylation (Table 3) as well as azo coupling (Table 5). In addition to the obvious difference in stoichiometry [eqn. (6) and (7)], the two processes differ in the following ways.

(*i*) Azo coupling requires a relatively activated aromatic substrate. For example, *m*-xylene (entry 1 in Table 5) reacts slowly with $C_6F_5N_2^+$ over a course of 14 d for only partial conversion to the diazene; and substrates such as naphthalene and toluene are inert. By contrast, biaryl coupling could be effectively carried out on benzene and toluene, and even on deactivated arenes such as nitrobenzene.

(*ii*) Azo coupling yields only a single diazene isomer with anisole, *m*-xylene and *o*-dimethoxybenzene. By contrast, the biaryls are formed as mixtures of isomers, and the isomeric distributions are rather unselective.

(*iii*) Diazoniative arylation is rather insensitive to temperature, and it occurs relatively readily at even −40 °C. By contrast, azo coupling is severely retarded at these low temperatures.

(*iv*) Diazoniative arylation is subject to strong catalysis by added iodide salts, whereas azo coupling is singularly unaffected by the presence of such a reducing agent.

Most notably, facets (*iii*) and (*iv*) allow the reactivity of $C_6F_5N_2^+$ to be selectively controlled. For example, the arylations of ArH = mesitylene, anisole and *o*-dimethoxybenzene can be effected under an argon atmosphere to afford high yields of the mixed biaryls C_6F_5–Ar merely by adding catalytic amounts of iodide salt to the reaction mixture at <−40 °C. The alternative azo coupling of the same aromatic substrates is readily achieved by merely allowing the reaction mixture to equilibrate in air at room temperature (in the absence of iodide). Indeed, such a clean separation of arylation from azo coupling follows from the mechanisms of these processes, as presented in Scheme 1 and Scheme 2, respectively. Thus, the free-radical intermediates inherent to homolytic arylation (Scheme 1) are distinct from the cationic intermediates important to electrophilic azo coupling (Scheme 2). Furthermore, the relatively low activation energies of the homolytic steps[43] in the radical-chain sequence (Scheme 1) ensures that they are rapid relative to the sequential electrophilic steps (Scheme 2), especially at low temperatures. Having said this, we are particularly intrigued by the behaviour of mesitylene and 3-methylanisole in Table 6 (entries 4 and 9), in which arylation competes with azo coupling in the absence of an added iodide catalyst. The latter suggests that thermal initiation of arylation can proceed with these relatively electron-rich aromatic donors in a manner analogous to that presented in eqn. (11), *i.e.* eqn. (15), where

$$C_6F_5N_2^+ + ArH \xrightarrow{k_{ET}} C_6F_5N_2^\bullet + ArH^{+\bullet} \xrightarrow[-N_2]{\text{fast}} C_6F_5^\bullet, \textit{etc.} \qquad (15)$$

ArH = mesitylene, dimethoxybenzene, *etc.* Homolytic initiation by electron transfer [k_{ET} in eqn. (15)] also directly relates to the electron-donor properties of the aromatic substrate, as measured by the ionization potentials in Table 3 (column 2).[44] As such, the conversions to biaryls in Table 6 are the greatest with the most electron-rich donors such as *p*-dimethoxybenzene (entries 1 and 2). The question then arises as to why the isomeric *m*-dimethoxybenzene (with essentially the same ionization potential) is quantitatively converted to the product of azo coupling (entry 3). Clearly, the answer to this problem depends on the bimolecular rate of electron transfer [k_{ET} in eqn. (15)] relative to the rate of electrophilic addition [k_A in eqn. (13)]. Although the rate of electrophilic addition generally correlates with the ionization potential (E_i) of the aromatic donor,[40,41] perhaps a more appropriate measure is the proton affinity (E_a).[45] Indeed, Fig. 2 shows that the proton affinities of various aromatic hydrocarbons generally track the (negative) ionization potentials (The dashed line is arbitrarily drawn to connect the points for benzene and hexamethylbenzene at the extrema). Particularly noteworthy is the detailed comparison of points for mesitylene and *p*-xylene which have essentially the same value of E_i, but whose proton affinities are widely different; and a similar divergence pertains to the *o*-/*m*-xylene pair.

