# Thermal (Iodide) and Photoinduced Electron-Transfer Catalysis in Biaryl Synthesis *via* Aromatic Arylations with Diazonium Salts

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**Abstract:** The dediazoniative arylation of various aromatic hydrocarbons (Ar′H) with diazonium salts (ArN$_2^+$) in acetonitrile can be readily effected to biaryls (Ar-Ar′) in high yields, simply by the addition of small (catalytic) amounts of sodium iodide. [In the absence of Ar′H, the competitive iodination to ArI is nearly quantitative.] Iodide catalysis of biaryl formation is efficiently mediated by aryl radicals (Ar•) that participate in an efficient homolytic chain process in which ArN$_2^+$ acts as a 1-electron oxidant. The complex kinetics of such an *electron-transfer chain* or ETC process (Scheme 1) is quantitatively verified by computer simulation of the Ar′H-dependent (a) competition between arylation *vs* iodination and (b) catalytic efficiency of iodide, using the GEAR algorithms. ETC catalysis also pertains to the alternative photochemical procedure for arylation (in the absence of iodide), in which the deliberate irradiation of the charge-transfer band of the precursor complex [ArN$_2^+$, Ar′H] initiates the same homolytic chain arylation. The latter underscores the mechanistic generality of the ETC formulation for various types of catalytic dediazoniations of aromatic diazonium salts.

## Introduction

Aromatic diazonium cations (ArN$_2^+$) represent activated aryl group (synthons) owing to the relatively facile loss of dinitrogen.[1] Despite their widespread use, it is often not clear as to whether an electrophilic (*via* Ar$^+$) or a homolytic (*via* Ar•) process is involved for dinitrogen loss in even the conceptually simple replacement by various nucleophiles (X$^-$), *i.e.*

$$\text{ArN}_2^+ + \text{X}^- \xrightarrow{-\text{N}_2} \text{ArX} \qquad (1)$$

where X$^-$ = halide, cyanide, sulfide, hydroxide, etc.[2,3] The mechanistic ambiguity is further exacerbated by the efficient catalysis of eq 1 by (trace) metal species, such as in the Sandmeyer, Gatterman, Meerwein, and related reactions.[4,5] When weak (uncharged) aromatic nucleophiles (*i.e.* X$^-$ = Ar′H) are employed, the arylation reactions leading to biaryls, *i.e.*

$$\text{ArN}_2^+ + \text{Ar′H} \xrightarrow{-\text{N}_2} \text{Ar−Ar′} + \text{H}^+ \qquad (2)$$
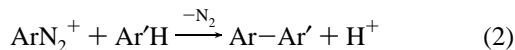
are commonly inefficient owing to competition from myriad side reactions leading to reduced arene (ArH), diazenes (ArN=NAr′), triazenes (ArN=NNHAr′), and other colored byproducts.[6] As such, we view the arylation reaction as an opportunity to utilize a mechanistic investigation to develop optimum procedures for the efficient dediazoniation of aromatic diazonium cations according to eq 2.

Conventionally, the synthetic transformation in eq 2 is realized in aqueous media with aromatic diazonium cations generated *in situ* with use of the Gomberg−Bachmann procedures (and its intramolecular analogue, the Pschorr synthesis) that are promoted by the addition of base.[7,8] Since a wide variety of other (undesired) reactions of ArN$_2^+$ are known to be induced by basic water,[9] we focussed in this study on the alternative use of nonaqueous solvents and highly electrophilic diazonium cations that are separately prepared in pure (crystalline) form. Accordingly, we report on how the pentafluorobenzenediazonium salt (C$_6$F$_5$N$_2^+$BF$_4^-$ (**I**)) can be employed in the high-yield synthesis of various "push-pull" biaryls (C$_6$F$_5$-Ar′) of potential use in nonlinear laser applications and liquid-crystal displays.[10] For comparative purposes, some additional studies were also carried out with the novel trichloro derivative[11] **II** that is readily available from **I** by mild treatment with hydrogen chloride.

Particularly relevant to aromatic diazonium salts in nonaqueous solvents is the spontaneous appearance of bright colorations

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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(2) Galli, C. *Chem. Rev.* **1988**, *88*, 765.

(3) (a) Lewin, A. H.; Cohen, T. *J. Org. Chem.* **1967**, *32*, 3844. (b) Lewis, E. S.; Johnson, M. D. *J. Am. Chem. Soc.* **1959**, *81*, 2070. (c) Waters, W. A. *J. Chem. Soc.* **1942**, 266.

(4) (a) Cowdrey, W. A.; Davies, D. S. *Chem. Soc. Quart. Rev.* **1952**, *6*, 358. (b) Cohen, T.; Lewarchik, R. J.; Tarino, J. Z. *J. Am. Chem. Soc.* **1974**, *96*, 7753.

(5) (a) Rondestvedt, C. S. *Org. React.* **1960**, *11*, 189. (b) Kochi, J. K. *J. Am. Chem. Soc.* **1957**, *79*, 2942.
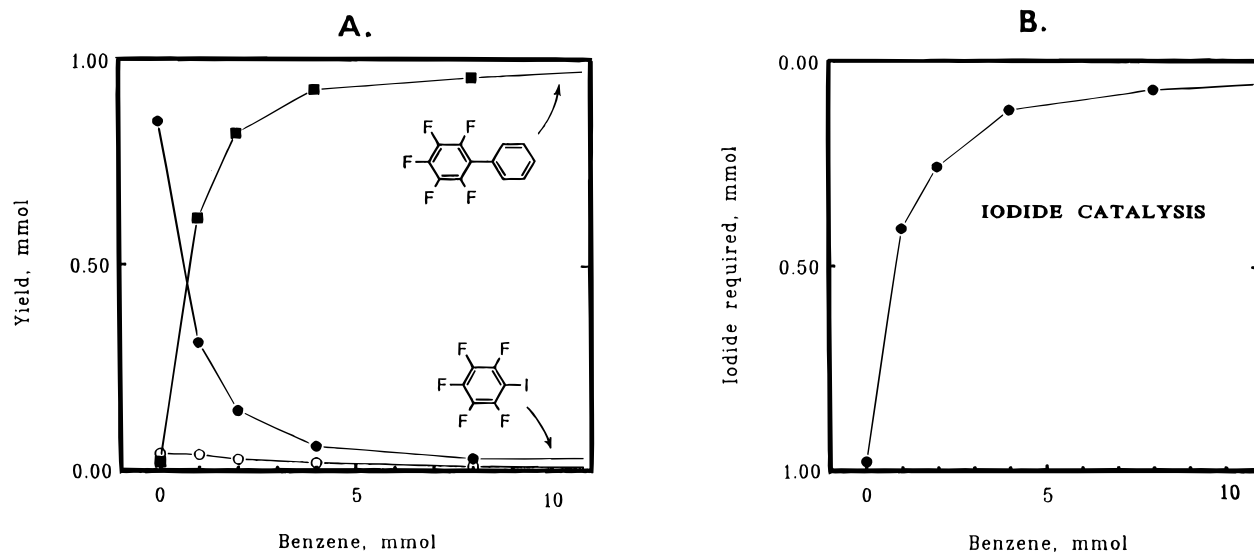
(6) (a) Beadle, J. R.; Korzeniowski, S. H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* **1984**, *49*, 1594. (b) Rüchardt, C.; Merz, E.; Freudenberg, B.; Opgenorth, H.-J.; Tan, C. C.; Werner, R. *Essays on Free-Radical Chemistry*; Special Publication No. 24, Norman, R. O. C., Ed.; Chemical Society London: London, 1970; p 51ff and references therein.

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(8) (a) Pschorr, R. *Chem. Ber.* **1896**, *29*, 496. (b) Abramovitch, R. A. *Adv. Free Radical Chem.* **1966**, *2*, 4787.

(9) Dreher, E.; Niederer, P.; Schwarz, W.; Zollinger, H. *Helv. Chim Acta* **1981**, *64*, 488.

(10) See, *e.g.*: (a) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for Nonlinear Optics: Chemical Perspectives*; American Chemical Society: Washington, DC, 1991. (b) Okada, M.; Shiuchi, K.; Funada, F.; Numada, H.; Ichinose, H.; Sasake, K.; Plach, H.; Poetsch, E. German Patent 4,426,904; 4,426,905 [*Chem. Abstr. 122*, 27861, 278762].

(11) (a) Treatment of **I** with excess HCl in nitromethane at 25 °C affords crystalline 2,4,6-trichloro-3,5-difluorobenzenediazonium hexafluorophosphate in 80% yield. (b) Bockman, T. M.; Kosynkin, D.; Kochi, J. K. To be submitted for publication.

**Figure 1.** (A) Reaction profile for iodide catalysis leading to arylation, iodination, and reduction of pentafluorobenzenediazonium with various amounts of benzene in acetonitrile at 24 °C: (■) $C_6F_5$-Ph + 2$(C_6F_5)_2C_6H_4$, (●) $C_6F_5I$, and (○) $C_6F_5H$. (B) Iodide requirements for the full conversion of $C_6F_5N_2^+$ (see text).

when various aromatic hydrocarbons are added.[12] The progressive bathochromic (red) shifts of the colors that follow the decreasing trend in the ionization potentials are in accord with the Mulliken formulation of intermolecular charge-transfer complexes,[13] *i.e.*

$$ArN_2^+ + Ar'H \rightleftharpoons [ArN_2^+, Ar'H] \qquad (3)$$
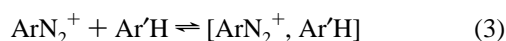
Thus, the critical part of any mechanistic investigation of eq 2 must specifically address the role of these colored charge-transfer complexes as intermediates in arylations with aromatic diazonium salts.[14]

**Results**

The dediazoniation of the pentafluorobenzenediazonium cation was examined in anhydrous acetonitrile solutions under two widely different conditions. In the *thermal* method, a small (catalytic) amount of an iodide salt was added to the colored mixture of $C_6F_5N_2^+$ and the aromatic hydrocarbon (Ar'H) at room temperature. In the alternative *photochemical* method, similar (diazonium) mixtures with Ar'H were initially cooled to low temperatures (at which any thermal process was inhibited), and the colored solutions were then deliberately irradiated with visible light. In order to avoid contamination by air, all reactions were carried out under an argon atmosphere as follows.