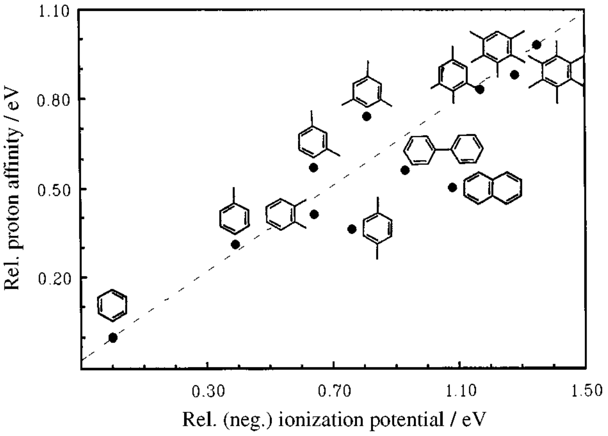

Fig. 2 Correlation of the relative (negative) ionization potentials and proton affinities for various aromatic hydrocarbons. The dashed line is arbitrarily drawn to connect benzene and hexamethylbenzene in order to emphasise the positive lie (above the line) of *m*-xylene and mesitylene relative to *p*-xylene.

On the basis of the comparisons, we deduce that *m*-dimethoxybenzene has a substantially greater proton affinity than the isomeric *p*-dimethoxybenzene.[46] Such a conclusion would thus account for their different behavior toward $C_6F_5N_2^+$ in arylation and azo coupling (Table 6). We hope that further comparative studies of electron transfer and electrophilic reactions of aromatic donors will shed additional light on this interesting dichotomy.

Summary and conclusions

Pentafluorophenylation of aromatic substrates is achieved by their iodide-promoted coupling with $C_6F_5N_2^+$ in acetonitrile solution. The reaction can be promoted either homogeneously (with NaI) or heterogeneously (with KI), and the yields and distributions of the isomeric products are essentially the same for both procedures. The catalysed reactions proceed rapidly at room temperature or below (−40 °C) and are applicable to arenes (ArH) with both activating and deactivating substituents. The role of the iodide catalyst and the lack of selectivity in the isomer distribution of arylation products points to a radical-chain process, with the pentafluorophenyl radical ($C_6F_5^\bullet$) as the active arylating reagent. Arylation (with the loss of N_2) is to be contrasted with the uncatalysed azo coupling of some of the same ArH substrates which yields the corresponding 1-pentafluorophenyl-2-aryl diazenes. Azo coupling of $C_6F_5N_2^+$ occurs with only the most electron-rich arenes, typical of other electrophilic aromatic substitutions. As such, arylation and azo coupling do not share reactive intermediates in common, and quite distinctive (competing) pathways are observed in the interaction of some of the $Ar'N_2^+$/ArH pairs in Table 6.