**I. Pentafluorophenylation of Benzene with $C_6F_5N_2^+BF_4^-$ and Catalytic Amounts of Sodium Iodide.** The diazonium group in the pentafluorobenzenediazonium cation could be readily replaced with an iodo substituent.[15] Thus, the addition of 1 equiv of sodium iodide to a colorless solution of $C_6F_5N_2^+BF_4^-$ in acetonitrile at 24 °C (in the dark) immediately led to the evolution of 1 equiv of dinitrogen. Workup of the

(12) Kampar, V. E.; Kokars, V. R.; Neiland, O. Ya. *Zh. Obs. Khim. (Engl. Transl.)* **1977**, *47*, 858. See also: Koller, S.; Zollinger, H. *Helv. Chim. Acta* **1970**, *53*, 78.

(13) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. See also: Foster, R. F. *Organic Charge-Transfer Complexes*; Academic: New York, 1965. Briegleb, G. *Elektronen Donator-Acceptor Komplexe*; Springer: Berlin, 1961. (b) This charge-transfer formulation is now confirmed by the isolation and X-ray crystallography of various types of intermolecular complexes in eq 3 (to be submitted for publication).

(14) Compare: Kochi, J. K. *Pure. Appl. Chem.* **1991**, *63*, 255.

(15) (a) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Org. Chem.* **1987**, *52*, 2768. (b) Carey, J. G.; Jones, G.; Millar, I. T. *Chem. Ind.* **1959**, 1018. (c) Carey, J. G.; Millar, I. T. *Chem. Ind.* **1960**, 97.

reaction mixture afforded the iodination product pentafluoroiodobenzene in 85% yield, *i.e.*

$$C_6F_5N_2^+ + I^- \rightarrow C_6F_5I + N_2 \qquad (4)$$
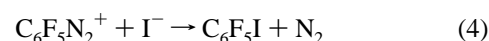
However, in the presence of benzene, the reaction took an entirely different course. For example, the addition of very small amounts of either sodium or potassium iodide to a yellow solution of $C_6F_5N_2^+BF_4^-$ and benzene led to the complete reaction of the diazonium salt and the evolution of a full equivalent of $N_2$. The major product of the reaction was 2,3,4,5,6-pentafluorobiphenyl, which was formed in high yield, together with minor amounts of pentafluoroiodobenzene and the bis-arylated derivative.[16] The reaction was thus designated as the *thermal arylation* of benzene catalyzed by iodide, *i.e.*

$$C_6F_5N_2^+ + PhH \xrightarrow{[I^-]} C_6F_5\text{-}Ph + N_2 + H^+ \qquad (5)$$
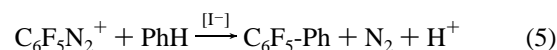
The iodinated product ($C_6F_5I$) together with a small amount of $I_2$ accounted for all of the added iodide salt. In the absence of sodium iodide, the colored acetonitrile solution of $C_6F_5N_2^+BF_4^-$ and benzene remained unchanged for prolonged periods, and no evolution of dinitrogen was evident (provided even adventitious room light was excluded).

**A. Effect of Benzene Concentration.** 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 as the catalyst owing to its ready solubility in anhydrous acetonitrile. Figure 1 shows that the progressive increase in the initial concentration of benzene resulted in a corresponding increase in the yields of the arylation product ($C_6F_5$-Ph) at the expense of the iodination product ($C_6F_5I$). Concomitant with these trends, the amount of NaI needed to effect complete reaction decreased (see Figure 1B). In the presence of a large excess of benzene, less than 1 mol % of NaI was sufficient to promote the complete arylation (Table 1), and the yield of pentafluorobiphenyl was close to quantitative. The overall trend is presented in column 4 of Table 1, in which the turnover number (*i.e.* T.N. = extent of reaction induced by each equivalent of NaI) is tabulated.

(16) The mixture consisted of *ortho, meta,* and *para* isomers of bis-(pentafluorophenyl)benzene.[11b]

**Table 1.**   Pentafluorophenylation of Benzene Induced by Sodium Iodide[a]

| | | | | products (%)[d] | | | | |
|---|---|---|---|---|---|---|---|---|
| PhH (M) | NaI[b] (mmol) | additive (mmol) | T. N.[c] | $C_6F_5Ph$ | $C_6F_5I$ | $C_6F_5H$ | Bis[e] | $I_2$[f] |
| 0 | 0.98 | 0 | 1.0 | 0 | 85 | 4 | 0 | 0.031 |
| 0.17 | 0.41 | 0 | 2.8 | 36 | 31 | 4 | 13 | 0.075 |
| 0.34 | 0.26 | 0 | 6.9 | 56 | 14 | 3 | 14 | 0.039 |
| 0.67 | 0.12 | 0 | 16 | 73 | 6 | 2 | 10 | 0.028 |
| 1.38 | 0.07 | 0 | 31 | 83 | 3 | 0.9 | 6 | 0.019 |
| 5.52 | 0.02 | 0 | 74 | 93 | 0.6 | 0.3 | 3 | 0.003 |
| 11.0 | 0.01 | 0 | 85 | 94 | 0.5 | 0 | 2 | <0.001 |
| 1.38 | 0.24 | $O_2$ (0.2) | 4.2 | 74 | 5 | | | 0.062 |
| 1.38 | 0.47 | $O_2$ (0.8) | 2.1 | 67 | 10 | | | 0.15 |
| 1.38 | 0.22 | $I_2$ (0.1) | 4.5 | 76 | 11 | | | |
| 1.38 | 0.44 | $I_2$ (1.0) | 2.3 | 55 | 38 | | | |
| 1.38 | 0.83 | $CH_2I_2$ (8.0) | 1.2 | 19 | 70 | | | 0.050 |
| 1.38 | 0.24 | $CBrCl_3$ (8.0) | 4.2 | 67 | 6[g] | | | 0.048 |

[a] In acetonitrile (6 mL) containing 1.0 mmol $C_6F_5N_2^+BF_4^-$ and benzene at 24 °C. [b] Added in 0.01−0.05-mmol aliquots. [c] Turnover number defined as mmol of $N_2$ evolved per mmol of NaI for the initial phase of reaction. [d] Based on $ArN_2^+$, unless noted otherwise. [e] Isomeric mixture of bis-substituted benzenes $(C_6F_5)_2C_6H_4$, see Bockman et al.[11b] [f] In mmol, based on iodometry. [g] In addition, 5 mmol $C_6F_5Br$ formed.

**Table 2.**   Iodide Catalysis in the Thermal Arylations of Various Arenes with $C_6F_5N_2^+BF_4^-$ [a]

| arene Ar′H | NaI[b] (mmol) | T.N.[b] | Products (%)[b] | | isomer distribution |
|---|---|---|---|---|---|
| | | | $C_6F_5$-Ar′ | $C_6F_5I$ | |
| toluene | 0.08 | 12.5 | 78 | 2.1 | *o:m:p* 49:27:24 |
| isopropylbenzene | 0.17 | 5.9 | 64 | 3.6 | 33:37:30 |
| *tert*-butylbenzene | 0.17 | 5.9 | 73 | 5.0 | 32:40:28 |
| *o*-xylene | 0.19 | 5.3 | 76 | 3.2 | 3:4   53:47 |
| *p*-xylene | 0.14 | 7.1 | 79 | 3.1 | |
| chlorobenzene | 0.22 | 4.5 | 64 | 10 | *o:m:p* 43:28:29 |
| *p*-dichlorobenzene | 0.55 | 1.8 | 43 | 31 | |
| nitrobenzene | 0.62 | 1.6 | 24 | 37 | *o:m:p* 23:61:16 |
| naphthalene | 0.16 | 17 | 76 | 2.1 | α:β 64:36 |

[a] In acetonitrile (3 mL) containing 1.0 mmol of $C_6F_5N_2^+BF_4^-$ and 8.0 mmol of arene at 24 °C. [b] Turnover number; see Table 1.

**Table 3.**   Other (Nonionic) Reducing Agents as Catalysts for Pentafluorophenylation[a]

| catalyst (mmol) | T.N.[b] | yield of $C_6F_5Ph$ (%)[c] |
|---|---|---|
| iodide (Na$^+$) (0.07) | 31 | 83 |
| iodide (K$^+$) (0.20) | *d* | 84 |
| ferrocene (0.11) | 9.0 | 83 |
| *p*-dimethoxybenzene (0.05) | 6.7 | 85 |
| zinc (granule) (0.40) | 1.3 | 43 |
| | 2.5[e] | 56 |

[a] In acetonitrile solution containing $C_6F_5N_2^+BF_4^-$ (1 mmol) and benzene (8 mmol) at 24 °C, unless noted otherwise. [b] Turnover number; defined as mmol of $N_2$ evolved per mmol of catalyst added. [c] Isolated yield of 2,3,4,5,6-pentafluorobiphenyl. [d] Indeterminate (owing to insolubility). [e] With 64 mmol of benzene.

**B.   Retardation of Iodide Catalysis.**  The effect of additives on the arylation reaction was explored by the addition of either dioxygen, diiodine, or polyhalomethane. The results in Table 1 show that $O_2$ drastically reduced the efficiency of the reaction (as reflected in the turnover number in column 4), but had only a minor effect on the distribution of products between $C_6F_5$-Ph and $C_6F_5I$. Added $I_2$ had a similar deleterious effect on the catalytic efficiency, but was more effective in diverting the course of the reaction from arylation to iodination (compare columns 5 and 6 in Table 1). The polyhalomethanes, $CH_2I_2$ and $BrCCl_3$, also retarded the reaction (note the lower turnover number in entries 12 and 13). However, diiodomethane was more effective in altering the reaction pathway, as shown by a comparison of the relatively low yield of $C_6F_5Br$ in entry 13 with the high yield of $C_6F_5I$ in entry 12.

**II.   Iodide-Promoted Pentafluorophenylation of Aromatic Donors.**  The arylations of various aromatic substrates (Ar′H) with $C_6F_5N_2^+BF_4^-$ were also carried out under the conditions that pertained to benzene. High yields of pentafluorophenylation products ($C_6F_5$-Ar′) could be obtained by the addition of small amounts (10−20 mol %) of sodium iodide to an acetonitrile solution of $C_6F_5N_2^+BF_4^-$ and the aromatic compound under an argon atmosphere. The isomer distributions of the pentafluorophenylated arenes in Table 2 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 also rather insensitive to steric hindrance, as shown by the slightly lower yields of the *ortho*-arylated products of the reactions of cumene and *tert*-butylbenzene (entries 2 and 3). Nitrobenzene yielded a preponderance of the *m*-pentafluorophenylated nitrobenzene, but again, the selectivity was poor. Naphthalene reacted preferentially at the α-position.

Catalysis by iodide was most effective for the arenes substituted with electron-donating alkyl groups. For chlorobenzene, dichlorobenzene, and nitrobenzene, on the other hand, the turnover number was diminished, and the yield of the pentafluorophenylated arene was significantly decreased. The lower yields were accompanied by increased yields of pentafluoroiodobenzene, to indicate competition from the iodination reaction (eq 4).

**III.   Catalysis of Pentafluorophenylation by (Nonionic) Reducing Agents.**  The catalytic role of iodide (by the use of NaI in Tables 1 and 2) was underscored by the equivalent promotion of the pentafluorophenylation by potassium iodide which was quite insoluble in acetonitrile. Effective catalysis of the pentafluorophenylation was also achieved with other nonionic reducing agents, such as ferrocene ($E_{ox}^0 = 0.40$ V vs SCE)[17] and a heterogeneous suspension of a zinc granule, as indicated by the turnover numbers listed in Table 3 (column 3). More striking was the catalytic role of the aromatic donor *p*-dimethoxybenzene ($E_{ox}^0 = 1.3$ V vs SCE).[18] Thus, a pale yellow solution of $C_6F_5N_2^+$ and benzene in acetonitrile was quiescent for rather prolonged periods in the dark. When a catalytic amount (0.05 mmol) of *p*-dimethoxybenzene was added, the solution immediately turned distinctly pink and began to slowly evolve dinitrogen and finally produced pentafluorobiphenyl (85% yield). The fate of *p*-dimethoxybenzene was traced to the arylated product pentafluorophenyl-1,4-dimethoxybenzene and the dimeric 2,2′,5,5′-tetramethoxybiphenyl.[19]

**IV.   Spontaneous Formation of Charge-Transfer Complexes of Pentafluorobenzenediazonium and Aromatic Compounds.**  When pentafluorobenzenediazonium fluoroborate

(17) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.
(18) Rathore, R.; Bosch, E.; Kochi, J. K. *Tetrahedron* **1994**, *23*, 6727.
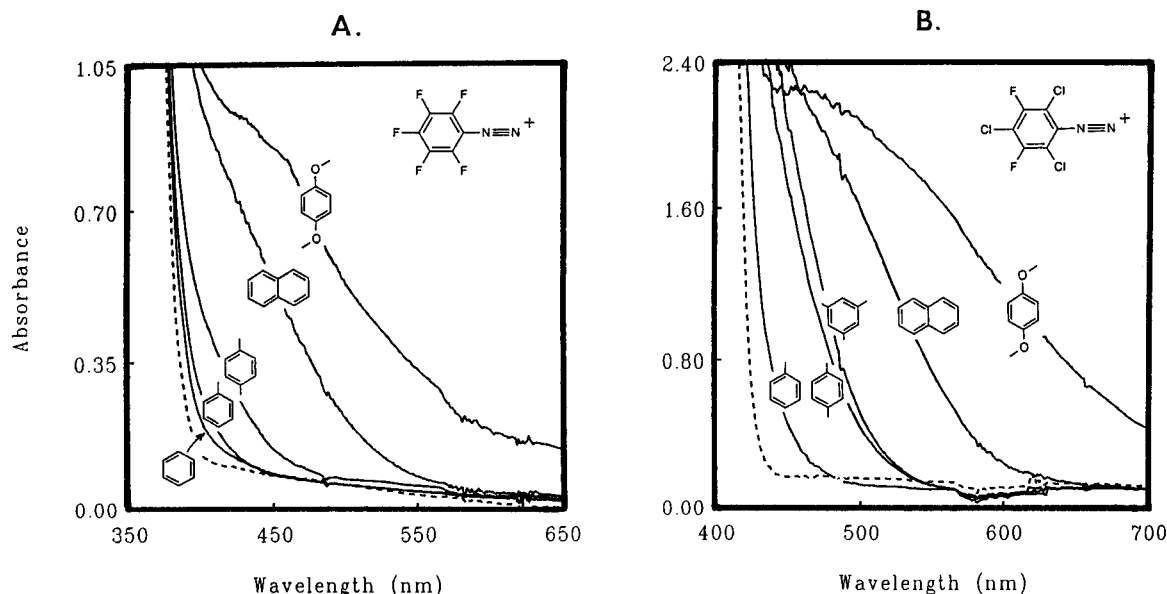(19) Margaretha, P.; Tissot, P. *Org. Synth.* **1977**, *57*, 92.

**Figure 2.** Charge-transfer spectra of the intermolecular complexes of various arenes (as indicated) with (A) $C_6F_5N_2^+$ and (B) $C_6F_2Cl_3N_2^+$ in acetonitrile. The dashed curves are the absorption tails of the uncomplexed diazonium cations.

**Table 4.** Charge-Transfer Absorption of Aromatic Diazonium Complexes with Various Arenes[a]

| arene (Ar′H) | IP[b] (eV) | $C_6F_5N_2^+$ (nm)[c] | | $C_6F_2Cl_3N_2^+$ (nm)[c] | |
|---|---|---|---|---|---|
| | | $\lambda_{0.1}$ | $\lambda_{0.5}$ | $\lambda_{0.5}$ | $\lambda_{1.0}$ |
| benzene | 9.08 | 391 | d | | |
| toluene | 8.81 | 400 | 381 | 448 | 434 |
| p-xylene | 8.84 | 447 | 388 | 496 | 473 |
| mesitylene | 8.40 | | | 501 | 479 |
| naphthalene | 8.12 | 510 | 450 | 568 | 533 |
| p-dimethoxybenzene | 7.90 | 579 | 490 | 668 | 620 |

[a] In acetonitrile containing 0.02 M $C_6F_5N_2^+BF_4^-$ or 0.05 M $C_6F_2Cl_3N_2^+BF_4^-$ and 0.4 M Ar′H at $-30$ °C. [b] Ionization potential from ref 20. [c] $\lambda_n$ is the CT wavelength at which the absorbance reached $A_n$. [d] $A_n$ too low.

dissolved in acetonitrile was treated with benzene, the solution immediately took on a distinctive yellow coloration (but no gas was evolved and the constituents could be recovered intact). The pale yellow color progressively deepened when either toluene or p-xylene was added. An orange color developed with naphthalene, and the solution turned red when p-dimethoxybenzene was added. The quantitative effect of these color changes is represented by the series of UV−vis absorption spectra (Figure 2A) that were measured at $-30$ °C to minimize any complications arising from competing thermal reactions. The progressive bathochromic shifts of the low-energy spectral tails in the order Ar′H = benzene < toluene < p-xylene < naphthalene < p-dimethoxybenzene followed the decreasing trend of the ionization potential of the aromatic compounds (Table 4).[20] Indeed, such a spectral behavior was predicted for the charge-transfer bands of intermolecular $(\pi,\pi)$ complexes, *i.e.* [ArN$_2^+$, Ar′H], which are of the type originally described by Mulliken (compare eq 3).[13b] The analogous charge-transfer absorptions (Figure 2B) obtained with the trichloro derivative **II** were slightly red-shifted relative to those of **I**, in accord with expectations based on the Mulliken theory.[13] The spectral maxima of these new absorption bands were unfortunately obscured by the low-energy cutoffs of the uncomplexed aromatic diazonium cations (see Figure 2, dashed curves). Thus for purposes of quantitative comparison, we chose to evaluate the charge-transfer band of the aromatic complexes with pentafluo-

robenzenediazonium **I** as the wavelength ($\lambda_{CT}$) at which it arbitrarily reached the critical absorbance of $A_n$ (see Table 4), as previously proposed by Tsubomura and Mulliken.[21] A similar treatment was also applied to the charge-transfer spectra from the trichloro derivative **II**, and the results are included in Table 4.

**V. Direct Arylations with [ArN$_2^+$, Ar′H] Complexes *via* the Photoirradiation of Their Charge-Transfer Bands.** Inspection of Figure 2 and Table 4 revealed that visible (excitation) light with $\lambda_{exc} > 410$ nm[22] was sufficient to selectively photoactivate only the intermolecular [C$_6$F$_5$N$_2^+$, Ar′H] complexes comprised of aromatic donors with ionization potentials (IP) lower than that of p-xylene in Table 4. [This excitation light ensured that there could be no ambiguity as to the adventitious photoexcitation of the local bands of either the uncomplexed C$_6$F$_5$N$_2^+$ or Ar′H.]

**A. Charge-Transfer Arylation.** The deliberate irradiation of the clear yellow solution of $C_6F_5N_2^+$ and p-xylene in acetonitrile (under an argon atmosphere) with $\lambda_{exc} > 410$ nm led to the steady evolution of roughly 1 equiv of dinitrogen and to the complete conversion of $C_6F_5N_2^+$ to afford pentafluorophenyl-p-xylene in 62% (isolated) yield, *i.e.*

$$C_6F_5N_2^+ + Ar'H \xrightarrow[-48\,°C]{h\nu_{CT}} C_6F_5\text{-}Ar' + N_2 + H^+ \qquad (6)$$
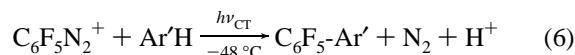
where Ar′H = p-xylene. The photolysate was always maintained at low temperature ($-48$ °C) to obviate any complication from thermal processes, and the photochemical transformation is thus designated hereafter as *charge-transfer or CT arylation*. Most importantly, Table 5 also shows that similar results were obtained with naphthalene to yield a mixture of $\alpha/\beta$ pentafluorophenylated isomers that was experimentally indistinguishable from that derived by iodide catalysis (compare Table 2, entry 9). Analogous arylations of benzene and toluene could not be unambiguously carried out owing to the very low CT absorbances (see Figure 2 and Table 4) derived from these rather weak aromatic donors. Nonetheless, the charge-transfer arylations of mesitylene and naphthalene with the trichloro acceptor **II** were successfully carried out to the same high conversions.