Experimental section

Materials

Nitrosonium tetrafluoroborate from a commercial source (Strem) was triturated with acetic anhydride (10%) in acetic acid. This was followed by filtration under an argon atmosphere, washing with dry dichloromethane and vacuum drying to provide a colorless free-flowing crystalline powder. The aromatic compounds were reagent grade commercial samples that were purified by distillation or recrystallization from alcohol followed by sublimation *in vacuo*: benzene, toluene, *o*- and *m*-xylenes (EM Science), isopropylbenzene, *tert*-butylbenzene, mesitylene, chlorobenzene, *p*-dichlorobenzene, anisole, *o*-, *m*- and *p*-dimethoxybenzenes (Aldrich), and naphthalene (Matheson). The haloarenes, 2-iodotoluene, 3-iodotoluene, 4-iodotoluene, 2-iodonitrobenzene, 3-iodonitrobenzene, *p*-diiodobenzene, 2-iodoisopropylbenzene, 4-iodoisopropylbenzene, 2,3-dimethyliodobenzene, 3,4-dimethyliodobenzene, 2,5-dimethyliodobenzene, 2-chloroiodobenzene, 3-chloroiodobenzene, 4-chloroiodobenzene, 1-iodonaphthalene, 2-iodonaphthalene, hexafluorobenzene and pentafluorobenzene were obtained from Aldrich and used as received. The aminoarenes, 4-nitroaniline, 4-(trifluoromethyl)aniline, ethyl 4-aminobenzoate, 4-aminobenzonitrile, 3,5-bis(trifluoromethyl)aniline and 2,3,4,5,6-pentafluoroaniline (Aldrich) were used without further purification. Sodium and potassium iodides (Aldrich) were dried *in vacuo* for 2 h at 150 °C and stored under an atmosphere of argon. Acetonitrile (OmniSolv, EM Science) and nitromethane (Spectrophotometric grade, Aldrich) were stored in Schlenk flasks under an argon atmosphere. Dichloromethane (HPLC grade, EM Science) was initially stirred with concentrated sulfuric acid; the separated layer was neutralized, dried over anhydrous Na_2CO_3 and finally distilled from anhydrous P_2O_5 under an argon atmosphere. Absolute ether, methanol, ethyl acetate, chloroform, carbon tetrachloride (Reagent grade, EM Science) and ethanol (USP grade, McCormick) were used without further purification. Deuterated solvents for the NMR experiments (Aldrich) were stored over molecular sieves prior to use. UV–VIS absorption spectra were measured on a Hewlett-Packard 8450A diode-array spectrometer with 2 cm^{-1} resolution. The ^1H, ^{13}C and ^{19}F NMR spectra were obtained on a General Electric QE-300 FT-NMR spectrometer with internal $(CH_3)_4Si$ or external CF_3COOH standards. *J* values are given in Hz. The infrared spectra were recorded on either a Nicolet 10DX, Nicolet 560 FTIR or a Mattson Genesis spectrophotometer. Gas chromatography was performed on a Hewlett-Packard 5790A series FID gas chromatography equipped with a 3392 integrator, the fused silica capillary column (WCOT, 0.25 mm i.d. × 12 m, coating CF-Sil-5-CB, Chrompak). All inert atmosphere manipulations were carried out in a Vacuum Atmospheres MO-41 dry box filled with high purity argon. GC–MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 quadrupole mass selective detector (EI, 70 eV).

Pentafluorobenzenediazonium tetrafluoroborate

An aqueous solution of fluoroboric acid (130 ml, 1 mol) was placed in a 1 l three-necked round-bottomed flask equipped with a mechanical stirrer and immersed in an ice bath. Acetic anhydride (595 ml, 6.28 mol) was added through a dropping funnel at such a rate as to keep the temperature of the reaction mixture below 10 °C. To this solution of HBF_4 in acetic acid and acetic anhydride, liquid N_2O_3 (76 g, 1 mol) was added at once to cause the immediate formation of a voluminous precipitate. The precipitate was filtered off under an argon atmosphere, washed with an acetic acid–dichloromethane (1:1 v/v, 3 × 50 ml) followed by dichloromethane (3 × 50 ml) and dried *in vacuo* overnight to yield a free-flowing white powder (69.4 g, 59%) having an IR spectrum identical to a purified commercial sample of nitrosonium tetrafluoroborate from Strem (*vide supra*). A 250 ml Schlenk flask equipped with a magnetic stirring bar and a rubber septum was charged with finely dispersed nitrosonium tetrafluoroborate (11.8 g, 0.10 mol) under argon. Dry acetonitrile (20 ml) was then injected with the aid of a hypodermic syringe and the flask was immersed in an acetonitrile–dry ice bath. After the solution had cooled to −30 °C, 2,3,4,5,6-pentafluoroaniline (18.3 g, 0.10 mol) in acetonitrile (20 ml) was added over 30 min. The yellow reaction mixture with an abundant heavy precipitate was stirred for 1 h at −30 °C, treated with dry dichloromethane (150 ml) and filtered. The white crystalline precipitate was washed with dry dichloromethane (3 × 50 ml), dissolved in a minimum volume of dry acetonitrile (*ca.* 60 ml) and reprecipitated by the slow addition of dichloromethane (200 ml) to yield shiny clear octahedra of the diazonium salt (22.9 g, 81%) mp 124–126 °C (decomp.); ν/cm^{-1}(Nujol) 2314, 1655, 1648, 1578, 1571, 1561, 1538, 1524, 1504, 1438, 1326, 1158, 1112, 1070, 1052, 1037, 1020, 1005, 980, 956, 943; $\delta_C(CD_3CN)$ 139.87 (dm, *J* 260), 149.08 (dm, *J* 280), 154.43 (dm, *J* 278); $\delta_F(CD_3CN)$ −40.09 (m, 1F), −43.70 (m, 2F), −71.82 (s, 4F), −73.02 (m, 2F). Anal. Calc. for $C_6BF_9N_2$: C, 25.57; H, 0.00; N, 9.95. Found: C, 25.37; H, 0.11; N, 9.90%. The diazonium salt was stable overnight at room temp. in an argon atmosphere, but further storage at 24 °C led to appreciable decomposition. Exposure of the diazonium salt to the atmospheric moisture caused yellow discoloration after 2–3 h and total degradation after 2 d.