(20) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970, p 457ff. (b) Bock, H.; Wagner, G. *Tetrahedron Lett.* **1971**, 3713.

(21) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966.
(22) For $\lambda_{exc} > 410$ nm, the output of a 500-W high-pressure mercury light was successively passed through a Pyrex sharp cutoff filter (Corning CS 3-74) and a IR water filter.

**Table 5.** Charge-Transfer Arylations of Aromatic Hydrocarbons with Various Aromatic Diazonium Salts[a]

| arene (Ar′H) | diazonium ($ArN_2^+$) | add.[b] | conv (%)[c] | products (%)[c] | | |
|---|---|---|---|---|---|---|
| | | | | ArAr′ | ArH | ArX |
| *p*-xylene | $C_6F_5N_2^+$ | 0 | 100 | 62 | *d* | |
| mesitylene | $C_6F_2Cl_3N_2^+$ | 0 | 100 | 60 | 34 | |
| naphthalene | $C_6F_5N_2^+$ | 0 | 100 | 66 (3.6)[e] | *d* | |
| naphthalene | $C_6F_2Cl_3N_2^+$ | 0 | 100 | 43 (2.9)[e] | 35 | |
| naphthalene | $(O_2N)_2C_6H_3N_2^+$ | 0 | 95 | 90 (5.0)[e] | 1 | |
| naphthalene | $(O_2N)_2C_6H_3N_2^+$ | $CH_2I_2$ | 10 | 2 (−)[d] | *d* | 8 (ArI) |
| naphthalene | $(O_2N)_2C_6H_3N_2^+$ | $CBr_4$ | 51[f] | 31 (4.2)[e] | *d* | 5 (ArBr) |
| naphthalene | $(O_2N)_2C_6H_3N_2^+$ | $CCl_4$ | 82 | 75 (5.8)[e] | *d* | *d* |

[a] In acetonitrile (6 mL) containing $ArN_2^+$ (1 mmol) and aromatic hydrocarbon (Ar′H = 3 mmol) and irradiated with $\lambda_{exc} > 410$ mm at −48 °C. [b] Additive (8.0 mmol). [c] Conversion based on $ArN_2^+$. [d] Not determined. [e] Ratio of $\alpha/\beta$ isomers. [f] At 0 °C.

**Table 6.** Inhibitory Effects of Diiodomethane on Charge-Transfer Arylations[a]

| $ArN_2^+$ [b] | $\lambda_{exc}$[c] (nm) | add.[d] | conv[e] (%) | products(%)[e] | | |
|---|---|---|---|---|---|---|
| | | | | ArAr′ | ArH | ArI |
| 3,5-dinitro | 410 | 0 | 99 | 83 | 10 | 0[f] |
| | 410 | $CH_2I_2$ | 92 | 13 | *g* | 79 |
| 4-nitro | 410 | 0 | 44 | 23 | 8 | 0 |
| | 410 | $CH_2I_2$ | 55 | 4 | 3 | 42 |
| 3-nitro | 400 | 0 | 40 | 20 | 11 | 0 |
| 3,5-bis(trifluoromethyl) | 380 | 0 | 40 | 36 | *g* | 0 |
| 4-bromo | 380 | 0 | 30 | 16 | 11 | 0 |
| | 380 | $CH_2I_2$ | 37 | 7 | *g* | 22 |
| 4-carboethoxy | 410 | 0 | 60 | 9 | 45 | 0 |
| | 410 | $CH_2I_2$ | 42 | *g* | *g* | 37 |
| 3,5-bis(carboethoxy) | 410 | 0 | 100 | 29 | 62 | 0 |

[a] In acetonitrile (6 mL) containing $ArN_2^+$ (1 mmol) and *p*-dimethoxybenzene (Ar′H = 3 mmol) at −48 °C. [b] As tetrafluoroborate or hexafluorophosphate salt. [c] High-energy cutoff. [d] Diiodomethane (8.0 mmol) added. [e] Conversion based on $ArN_2^+$. [f] 2,5-Dimethoxyphenylacetonitrile (5%) also observed. [g] Not determined.

Moreover, the charge-transfer arylation of naphthalene was readily effected with the nonfluorinated 3,5-dinitrobenzenediazonium cation, and the high yields of the 3,5-dinitrophenyl derivatives (Table 5, entry 5) enabled us to examine the strong inhibitory effects of diiodomethane (entry 6), carbon tetrachloride (entry 8), and tetrabromide (entry 7) on this charge-transfer arylation.

**B. Inhibition of Charge-Transfer Arylation.** In order to examine the inhibitory effects of additives such as diiodomethane, the charge-transfer arylation of *p*-dimethoxybenzene was examined with a series of aromatic diazonium ($ArN_2^+$) salts containing different (nuclear) substituents. The results in Table 6 show that the reduced yields of arylated products were directly traceable to the diversion of the aromatic moiety to the corresponding aromatic iodide (ArI). The material balance was largely made up by small (but significant) amounts of the reduced arene (ArH).

**V. Photoefficiency of Charge-Transfer Arylation.** The charge-transfer complex of the trichlorodiazonium derivative **II** with naphthalene was particularly useful in quantitative photochemical reactions since the irradiation of its charge-transfer absorption band cleanly led to the steady bleaching of the orange color to finally yield a completely colorless photolysate.[23] Accordingly, the quantum yield ($\Phi$) was determined with the aid of ferrioxalate actinometry[24] by continuously monitoring the progressive diminution of the charge-transfer (tail) absorbance upon irradiation of the acetonitrile solution with monochromatic light at $\lambda_{exc} = 420 \pm 10$ mm (compare

**Table 7.** Quantum Yields for Charge-Transfer Arylation. The Deleterious Effect of Dioxygen[a]

| benzenediazonium substituent | mmol | Ar′H[b] (mmol) | Ar′H/$ArN_2^+$ | $\Phi$ |
|---|---|---|---|---|
| 3,5-difluoro-2,4,6-trichloro | 0.055 | 3.0 N | 54 | 11.0 |
| | 0.096 | 1.9 N | 20 | 7.5 |
| | 0.087 | 2.0 N | 23 | 6.7 (6.0)[c] |
| | 0.15 | 1.2 N | 8.2 | 4.5 |
| | 0.10 | 1.4 N | 14 | 4.6 (0.11)[d] (5.5)[e] |
| | 0.095 | 1.2 N | 13 | 5.0 (0.20)[d] (6.6)[e] |
| 3,5-dinitro | 0.12 | 0.93 N | 8.0 | 2.9 |
| | 0.16 | 0.66 N | 4.0 | 1.5 |
| | 0.088 | 8.1 X | 90 | 4.5 |
| | 0.025 | 8.1 X | 320 | 3.1 |

[a] Irradiation at $\lambda_{exc} = 420 \pm 10$ nm of acetonitrile (3 mL) solutions containing $ArN_2^+$ and Ar′H, as specified, at 24 °C. [b] N = naphthalene, X = *p*-xylene. [c] In the presence of 0.5 mmol of $BrCCl_3$. [d] After the introduction of 0.04 mmol of dioxygen. [e] Following 3 successive freeze−pump−thaw cycles.
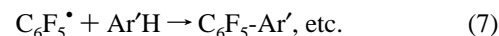
Figure 2B).[25] Quantum yields significantly greater than unity were consistently measured (Table 7), and they generally increased with the molar ratio of [Ar′H]/[$ArN_2^+$] (see column 4). Highly reproducible measurements of $\Phi$ were difficult to obtain, since they were subject to a rather strong negative effect by air contamination. For example, the deliberate addition of as little as 0.04 mmol of dioxygen to the argon atmosphere over the orange solution prior to irradiation was sufficient to drastically decrease the quantum yield from 5 to only $\Phi = 0.1$ (entry 5). [The quantum yield was completely restored after the (partially transformed) photolysate was deaerated by 3 successive freeze−pump−thaw cycles.] The presence of small amounts of bromotrichloromethane also led to reduced values of $\Phi$ (entry 3).

The quantum yields for charge-transfer arylations with the 3,5-dinitrobenzenediazonium complexes of naphthalene and *p*-xylene were slightly lower than that from **II**, but otherwise they more or less followed the same (concentration) trend as listed in Table 7 (last 4 entries).

## Discussion

The facile iodo-dediazoniation of aromatic diazonium cations ($ArN_2^+$ in eq 1 with $X^- =$ iodide) bears a direct mechanistic relationship to the dediazoniative arylation in eq 2, in that the iodination product (ArI) is easily diverted to the arylation product (Ar-Ar′) when the reaction in eq 4 is simply carried out in the presence of an aromatic donor (Ar′H). As described in Table 1, the diversionary pathway is so efficient that the biaryl synthesis in eq 5 can be made quantitative with only catalytic amounts (<1 mol %) of added iodide. Indeed, the monotonic changeover from ArI to Ar-Ar′ in the presence of increasing amounts of Ar′H, as illustrated in Figure 1, indicates that these products are derived from a common intermediate.[26]

**I. ETC Mechanism for Iodide (Thermal) Catalysis of Arylation.** The quantitative comparisons of the isomeric pentafluorophenylated biaryls ($C_6F_5$-Ar′) obtained in Table 2 coincide (within experimental uncertainty) with the isomeric product distributions in Table 8 that were previously observed in homolytic arylations effected with the pentafluorophenyl radical from various sources,[27,28] *i.e.*

$$C_6F_5^\bullet + Ar′H \rightarrow C_6F_5\text{-}Ar′, \text{ etc.} \tag{7}$$

As applied to pentafluorobenzenediazonium, the most economi-

(23) The extreme sensitivity of **I** to even traces of moisture caused (yellow) coloring and thus precluded the use of $C_6F_5N_2^+$ for quantitative photochemical studies.

(24) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc.* **1956**, *253*, 518.

(25) The output of a 450-W Xenon lamp was passed through an interference filter (Oriel 53810) with bandwidth (fwhm) ±10 nm.

(26) The cation $ArN_2^+$ cannot be the common precursor since it does not directly react (thermally) with the arenes in Tables 1 and 2.

**Table 8.** Pentafluorophenylation of Toluene, Nitrobenzene, and Anisole

| arene (ArH) | reagent | isomer distribution[a] of $C_6F_5$-Ar | | | ref |
| | | $o$ | $m$ | $p$ | |
| --- | --- | --- | --- | --- | --- |
| toluene | $C_6F_5CO_2$–$O_2CC_6F_5$ | 44 | 19 | 37 | 27e |
| | $C_6F_5I/h\nu$ | 38 | 20 | 42 | 28c |
| | $C_6F_5Xe^+$ | 44 | 19 | 37 | 28a |
| | $C_6F_5NH_2/RONO$ | 49 | 25 | 26 | 27f |
| | $C_6F_5N_2^+$/cat. NaI | 39 | 22 | 39 | this work |
| nitrobenzene | $C_6F_5NH_2/RONO$ | 17 | 42 | 41 | 27f |
| | $C_6F_5Xe^+$ | 18 | 53 | 29 | 28a |
| | $C_6F_5N_2^+$/cat. NaI | 20 | 52 | 28 | this work |
| anisole | $C_6F_5CO_2$–$O_2CC_6F_5$ | 35 | 7 | 57 | 27e |
| | $C_6F_5N_2^+$/cat. KI | 29 | 10 | 61 | this work |

[a] Corrected statistically for two *ortho* and *meta* positions.

cal pathway for the source of $C_6F_5^{\bullet}$ involves an initial 1-electron reduction, as in eq 8.[2,29]

$$C_6F_5N_2^+ + I^- \xrightarrow{k_I} C_6F_5^{\bullet} + N_2 + I^{\bullet} \qquad (8)$$
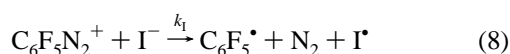
Such a redox process is consistent with the catalytic efficiency of other (nonionic) reducing agents in Table 3, such as ferrocene, the well-known 1-electron reagent,[32] *i.e.*

$$C_6F_5N_2^+ + Cp_2Fe \rightarrow C_6F_5^{\bullet} + N_2 + Cp_2Fe^+ \qquad (9)$$
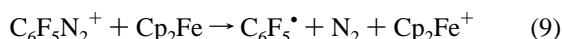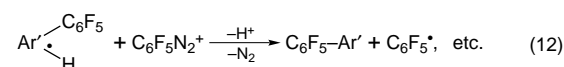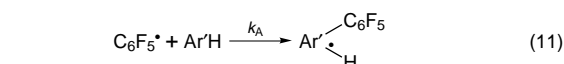
If so, the subsequent arylation of Ar'H must involve a homolytic chain process in order to account for (a) the catalytic turnover numbers (in excess of unity) found in Tables 1 and 2, and (b) the drastically reduced catalytic efficiency observed in the presence of aryl radical traps (Table 1). Thus, the diminished turnover numbers induced by dioxygen (entries 8 and 9), without materially affecting the product ratio $[C_6F_5$-Ph]/$[C_6F_5I]$, point to the interception of the aryl radicals prior to both arylation and iodination.[33] Moreover, the reduced efficiency inflicted by diiodine and diiodomethane (entries 10–12), which is accompanied by the progressively diminished ratio of $[C_6F_5$-Ar']/$[C_6F_5I]$, derives from the facile iodine-atom transfer,[34] *i.e.*

$$C_6F_5^{\bullet} + CH_2I_2 \rightarrow C_6F_5I + CH_2I^{\bullet}, \text{ etc.} \qquad (10)$$
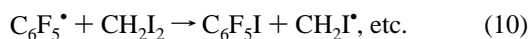
In order to accommodate the arylation step (eq 7) in the catalytic cycle, we propose that the well-known homolytic addition of $C_6F_5^{\bullet}$ onto Ar'H (eq 11) is followed by the rapid oxidation of

the cyclohexadienylic (radical) adduct, *i.e.*[35]

**Scheme 1**

$$C_6F_5^{\bullet} + Ar'H \xrightarrow{k_A} Ar'\overset{C_6F_5}{\underset{H}{\cdot}} \qquad (11)$$

$$Ar'\overset{C_6F_5}{\underset{H}{\cdot}} + C_6F_5N_2^+ \xrightarrow[-N_2]{-H^+} C_6F_5\text{–}Ar' + C_6F_5^{\bullet}, \text{ etc.} \qquad (12)$$

The overall 1-electron oxidation in eq 12 most likely proceeds via a rate-limiting electron transfer ($k_{ET}$) that is followed by the rapid deprotonation of the cationic Wheland adduct ($C_6F_5$-Ar'H$^+$)[36] to afford the biaryl ($C_6F_5$-Ar') and the rapid dediazoniation of the transient pentafluorophenyldiazenyl radical ($C_6F_5N_2^{\bullet}$)[31] to regenerate the aryl radical ($C_6F_5^{\bullet}$). According to this formulation, iodide catalysis proceeds via an initial reduction of $ArN_2^+$ in eq 8 to generate the critical aryl radical (Ar$^{\bullet}$), which is then involved in the homolytic chain process shown in Scheme 1.[37] Since the overall catalytic cycle includes a critical electron-transfer step (eq 12), the iodide-induced arylation is appropriately described as an *electron-transfer chain or ETC catalysis*,[38] of which a number of examples have been previously identified in various organic and organometallic reactions.[39,40]

**II. Competition between Arylation and Iodination.** Any mechanistic formulation of iodide catalysis must quantitatively account for the two important facets of the iodide-promoted arylation that are illustrated in Figure 1, namely, (a) the countercurrent trends in the yields of the arylation ($C_6F_5$-Ph) and iodination ($C_6F_5I$) products with changes in benzene concentration (Figure 1A) and (b) the steep monotonic fall in

(27) (a) Bolton, R.; Williams, G. H. *Adv. Free Radical Chem.* **1975**, *5*, 1. (b) Burdon, J.; Campbell, J. G.; Tatlow, J. C. J. *J. Chem. Soc. (C)* **1969**, 822. (c) Oldham, P. H.; Williams, G. H. *J. Chem. Soc. (C)* **1970**, 1260. (d) Bolton, R.; Coleman, M. W.; Williams, G. H. *Fluorine Chem.* **1974**, *4*, 363. (e) Bolton, R.; Williams, G. H. *Chem. Soc. Rev.* **1986**, *15*, 261. (f) Oldham, P. H.; Williams, G. H.; Wilson, B. A. *J. Chem. Soc. (C)* **1971**, 1094.

(28) (a) Frohn, H. J.; Klose, A.; Bardin, V. V. *J. Fluorine Chem.* **1993**, *64*, 201. (b) Birchall, J. M.; Haszeldine, R. N.; Wilkinson, M. J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1740. (c) Birchall, J. M.; Hazard, R.; Haszeldine, R. N.; Wakalski, W. W. *J. Chem. Soc. (C)* **1967**, 47.

(29) Equation 8 proceeds via a 2-step process involving the rate-limiting electron transfer ($k_{ET}$)[30] followed by the rapid dediazoniation in eq 18.[31] Such a two-step sequence was originally proposed as the initial stage of the iododediazoniation reaction.[30a]

(30) See: (a) Singh, P. R.; Kumar, R. *Aust. J. Chem.* **1972**, *25*, 2133. (b) Pladziewicz, J. R.; Doyle, M. P. *J. Imaging Sci.* **1989**, *33*, 57. (c) Brown, K. C.; Doyle, M. P. *J. Org. Chem.* **1988**, *53*, 3255. (d) Andersen, M. L.; Handoo, K. L.; Parker, V. D. *Acta Chem. Scand.* **1991**, *45*, 983. (e) Gilbert, B. C.; Hanson, P.; Jones, J. R.; Whitwood, J. C.; Timms, A. W. *J. Chem. Soc., Perkin Trans. 2* **1992**, 629.

(31) Suehiro, T. *Rev. Chem. Intermed.* **1988**, *10*, 101.

(32) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(33) DeTar, D. F.; Turetzky, M. N. *J. Am. Chem. Soc.* **1955**, *77*, 1745.

(34) Ingold, K. U. In *Free Radicals*; Kochi J. K., Ed; Wiley: New York, 1973; Vol. I, p 37.

(35) See: Bolton, R.; Williams, G. H. in ref 27e.

(36) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990; p 278ff.

(37) Although there are previous examples of $ArN_2^+$ undergoing homolytic chain reactions,[1,2] this is the first unequivocal example in which the intermolecular (Gomberg–Bachmann) arylation is shown to proceed via a *chain* process.

(38) We suggest that the iodide-promoted intramolecular Pschorr cyclization also proceeds via an analogous ETC mechanism. Compare: (a) Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1995**, *60*, 196. (b) Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.* **1987**, *52*, 1922. (c) Karady, S.; Abramson, N. L.; Dolling, U.-H.; Douglas, A. W.; McManemin, G. J.; Marcune, B. *J. Am. Chem. Soc.* **1995**, *117*, 5425.

(39) (a) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (b) Darchen, A.; Mahe, C.; Patin, H. *New J. Chem.* **1983**, *7*, 453. (c) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139. (d) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 943.