3,5-Difluoro-2,4,6-trichlorobenzenediazonium hexafluorophosphate

Pentafluorobenzenediazonium tetrafluoroborate (9.15 g, 0.05 mol) was dissolved in nitromethane (50 ml) at −20 °C, and a stream of dry HCl was passed through the solution until it was saturated. The yellow residue was dissolved in concentrated hydrochloric acid (50 ml) and treated with 60% aqueous HPF_6 (8 ml, 0.06 mol) to form a yellowish precipitate, which was collected by filtration, dried *in vacuo* at room temp. and reprecipitated from acetonitrile with absolute ether three times to give yellow needles (12.8 g, 77%): $\delta_C(CD_3CN)$ 156.3 (dd, J_1 257, J_2 5), 131.1 (t, *J* 20), 125.1 (d, *J* 30), 121.2. Anal. Calc. for $C_6F_8Cl_3N_2P$: C, 18.51; H, 0.00; N, 7.20. Found: C, 18.55; H; 0.09; N, 7.23%.

Preparation of the other diazonium salts

A solution of the aniline (0.06 mol) in hot concentrated hydrochloric acid (50 ml, 0.6 mol) was prepared in a 250 ml beaker and cooled in a dry ice–ethanol bath until it began to freeze. A cold solution of $NaNO_2$ (5.6 g, 0.08 mol) in water (10 ml) was added, and the reaction mixture was stirred at 0 °C until clear. It was then treated with activated charcoal (0.5 g) and filtered through a Celite pad. The clear yellowish filtrate was treated 48% aqueous HBF_4 (13 ml) or 60% aqueous HPF_6 (11 ml) to give a colorless crystalline precipitate. The precipitate was filtered off under an argon atmosphere, washed with either aqueous HBF_4 or HPF_6 (3 × 10 ml), dried at 0.3 Torr and reprecipitated from acetonitrile with absolute ether.

3,5-Dinitrobenzenediazonium tetrafluoroborate. Colorless flakes (13.5 g, 80%) from 3,5-dinitroaniline. ν/cm^{-1}(KBr) 3102, 3090, 3079, 3042, 2319, 1616, 1605, 1557, 1352, 1105, 1082, 1035, 1024, 998, 925, 899; $\delta_H(CD_3CN)$ 9.619 (d, 2H, *J* 1.8), 9.506 (t, 1H, *J* 1.8); $\delta_C(CD_3CN)$ 150.1, 133.6, 131.6, 119.7. **CAUTION should be used in handling this material due to its potentially explosive nature.**

3-Nitrobenzenediazonium hexafluorophosphate. Colorless needles (13.0 g, 74%) from 3-nitroanilines. $\delta_H(CD_3CN)$ 9.256 (t, 1H, *J* 2.1), 8.955 (dd, 1H, J_1 9.3, J_2 2.1), 8.791 (dd, 1H, J_1 9.3, J_2 2.0), 8.172 (t, 1H, *J* 9.3).

4-Nitrobenzenediazonium hexafluorophosphate. Yellow needles (13.6 g, 78%) from 4-nitroaniline. $\delta_H(CD_3CN)$ 8.760 (m, 2H), 8.645 (m, 2H); $\delta_C(CD_3CN)$ 155.4, 135.4, 127.7, 121.4.

4-(Ethoxycarbonyl)benzenediazonium hexafluorophosphate. Colorless crystals (16.6 g, 86%) from ethyl 4-aminobenzoate. $\delta_H(CD_3CN)$ 8.575 (m, 2H), 8.415 (m, 2H), 4.420 (q, 2H, *J* 7.2), 1.380 (t, 3H, *J* 7.2); $\delta_C(CD_3CN)$ 164.2, 142.7, 133.8, 132.9, 119.2, 63.9, 14.3.