(40) In a more general context, the ETC catalysis, as presented in eq 18 and Schemes 1–3, relates directly to other catalytic reactions of diazonium cations by various metal species,[2] as well as other radical-chain reactions such as the $S_{RN}1$ and hole-catalyzed processes.[41]

(41) See: (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Rossi, R. A.; De Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; American Chemical Society: Washington, DC, 1983. (c) Mirafzal, G. A.; Liu, J. P.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 6072. (d) Bosch, E.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 1319.
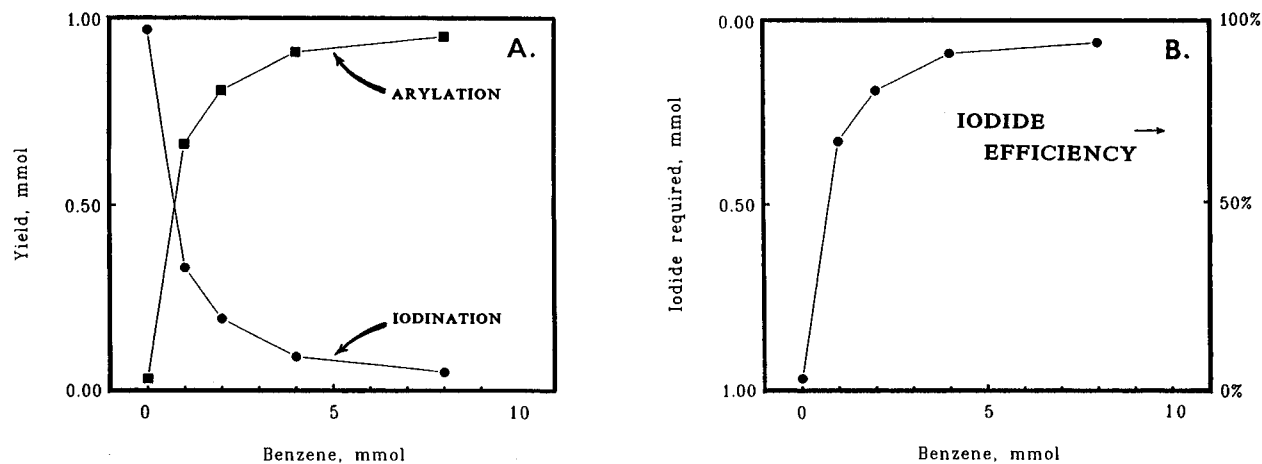
**Figure 3.** Computer simulation of the kinetics based on eq 8 and Scheme 1−3 for the effect of benzene concentration on (A) the formation of arylation and iodination products and (B) catalytic efficiency of iodide (right scale). The simulated points in parts A and B correspond to the experimental data described in Figure 1, parts A and B, respectively.

the iodide requirement for efficient catalysis (Figure 1B). If the propagation steps for arylation are described by Scheme 1, the homolytic (chain-transfer) process for iodination stemming from the initiation (eq 8) is

**Scheme 2**

$$C_6F_5^\bullet + I_2 \xrightarrow{k_P} C_6F_5I + I^\bullet \qquad (13)$$
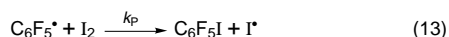
and the termination process is then described by the pair of radical-annihilation steps

**Scheme 3**

$$C_6F_5^\bullet + I^\bullet \xrightarrow{k_C} C_6F_5I \qquad (14)$$

$$I^\bullet + I^\bullet \xrightarrow{k_D} I_2 \qquad (15)$$
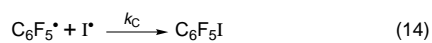
In order to validate the participation of the initiation step (eq 8), the propagation steps (Schemes 1 and 2), and the termination steps (Scheme 3), we carried out the computer simulation of the kinetics based on the GEAR Iterator developed by Weigert.[42] As presented in Figure 3A, the successful simulation of the opposed trends for arylation ($C_6F_5$-Ph) and iodination ($C_6F_5I$) in the experimental Figure 1A derives from the competition between homolytic addition (eq 11) and iodine-atom transfer (eq 13),[43] and the quantitative curve fittings largely reflect the relative magnitudes of the second-order rate constants, $k_A/k_P \sim 10^{-2}$, as described in the Experimental Section. Furthermore, the simulation in Figure 3B correctly predicts the sharp rise in the catalytic efficiency of iodide at rather low benzene concentrations (compare Figure 1B) to derive from the chain character of the ETC arylation, as described in Scheme 1.

**III. ETC Mechanism for Charge-Transfer Arylation.** The charge-transfer arylations exemplified by eq 6 represent the photochemical equivalent to the thermal (iodide) process in eq 5, without the obvious complications arising from competing iodinations. Otherwise, the charge-transfer arylations in Table 5 show the same mechanistic earmarks as those

observed in the thermal catalysis. Thus, the isomeric product distribution obtained in the charge-transfer arylations of naphthalene with $ArN_2^+$ accord with the low selectivities characteristic of other homolytic arylations with aryl radicals generated from unambiguous (Ar$^\bullet$) sources.[44] Such aryl radicals are rapidly trapped by diiodomethane (Table 6) and other halogen-atom transfer agents such as $CBr_4$ (Table 5). Most importantly, the enhanced magnitude of the quantum yields (consistently in excess of unity in Table 7) for photochemical promotion indicates that a chain process is operative. The latter can be readily formulated as the electron-transfer chain or ETC mechanism presented in Scheme 1, which does not depend on any species (such as I$^\bullet$) derived from the initiator. Further diagnostic of the homolytic chain mechanism based on Scheme 1 for charge-transfer arylation is the marked attenuation of the quantum yields in the presence of the radical-trap (dioxygen) and the halogen-atom transfer agents found to be effective in the retardation of thermal catalysis (compare the results in Tables 1 and 7).

**IV. Importance of Charge-Transfer Complexes in ETC Initiation.** Relevant to the photochemical procedure for arylations with aromatic diazonium salts is the specific irradiation of the charge-transfer absorption bands ($h\nu_{CT}$) described in Table 4. Figure 4 illustrates the direct relationship of these charge-transfer bands from diazonium salts **I** and **II** with the electron-donor strength of the aromatic hydrocarbon (Ar′H), as measured by the ionization potential (IP). According to Mulliken,[45] such a direct correlation derives from the photoinduced electron transfer that occurs within the precursor complex (see eq 3) to generate the radical-ion pair, *i.e.*[46,47]

$$[ArN_2^+, Ar'H] \xrightarrow{h\nu_{CT}} [ArN_2^\bullet, Ar'H^{\bullet+}] \qquad (16)$$

Loss of dinitrogen from the transient diazenyl radical ($ArN_2^\bullet$) yields the aryl radical required for the propagation sequence in Scheme 1.[48]

The photochemical activation of the aromatic diazonium cation as presented in eq 16 has its thermal (dark) counterpart

(42) (a) Weigert, F. *J. Comput. Chem.* **1987**, *11*, 273. (b) The program is available from Project Seraphim, 1101 University Ave., Madison, WI 53706.

(43) The reaction of Ar$^\bullet$ with I$^-$ to give the iodoarene radical anion ArI$^{\bullet-}$ followed by its reduction of $ArN_2^+$ has been proposed as a propagation sequence for iododediazoniation.[30a] However, the intermediacy of ArI$^{\bullet-}$ has been challenged[2] on account of its very rapid reversion to Ar$^\bullet$ and iodide, with a rate constant of $10^{10}$ s$^{-1}$. (See: Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.) We find that the inclusion of ArI$^{\bullet-}$ (its formation, decomposition, and reaction with $ArN_2^+$) as an intermediate in the GEAR simulations of Schemes 1−3 does not alter the predicted yields of either Ar−Ar′ or ArI (see the Experimental Section).

(44) See: Williams, G. H. et al. in ref 27.

(45) Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley: New York, 1969.

(46) The charge-transfer activity of various $ArN_2^+$ ions has been demonstrated: Becker, H. G. O.; Israel, G.; Oertel, U.; Vetter, H.-U. *J. Prakt. Chem.* **1985**, *327*, 399 and related papers.

(47) For a review of time-resolved (spectral) studies of photogenerated radical-ion pairs as in eq 16, see: Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409.
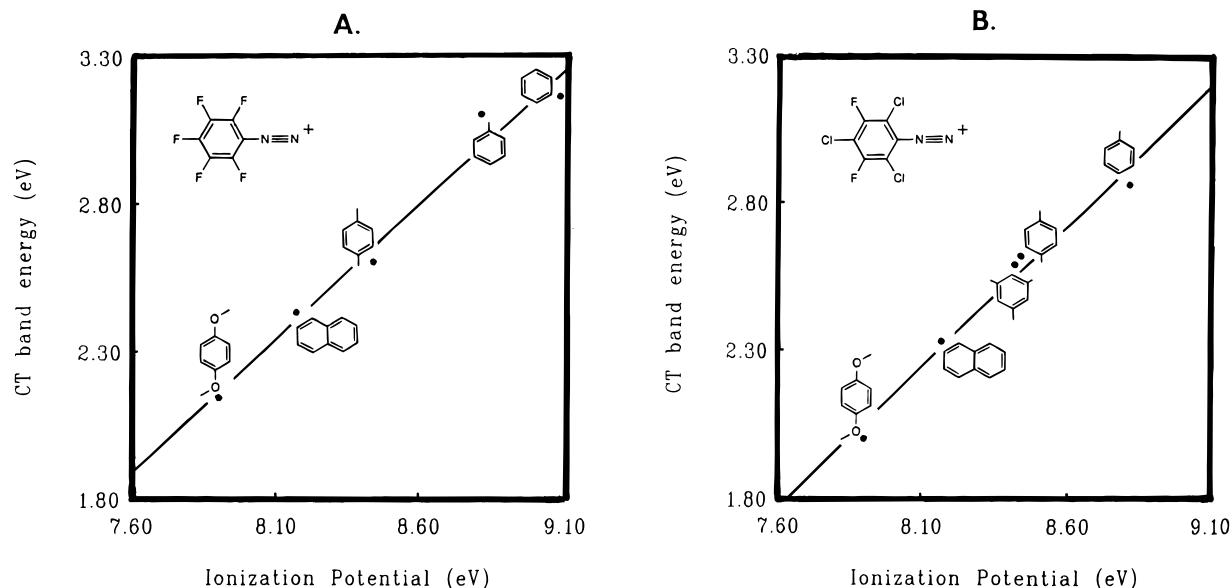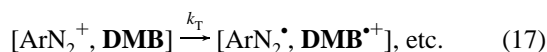
**Figure 4.** Mulliken correlation of the charge-transfer energy ($h\nu_{CT}$) of intermolecular complexes of (A) $C_6F_5N_2^+$ and (B) $C_6F_2Cl_3N_2^+$ with various arenes (as indicated).

$k_T$, which is especially applicable to electron-rich Ar'H such as *p*-dimethoxybenzene (**DMB**), *i.e.*

$$[ArN_2^+, \textbf{DMB}] \xrightarrow{k_T} [ArN_2^\bullet, \textbf{DMB}^{\bullet+}], \text{ etc.} \qquad (17)$$

owing to the enhanced stability of the cation radical (**DMB**$^{+\bullet}$).[18] Such an adiabatic charge-transfer process[49] is responsible for the thermal initiation of arylation by **DMB** (in the absence of iodide), as described in Table 3 (entry 4). Viewed from a slightly different perspective, the adiabatic charge transfer in eq 17 represents a simple oxidation-reduction reaction associated with the redox interaction of a relatively strong oxidant (*e.g.*, $C_6F_5N_2^+$ with $E_{red}^0 \sim 0.8$ V)[50] coupled with a reasonable reducing agent (**DMB** with $E_{ox}^0 = 1.3$ V).[18]

In a more general context, the same charge (electron) transfer formulation applies to the iodide-induced reductive dediazoniation of $ArN_2^+$ in eq 8 via the contact (charge-transfer) ion pair,[51] *i.e.*

$$[ArN_2^+, I^-] \xrightarrow{k_{ET}} [ArN_2^\bullet, I^\bullet] \xrightarrow{\text{fast}} Ar^\bullet + N_2 + I^\bullet \qquad (18)$$
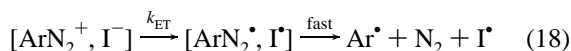
Most importantly, the radical pair in eq 18 does not undergo cage collapse as in a conventional mechanism for iododediazoniation of $ArN_2^+$,[52] since the efficient diversion of iodination to arylation by added benzene, as well as the GEAR simulations shown in Figure 3, indicates that virtually all the aryl radicals (Ar$^\bullet$) can be scavenged by benzene. Clearly, diffusive separation of the radical pair, followed by chain transfer (eq 13) and termination (eqs 14 and 15), is needed to account for iododed-

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(48) Alternatively, the aryl radical Ar$^\bullet$ can react with the aromatic cation radical to directly afford the Wheland intermediate (Ar$-$Ar'H$^+$), which yields the biaryl following deprotonation. For related examples, see: Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521. Bockman, T. M.; Kochi, J. K. *J. Phys. Org. Chem.* **1994**, *7*, 325.

(49) For some examples in which charge-transfer complexes (that contain very good electron donors) readily undergo thermal electron transfer as in eq 17, see: Kochi, J. K. *Adv. Phys. Org. Chem.* **1994**, *29*, 185 and related papers.

(50) Estimated from: Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854. Compare: Kochi, J. K. *J. Am. Chem. Soc.* **1955**, *77*, 3208.

(51) Based on the 1-electron oxidation potential of iodide ($E_{ox}^0 \approx 1.0$ V),[2] the driving force for oxidation by $ArN_2^+$ is roughly isergonic, and the rate of electron transfer is thus expected to be very fast (see GEAR simulation in the Experimental Section).

(52) See, *e.g.*: Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry*; Cambridge: London, 1974; p 356.

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ediazoniation. Indeed, the time scale for diffusive separation of the radical pair ($\tau \sim 10^{-10}$ s), which is at least an order of magnitude shorter than that required for dediazoniation ($k_{N_2} \sim 10^8$ s$^{-1}$),[31] accounts for the high efficiencies that can be attained in iodide catalysis of arylation.[53]

## Summary and Conclusions

The arylation of various aromatic hydrocarbons (Ar'H) can be effected by pentafluorobenzenediazonium and related cations ($ArN_2^+$) to afford the biaryls (Ar-Ar') by two independent procedures. Thus, the *thermal* arylation is promoted by small (catalytic) amounts of sodium iodide at 24 °C, and the biaryls (Ar-Ar') are produced in high yields together with the iodination products (ArI). The product ratio [Ar-Ar']/[ArI] increases markedly with Ar'H concentration, and the catalytic efficiency of iodide for biaryl formation can be made to exceed turnover numbers in excess of 85. Comparisons of the isomer distribution obtained from toluene, nitrobenzene, and naphthalene with those reported previously for free-radical aromatic substitutions with aryl radicals (generated from unambiguous sources) identify Ar$^\bullet$ as the reactive intermediate. According to the catalytic chain mechanism presented in Scheme 1, the homolytic addition of Ar$^\bullet$ onto the aromatic hydrocarbon (eq 11) is followed by a rapid electron transfer from the adduct (Ar-Ar'H$^\bullet$) to the diazonium cation acting as a 1-electron oxidant in eq 12. Such an oxidation−reduction is thus characteristic of an electron-transfer chain or ETC mechanism, which is verified by the computer simulation of the complex kinetics with the GIT program based on the GEAR algorithm.[42]

The *photochemical* arylation (in the absence of iodide) is alternatively induced by the deliberate irradiation of the charge-transfer absorption bands of the intermolecular complexes of $ArN_2^+$ and various arenes (Ar'H) that are characterized in Table 4. The charge-transfer activation of these precursor complexes according to eq 16 affords aryl radicals to initiate the homolytic chain mechanism in Scheme 1. Otherwise the catalytic process

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(53) (a) Iodide efficiencies approaching 100% in Figure 3 are to be contrasted with the more limited escape efficiencies measured in other azo decompositions. See: Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 157. (b) Note that the rate of initiation in eq 18 represents a lower limit for $k_{ET}$, since back electron transfer to regenerate [$ArN_2^+$, I$^-$] cannot be evaluated. Compare the CIDNP observations of Becker *et al.* in ref 46.

for the photochemical arylation is equivalent to the mechanism of the thermal (iodide) process.

## Experimental Section

**Preparation of Pentafluorobenzenediazonium Tetrafluoroborate.** 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 needle, and the flask was immersed in an acetonitrile/dry ice bath. After the solution 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 (syringe). The yellow reaction mixture containing an abundant heavy precipitate was stirred for an hour 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 dec; IR (Nujol) 2314, 1655, 1648, 1578, 1571, 1561, 1538, 1524, 1504, 1438, 1326, 1158, 1112, 1070, 1052, 1037, 1020, 1005, 980, 956, 943 cm$^{-1}$; $^{13}$C NMR (CD$_3$CN) $\delta$ 139.87 (dm, $J$ = 260 Hz), 149.08 (dm, $J$ = 280 Hz), 154.43 (dm, $J$ = 278 Hz); $^{19}$F NMR (CD$_3$CN) $\delta$ −40.09 (m, 1F), −43.70 (m, 2F), −71.82 (s, 4F), −73.02 (m, 2F). Anal. Calcd for C$_6$BF$_9$N$_2$: 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 temperature under 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 days. The synthesis of 3,5-difluoro-2,4,6-trichlorobenzenediazonium hexafluorophosphate (**II**) as well as that of the other diazonium salts utilized in Tables 5 and 6 is described separately.[11b]

**Iodide-Promoted Arylations with Diazonium Salts.** In a typical procedure, a 75-mL flask having two Teflon O-ring sidearm stopcocks was charged in a drybox equipped with a magnetic stirring bar and a rubber septum with the diazonium salt (1.00 mmol). The pressure transducer was attached to one of the sidearms, and the flask was evacuated and refilled with argon. Acetonitrile (5.8 mL) and arene (0.71 mL, 8 mmol) were injected with the aid of hypodermic syringes, and the flask was evacuated and refilled with argon three times. The evacuated flask was then closed off, and argon (25 mL at 24 °C) was then injected via a gas-tight syringe to calibrate the output of the transducer. The calibration was repeated with further additions of argon. Following the calibration procedure, the flask was degassed as described above and allowed to equilibrate until no observable change in the transducer output occurred over 5 min. The reaction was subsequently started by the injection of an oxygen-free solution of sodium iodide (20 $\mu$L, 0.500 M) in acetonitrile via a gas-tight microsyringe. The immediate appearance of a brown coloration (I$_2$) and gas evolution were observed. After the pressure remained unchanged for 2 min, a new aliquot of the iodide solution (20 $\mu$L, 0.500 M) was injected. If the addition of first three aliquots of sodium iodide (20 $\mu$L, 0.500 M) led to the evolution of less than 0.20 mmol of nitrogen, further addition was performed with larger aliquots (100 $\mu$L, 0.500 M). The initiation process was continued until no further pressure change was caused by addition of sodium iodide. The brown reaction mixture was quenched with water (30 mL) containing a few drops of a starch solution and titrated with 0.020 N sodium thiosulfate. Following the titration, the reaction mixture was 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 $\mu$L, 86.4 mg) as an internal standard.

**Inhibition of the Iodide-Promoted Pentafluorophenylation of Benzene.** After the degassing and calibration procedures (described above for the uninhibited reaction) were carried out, dry oxygen (5 mL, 0.2 mmol at 25 °C) was injected into the reaction flask containing pentafluorobenzenediazonium hexafluorophosphate (282 mg, 1.00 mmol), acetonitrile (5.8 mL), and benzene (0.71 mL, 8 mmol) via a gas-tight syringe. The amount of iodide required for the complete evolution of nitrogen (1 mmol) was determined by iodometric titration.