3,5-Bis(ethoxycarbonyl)benzenediazonium hexafluorophosphate. Colorless crystals (18.0 g, 76%) from diethyl 5-aminoisophthalate. $\delta_H(CD_3CN)$ 9.249 (d, 2H, *J* 1.2), 9.133 (t, 1H, *J* 1.2), 4.472 (q, 2H, *J* 7.1), 1.419 (t, 3H, *J* 7.1); $\delta_C(CD_3CN)$ 162.8, 142.0, 137.0, 135.6, 64.2, 14.3.

3,5-Bis(trifluoromethyl)benzenediazonium hexafluorophosphate. Colorless crystals (16.7 g, 72%) from 3,5-bis(trifluoromethyl)aniline. $\delta_H(CD_3CN)$ 9.07 (br s, 1H), 8.86 (br s, 2H); $\delta_C(CD_3CN)$ 136.9 (t, *J* 4.7), 135.3 (q, *J* 36), 134.6 (t, *J* 4.7), 12.3 (q, *J* 274), 116.9.

Pentafluoroarenes (ArC_6F_5)

A 50 ml Schlenk flask equipped with a magnetic stirring bar and a rubber septum was charged with the appropriate iodoarene (3.0 mmol) and absolute ether (10 ml) under an argon atmosphere. A solution of *n*-butyllithium in hexane (1.2 ml, 3.0 mmol) was injected with the aid of a syringe. After stirring at room temp. for 30 min, the mixture was transferred into a 50 ml Schlenk flask containing a magnetically stirred solution of hexafluorobenzene (1.116 g, 6.0 mmol) in diethyl ether (10 ml). The opaque solution was stirred for 30 min. Aqueous work-up and threefold extractions with diethyl ether afforded the pentafluorophenyl-substituted arene, ArC_6F_5, as a yellow crystalline residue that was further purified by sublimation *in vacuo* followed by recrystallization from ethanol.

2,3,4,5,6-Pentafluorobiphenyl,[47] **4′-methyl-2,3,4,5,6-pentafluorobiphenyl,**[16] **2′-methyl-2,3,4,5,6-pentafluorobiphenyl,**[16] **3′-methyl-2,3,4,5,6-pentafluorobiphenyl,**[16] **2′,3′-dimethyl-2,3,4,5,6-pentafluorobiphenyl,**[48] **3′,4′-dimethyl-2,3,4,5,6-pentafluorobiphenyl,**[48] **2′,5′-dimethyl-2,3,4,5,6-pentafluorobiphenyl,**[48] **2′-isopropyl-2,3,4,5,6-pentafluorobiphenyl,**[48] **4′-isopropyl-2,3,4,5, 6-pentafluorobiphenyl,**[48] **4′-*tert*-butyl-2,3,4,5,6-pentafluorobiphenyl,**[49] **2′,4′,6′-trimethyl-2,3,4,5,6-pentafluorobiphenyl,**[48] **3′-chloro-2,3,4,5,6-pentafluorobiphenyl,**[49] **4′-chloro-2,3,4,5,6-pentafluorobiphenyl,**[49] **2′,5′-dichloro-2,3,4,5,6-pentafluorobiphenyl,**[49] **1-pentafluorophenylnaphthalene,**[15] **2-pentafluorophenylnaphthalene,**[15] **2′-methoxy-2,3,4,5,6-pentafluorobiphenyl,**[49] **3′-methoxy-2,3,4,5,6-pentafluorobiphenyl,**[49] **4′-methoxy-2,3,4,5,6-pentafluorobiphenyl,**[50] **2′,3′-dimethoxy-2,3,4,5,6-pentafluorobiphenyl,**[49] **3′,4′-dimethoxy-2,3,4,5,6-pentafluorobiphenyl,**[49] **2′,5′-dimethoxy-2,3,4,5,6-pentafluorobiphenyl,**[49] **1,4-bis(pentafluorophenyl)benzene,**[15] **3′-nitro-2,3,4,5,6-pentafluorobiphenyl.**[51] The isomeric 1,2- and 1,3-bis(pentafluorophenyl)benzenes were not separately synthesized from *o*- and *m*-diiodobenzene. However, GC–MS analysis of the $(C_6F_5)_2C_6H_4$ fractions of the reaction mixture from $C_6F_5N_2^+$ and benzene (especially at low benzene concentrations) showed three separate peaks (with the same MS cracking patterns) in a roughly 1 : 2 : 0.5 (area) ratio for the *ortho, meta* and *para* isomers respectively. The last was identical to the authentic sample of 1,4-bis(pentafluorophenyl)benzene prepared above.

Aryl iodides. Pentafluoroiodobenzene, ethyl 4-iodobenzoate, diethyl 4-iodoisophthalate, and 4-iodobromobenzene obtained from Aldrich were used as received. 2,4,6-Trichloro-3,5-difluoroiodobenzene[49] and 3,5-dinitroiodobenzene[49] were synthesized by iododediazoniation of the corresponding diazonium tetrafluoroborate salts.

Pentafluorophenylation of aromatic compounds catalysed by iodide

In a typical procedure, a 50 ml Schlenk flask was charged with pentafluorobenzenediazonium tetrafluoroborate (282 mg, 1.00 mmol), equipped with a magnetic stirring bar and sealed with a rubber septum in a dry box. Acetonitrile (5.8 ml) and benzene (0.71 ml, 8 mmol) were injected *via* hypodermic syringes and a crystalline granule of potassium iodide (33 mg, 0.2 mmol) was added under a counter stream of argon. A vigorous gas evolution was observed immediately. The reaction mixture was stirred for 10 min and quenched with water (30 ml) containing a few drops of a starch solution, titrated with 0.020 M sodium thiosulfate and extracted with dichloromethane (3 × 25 ml). The combined dichloromethane extracts were washed with water (3 × 50 ml), dried over magnesium sulfate and subjected to GC analysis after the addition of *p*-xylene (100 µl, 86.4 mg) as an internal standard. Evaporation of the solvent and repeated sublimation (45 °C, 0.3 Torr) of the yellow crystalline residue afforded pure colorless 2,3,4,5,6-pentafluorobiphenyl (191 mg, 79.9%, purity 99.8% by GC). The same procedure was followed for the reactions with the other aromatic donors. The products were detected by GC and GC–MS analysis.[49] The arylation reactions of the arenes with pentafluorobenzenediazonium catalysed by sodium iodide in Tables 1 and 2 were taken from ref. 19.

Reaction of other diazonium salts induced by potassium iodide

In a typical procedure, a 50 ml Schlenk flask was charged with the diazonium salt (1.00 mmol), equipped with a magnetic stirring bar and sealed with a rubber septum in a dry box. Acetonitrile (5.8 ml) and arene (8 mmol) were injected *via* hypodermic syringes and a crystalline granule of potassium iodide (166 mg, 1.0 mmol) was added in the counter stream of argon. The reaction mixture was stirred for 1 h, quenched with water (30 ml) and worked up as usual and subjected to GC analysis after the addition of *p*-xylene (100 µl, 86.4 mg) as an internal standard. The data for each reaction follows in serial order as follows: **Diazonium salt:** *Arene*. Products (mmol).

3,5-Dinitrobenzenediazonium tetrafluoroborate: *Benzene*. *m*-Dinitrobenzene (0.001), 5-iodo-3,5-dinitrobenzene (0.195), 3,5-dinitrobiphenyl (0.730). Evaporation of the dichloromethane extracts followed by column chromatography on silica with CH_2Cl_2–hexane, recrystallization from ethanol and sublimation (0.3 Torr) afforded 3,5-dinitrobiphenyl (155 mg, 64%) as colorless flakes, mp 147–148 °C.

2,4,6-Trichloro-3,5-difluorobenzenediazonium hexafluorophosphate. *Benzene*. 2,4,6-Trichloro-3,5-difluorobenzene (0.083), 2,4,6-trichloro-3,5-difluoroiodobenzene (0.242), 2,4,6-trichloro-3,5-difluorobiphenyl (0.65). Evaporation of the dichloromethane extracts followed by column chromatography on silica with CH_2Cl_2–hexane, recrystallization from ethanol and sublimation (0.3 Torr) afforded 2,4,6-trichloro-3,5-difluorobiphenyl (153 mg, 52%) as colorless needles, mp 61–62 °C.