**Pentafluorophenylation of Benzene with Other Catalysts. (a) Ferrocene:** The experiment was run as described above for the reaction catalyzed by sodium iodide. The formation of the blue color of the ferrocenium cation was observed immediately after the addition of ferrocene (60 $\mu$L, 0.167 M in acetonitrile) to the yellow acetonitrile solution of pentafluorobenzenediazonium tetrafluoroborate (1.00 mmol) and the arene (8 mmol). The dark blue reaction mixture was treated with zinc granules (0.1 g), quenched with water (50 mL), and extracted with dichloromethane (3 × 25 mL). The combined yellow 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 $\mu$L, 86.4 mg) as an internal standard. Evaporation of the solvent, recrystallization from methanol, and repeated sublimation (45 °C, 0.3 Torr) of the yellowish crystalline residue afforded slightly yellowish 2,3,4,5,6-pentafluorobiphenyl (203 mg, 83%, purity 99.6% by GC). **(b) Dimethoxybenzene:** The addition of the dimethoxybenzene solution (20 $\mu$L, 0.500 M in acetonitrile) to the solution of benzene (8.0 mmol) and the diazonium salt (1.00 mmol) resulted in a relatively slow evolution of nitrogen that did not cease even after 30 min. An additional 0.05 mmol of dimethoxybenzene was added, and the dark green reaction mixture was finally treated with zinc granules (100 mg) to result in a complete bleaching of the coloration. After workup, evaporation of the solvent and repeated sublimation (45 °C, 0.3 Torr) of the yellowish crystalline residue afforded pure colorless 2,3,4,5,6-pentafluorobiphenyl (207 mg, 84.5%, purity 99.6% by GC). **(c) Zn Metal (with 64 mmol of Benzene):** The reaction was run with pentafluorobenzenediazonium tetrafluoroborate (282 mg, 1.00 mmol) and benzene (5.00 g, 5.71 mL, 64 mmol) in acetonitrile (5.8 mL). The reaction was started by dropping a zinc granule (17.6 mg, 0.54 mg·atom) into the degassed reaction mixture. After 23 ± 0.8 mL (0.94 mmol, 94% a 24 °C) of nitrogen was evolved, the pressure stabilized and the resulting orange reaction mixture was quenched with water (30 mL) and extracted with dichloromethane (3 × 25 mL). The consumption of zinc was determined to be 13.1 mg (0.40 mequiv). 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 $\mu$l, 86.4 mg) as an internal standard. The yield of the biphenyl was 0.60 mmol, 60%. 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 (136 mg, 56%). The reaction was repeated in the same conditions with 8 mmol of benzene (624 mg, 714 $\mu$L). The gas evolution was more sluggish, and the entire granule of zinc was consumed after 18 ± 0.8 mL (0.74 mmol at 24 °C) of nitrogen had evolved. The analysis of the product mixture showed the presence of 2,3,4,5,6-pentafluorobiphenyl (0.43 mmol, 43%) and small amounts of byproducts.

**Charge-Transfer Photoarylations of Aromatic Donors.** A Schlenk flask was typically charged with the diazonium salt (1.00 mmol) and the arene donor (3.00 mmol) under an argon atmosphere in a drybox and sealed with a rubber septum. Acetonitrile (20 mL) was added with the aid of a hypodermic syringe. The immediate appearance of the yellow to red coloration of the EDA complex was noted upon the dissolution of the reagents. The reaction mixture was irradiated at −48 °C with a 410-nm cut-off filter. The irradiation was continued until no gas evolution could be observed. The final colorless reaction mixture was poured in a separatory funnel containing water (100 mL), concentrated hydrochloric acid (20 mL), and chloroform (20 mL) several times. The combined chloroform extracts were washed with water (3 × 20 mL), dried over molecular sieves, and analyzed by GC and GC-MS after addition of *p*-xylene (100 $\mu$L, 86.4 mg) as an internal standard.

**Determination of the Quantum Yields.** The actinic output of a 150-W short arc xenon lamp equipped with a 420-nm interference filter was measured by using the original ferrioxalate technique by Hatchard and Parker.[24] A solution of the diazonium salt and arene in acetonitrile (3 mL) was prepared in a Schlenk cell for UV−vis spectroscopy (1.000-cm path) with the total volume of 21 mL at 24 °C in the dark. The cell was placed in a water bath at 24 °C and irradiated with the focused beam of the xenon lamp. The irradiation was periodically interrupted and the UV−vis spectra of the solution recorded. A steady bleaching of the charge-transfer absorption band was observed. The amount of the diazonium salt in the solution for each spectrum was determined by measuring the charge-transfer absorbance of the [diazonium, arene] EDA complex [C] and calculating the amount of the unreacted diazonium cation with use of the Benesi−Hildebrand approximation.

Thus, if $A = \epsilon_C[C]l$ (where $\epsilon_C$ is the extinction coefficient of the complex and $l$ is the optical path) and $K = [C]/(([D] - [C])([ArH] - [C])) \approx [C]/(([D] - [C])[ArH])$ (where ArH and D are the arene and diazonium cation, respectively), then $A = \epsilon_C l[D][ArH]/([ArH] - 1/K)$ $\approx [D_0]$ constant. The amount of the residual diazonium was calculated for each time point by using a wavelength value outside of the perturbed range (400−430 nm). The initial slope of the [D] versus time curve was considered the initial rate of the reaction, and the quantum yield was calculated by dividing this rate by the light flux. **(a) Inhibition with Oxygen.** A solution of the diazonium salt (40.3 mg, 0.102 mmol) and naphthalene (182 mg, 1.42 mmol) in acetonitrile (3 mL) was prepared and irradiated in a Schlenk UV cell as described above. After exposing the solution to light (15 min), dry oxygen (1 mL, 0.04 mmol) was injected via a gas-tight syringe. The quantum yield of the CT band bleaching dropped to 0.11. The solution was then degassed by 3 freeze−thaw cycles and subjected to further irradiation. The $\Phi$ value of 5.49 was determined. The experiment was repeated under the same conditions and yielded initial quantum yields of 5.02 and 4.98. Addition of oxygen (2 mL, 0.08 mmol) reduced these to 0.20 and 0.22. Oxygen removal restored the quantum yields to 6.02 and 5.26. Addition of a smaller amount of oxygen (0.100 mL, 0.004 mmol) reduced the quantum yield to 1.69 (0.008 mmol, 20 min of exposure). Further addition of oxygen (0.100 mL, 0.004 mmol) reduced the quantum yield again to 1.02 (0.008 mmol, 20 min exposure). **(b) Inhibition with Bromotrichloromethane.** A solution of the diazonium salt (38.0 mg, 0.0962 mmol) and naphthalene (198 mg, 1.89 mmol) in acetonitrile (3 mL) was irradiated in a Schlenk UV cell as described above. The initial $\Phi$ value of 6.73 fell to 6.00 upon addition of bromotrichloromethane (198 mg, 0.507 mmol).

**Simulation of the Kinetics of the ETC Mechanism in Schemes 1−3.** The system of six kinetic equations (eq 8 and Schemes 1−3) was simulated with use of the MS-FORTRAN program GEAR.[42,43] The rate constants for the simulation were chosen as follows. The rate constant for the initiation step (eq 8) was taken as $k_I = 1.2 \times 10^2$ M$^{-1}$ s$^{-1}$ from the simulation of the rate of nitrogen evolution. The rate constants $k_C$ and $k_D$ for the coupling of C$_6$F$_5$• with I• (eq 14) and I• dimerization (eq 15), respectively, were assumed to be diffusion controlled, and the rate constant of $10^{10}$ M$^{-1}$ s$^{-1}$ was used for both.[54] The chain transfer of C$_6$F$_5$• with I$_2$ (eq 13) was assumed to proceed with a rate constant of $k_P = 10^7$ M$^{-1}$ s$^{-1}$.[34] Preliminary simulation experiments indicated that varying the rate constant for the electron-transfer step (eq 12) between $10^6$ and $10^{10}$ M$^{-1}$ s$^{-1}$ had no effect on the yields of either the arylation products or C$_6$F$_5$I. Accordingly, the value was fixed at $k_{ET} = 10^9$ M$^{-1}$ s$^{-1}$. The rate constant for the addition step (eq 11) was treated as a variable parameter. Initially, the kinetics

(54) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993; p 207.

of the reaction of 0.17 M pentafluorobenzenediazonium and an equimolar amount of benzene in the presence of $8 \times 10^{-3}$ M sodium iodide was simulated, and allowed to run until the concentration of iodide fell to less than $10^{-7}$ M (0.5−5 s). The concentrations of C$_6$F$_5$N$_2^+$ and benzene calculated at this point were used as input for a second cycle of calculations, starting with a concentration of iodide of $8 \times 10^{-3}$ M. The process was repeated until the concentration of diazonium cation fell to less than $10^{-3}$ M. The amounts of aryl iodide and biaryl coupling products generated in each cycle of simulation were added to calculate the final (simulated) concentrations for comparison with the experimental yields in Table 1. The simulation was repeated for benzene concentrations of 0.34, 0.67, and 1.38 M to correspond with the experimental conditions in Table 1 and Figure 1A. The fit shown in Figure 3A corresponds to a rate constant for the addition step of $k_A = 6 \times 10^4$ M$^{-1}$ s$^{-1}$. Simulations using values of $k_A = 4 \times 10^4$ and $8 \times 10^4$ M$^{-1}$ s$^{-1}$ led to substantially worse fits, with all the calculated values of the yield of arylation products either less than (for $k_A = 4 \times 10^4$ M$^{-1}$ s$^{-1}$) or greater than (for $k_A = 8 \times 10^4$ M$^{-1}$ s$^{-1}$) the experimental yields. The overall rate constant for addition of C$_6$F$_5$• to benzene is thus estimated as $k_A = 6 \pm 2 \times 10^4$ M$^{-1}$ s$^{-1}$. For comparison of the experimental data with the simulation, the total yield for arylation was taken as the sum of yield of C$_6$F$_5$Ph and of twice the yield of the doubly-arylated products[11] in Table 1. No attempt was made to simulate the yield of the minor products (I$_2$ and C$_6$F$_5$H) or the participation of other iodine-containing species such as triiodide, etc.

To test for the intermediacy of C$_6$F$_5$I•$^-$, we repeated the calculation with the following reaction steps included: (a) the reaction of C$_6$F$_5$• with I$^-$ to form C$_6$F$_5$I•$^-$, which was assumed to proceed with a rate constant of $10^7$ M$^{-1}$ s$^{-1}$, (b) the reversion of C$_6$F$_5$I•$^-$ to C$_6$F$_5$• and I$^-$ for which a rate constant of $10^{10}$ s$^{-1}$ was used,[2] and (c) the reaction of C$_6$F$_5$I•$^-$ with C$_6$F$_5$N$_2^+$ to generate C$_6$F$_5$I, C$_6$F$_5$•, and N$_2$, which was assumed to proceed at a diffusion-controlled rate. The (simulated) yields of C$_6$F$_5$I and C$_6$F$_5$-Ph, as well as the amount of iodide required for complete conversion, were identical with those obtained without inclusion of reactions a−c. We conclude, therefore, that the reaction between C$_6$F$_5$• and I$^-$ does not control the partitioning between iododediazoniation and biaryl formation in eqs 4 and 5, respectively.

**Supporting Information Available:** Materials, instrumentation, charaterizations, and product yields for the thermal (iodide-catalyzed) and photochemical arylations in Tables 1−3, 5, and 6 (10 pages). See any current masthead page for ordering and Internet access instructions.

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