4-Nitrobenzenediazonium hexafluorophosphate. *Benzene.* Nitrobenzene (0.005), 4-iodonitrobenzene (0.788), 4-nitrobiphenyl (0.181).

Azo-coupling of pentafluorobenzenediazonium tetrafluoroborate with aromatics

In a typical procedure, a 100 ml two-neck Schlenk flask was charged with pentafluorobenzenediazonium tetrafluoroborate (282 mg, 1.00 mmol), equipped with a magnetic stirring bar, thermometer and a rubber septum in a dry box. Acetonitrile (5.8 ml) was injected with a hypodermic syringe, and the flask was carefully degassed three times and immersed in an acetonitrile–dry-ice bath. After the temperature of the reaction mixture had fallen to −40 °C, the solution of *m*-dimethoxybenzene (1.10 g, 8 mmol) in acetonitrile (2 ml) was slowly added with intense stirring. The fast transformation was manifested by the appearance of dark red coloration. The resulting dark red reaction mixture was quenched with water (30 ml) after 10 min and extracted with dichloromethane (3 × 25 ml). The combined dichloromethane extracts were washed with water (3 × 50 ml), dried over magnesium sulfate and subjected to GC analysis after the addition of *p*-xylene (100 µl, 86.4 mg) as an internal standard. Evaporation of the solvent and twofold recrystallization from methanol afforded pure 1-pentafluorophenyl-2-(2,4-dimethoxyphenyl)diazene[49] as red needles with metallic lustre (302 mg, 91%).

***m*-Xylene.** The reaction mixture was kept at 24 °C in the dark for 14 d. An aliquot (0.5 ml) of the resulting orange solution was withdrawn, incubated with *m*-dimethoxybenzene (138 mg, 1 mmol) for 10 min, quenched with water and extracted with dichloromethane (3 × 5 ml). A GC analysis of the combined extracts with *p*-xylene as an internal standard showed that 0.46 mmol of the diazonium salt remained unreacted. The rest of the original reaction mixture was poured into 20% hydrochloric acid (50 ml) and extracted with dichloromethane (3 × 20 ml). The combined dichloromethane extracts were washed with aqueous sodium hydrogencarbonate and water and evaporated to dryness. Twofold recrystallization of the orange residue thus obtained afforded pure 1-pentafluorophenyl-2-(2,4-dimethylphenyl)diazene[49] as light orange needles (110 mg, 68% based on the conversion of the diazonium salt).

Mesitylene. 1-Pentafluorophenyl-2-(2,4,6-trimethylphenyl)-diazene[52] was obtained as orange needles (297 mg, 95%).

Pentamethylbenzene. The reaction was complete within 30 s at room temp. A voluminous orange precipitate was collected and orange needles of 1-pentafluorophenyl-2-(2,3,4,5,6-pentamethylphenyl)diazene[49] were obtained after a twofold recrystallization (334 mg, 98%).

Anisole. The reaction was complete after 1 h at room temp., and 1-pentafluorophenyl-2-(4-methoxyphenyl)diazene[52] (278 mg, 92%) was obtained as orange scales.

1,2-Dimethoxybenzene. The coupling was complete within 1 min at room temp. The usual aqueous work up and recrystallization yielded 1-pentafluorophenyl-2-(3,4-dimethoxyphenyl)-diazene[49] as orange–brown needles (311 mg, 95%).

Thermal (dark) reactions of arenes with diazonium salts

In a typical procedure, a solution of the diazonium salt (1.00 mmol) and the arene (3.00 mmol) in acetonitrile (20 ml) was prepared in a Schlenk test tube and maintained under an argon atmosphere for 8 h in the dark. The reaction mixture quenched with water (10 ml) and extracted with chloroform (3 × 20 ml). The chloroform extracts were analysed by GC and GC–MS, and the products are listed in serial order: **Diazonium salt.** *Arene.* Products (mmol).

3,5-Dinitrobenzenediazonium tetrafluoroborate. p-*Dimethoxybenzene. m*-Dinitrobenzene (0.08), 2,5-dimethoxyphenylacetonitrile (0.03), 2,5-dimethoxy-3′,5′-dinitrobiphenyl (0.83). The amount of untreated diazonium salt was 0.10 mmol, 10%. m-*Dimethoxybenzene*. 1-(2,4-Dimethoxyphenyl)-2-(3,5-dinitrophenyl)diazene (1.00), was detected. Removal of the solvent from the combined chloroform extracts left an orange crystalline residue. 1-(2,4-dimethoxyphenyl)-2-(3,5-dinitrophenyl)-diazene[49] was isolated as orange needles (327 mg, 98%). 3-*Methylanisole*. 2-Methoxy-4-methyl-3′,5′-dinitrobiphenyl (0.09); 2-methyl-4-methoxy-3′,5′-dinitrobiphenyl (0.09); 1-(3,5-dinitrophenyl)-2-(2-methyl-4-methoxyphenyl)diazene (0.78). Removal of the solvent from the combined chloroform extracts left an orange solid residue, from which 1-(3,5-dinitrophenyl)-2-(2-methyl-4-methoxyphenyl)diazene[49] was isolated as orange needles (198 mg, 63%). *m*-Xylene. No products were detected. The amount of unreacted diazonium salt was 0.98 mmol, 98%.

Pentafluorobenzenediazonium tetrafluoroborate. *Naphthalene* (384 mg, 3.00 mmol) in acetonitrile (20 ml) prepared in a Schlenk test tube was kept in the dark at room temp. for 8 h. The final reaction mixture was treated with *m*-dimethoxybenzene (150 mg, 1.09 mmol) and kept for 10 min at room temp. No products other than 1-(2,4-dimethoxyphenyl)-2-pentafluorophenyldiazene (0.97 mmol, 97%) were detected. p-*Dimethoxybenzene*. 2,5-Dimethoxyphenylacetonitrile (0.03), 2′,5′-dimethoxy-2,3,4,5,6-pentafluorobiphenyl (0.72). No unreacted diazonium salt was found. p-*Xylene.* After 48 h the reaction mixture was treated with *m*-dimethoxybenzene (138 mg, 1.00 mmol) and kept for 10 min at room temp. 1-(2,4-Dimethoxyphenyl)-2-pentafluorophenyldiazene (0.12 mmol), 2′,5′-dimethyl-2,3,4,5,6-pentafluorobiphenyl (0.43). No peaks with *m/z* 300 in the GC–MS of the reaction mixture (as expected for the product of azo-coupling) were observed. The amount of unreacted diazonium salt was 0.12 mmol.

2,4,6-Trichloro-3,5-difluorobenzenediazonium hexafluorophosphate. *Naphthalene*. 2,4,6-Trichloro-3,5-difluorobenzene (0.02), 1-(2,4,6-trichloro-3,5-difluorophenyl)naphthalene (0.03), 2-(2,4,6-trichloro-3,5-difluorophenyl)naphthalene (0.01). The amount of unreacted diazonium salt was 0.92 mmol, 92%. *Mesitylene.* 2,4,6-Trichloro-3,5-difluorobenzene (0.01); 2,4,6-trichloro-3,5-difluoro-2′,4′,6′-trimethylbiphenyl (0.05), 1-(2,4,6-trichloro-3,5-difluorophenyl)-2-(2,4,6-trimethylphenyl)diazene (0.93 mmol). Removal of the solvent from the combined chloroform extracts left orange-brown crystals of 1-(2,4,6-trichloro-3,5-difluorophenyl)-2-(2,4,6-trimethylphenyl)diazene.[49] p-*Dimethoxybenzene.* The reaction mixture was quenched and worked up after 30 min. 2,4,6-Trichloro-3,5-difluorobenzene (0.27), 2,5-dimethoxyphenylacetonitrile (0.05), 2′,5′-dimethoxy-2,4,6-trichloro-3,5-difluorobiphenyl (0.67).[49] No unreacted diazonium salt was found. Solvent removal yielded a colorless crystalline residue. 2′,5′-Dimethoxy-2,4,6-trichloro-3,5-difluorobiphenyl[49] was isolated from the residue after passing it through a column of silica with diethyl ether–hexane, fractional vacuum sublimation and recrystallization from methanol as colorless needles (114 mg, 32%).

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