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I. Materials.

Benzene, toluene, o- and m-xylenes (EM Science), iso-propylbenzene, tertbutylbenzene, mesitylene, chlorobenzene, p-dichlorobenzene, anisole, and odimethoxybenzene (Aldrich) were purified by twofold distillation under an atmosphere of Naphthalene (Matheson) and p-dimethoxybenzene were recrystallized from argon. ethanol and sublimed in vacuo. p-Xylene (Kodak) was purified by repeated partial freezing (5 times) and distilled from sodium under an argon atmosphere. Pentafluoroaniline, pentafluorobenzene, iodopentafluorobenzene, diiodomethane, carbon tetrabromide, and bromotrichloromethane (Aldrich) were used as received. Sodium and potassium iodides (Aldrich) were dried in vacuo for 2 hours at 150 °C and stored under Pentafluoroiodobenzene, 3- and 4-nitroiodobenzene, 4-bromoiodobenzene 4argon. carboethoxy and 3,5-bis(carboethoxy)iodobenzene were commercial samples (Aldrich). Authentic samples of the 3,5-dinitro and 3,5-difluoro-2,4,6-trichloroiodobenzenes were prepared by treatment of sodium iodide with their diazonium salts and are reported separately.^{11b} Pentafluorobiphenyl was prepared from phenyllithium and hexafluorobenzene as described by Chen and Li.ª mp 111-112 °C (EtOH/acetone; litª, mp 110.5-112 °C); IR (KBr) 1525, 1495, 1440, 1072, 1063, 983, 723 cm⁻¹; ¹H NMR (CDCl₃) δ 7.391- 7.511 (m, 5H); ¹³C NMR (CDCl₃) δ 115.95 (m), 126.40, 128.70, 129.27, 130.14, 137.84 (dm, J = 251 Hz), 140.38 (dm, J = 252 Hz), 144.16 (dm, J = 246 Hz); 19 F NMR (CDCl₃) δ -62.73 (m, 2F), -75.18 (m, 1F), -81.79(m, 2F); MS m/z (%) 244(M,

100), 224(30). Syntheses of the pentafluorophenylated derivatives in Table II, as well as the other analogues in Tables V and VII are reported separately.^b

Acetonitrile (OmniSolv, EM Science), and nitromethane (Spectrophotometric grade, Aldrich) were transferred to Schlenk flasks under an argon atmosphere and used without further purification. Dichloromethane (HPLC grade, EM Science) was initially stirred with concentrated sulfuric acid; the separated layer was neutralized, dried over anhydrous Na₂CO₃ and finally distilled from anhydrous P₂O₅ under an argon atmosphere. Absolute ether. 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.

II. Instrumentation.

UV-Vis absorption spectra were measured on a Hewlett-Packard 8450A diodearray spectrometer with 2 cm⁻¹ resolution. The ¹H ,¹³C and ¹⁹F NMR spectra were obtained on a General Electric QE-300 FT-NMR spectrometer with internal (CH₃)₄Si or external CF₃COOH standards. The infrared spectra were recorded on either a Nicolet 10DX, Nicolet 560 FT-IR or a Matteson Genesis spectrophotometer. Gas chromatography was performed on a Hewlett-Packard 5790A series FID gas chromatograph equipped with a 3392 integrator, the fused silica capillary column (WCOT, 0.25mm i.d. x 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). Barometric experiments were performed employing a pressure transducer based on a pressure-sensitive transistor (B&F Instruments). Melting points were determined with a Laboratory Devices MEL-TEMP apparatus and were uncorrected.

III. Products from the Sodium Iodide Catalyzed Reaction

For each diazonium salt, the products follow in serial order: Diazonium salt: Arene Donor, mmol iodide consumed; mmol I_2 formed; products (mmol). Pentafluorobenzene-diazonium tetrafluoroborate: Benzene, 0.10; 0.038; 2,3,4,5,6pentafluorobenzene (0.009) 2,3,4,5,6-pentafluorobiphenyl (0.83), and bis-(2,3,4,5,6pentafluorophenyl)-benzene (0.032). The latter consisted of a mixture of o, m- and pisomers.11b Toluene, 0.08; 0.019; pentafluorobenzene (0.023 mmol, 2.3%), iodopentafluorobenzene (0.021), 2'-methyl-2,3,4,5,6-pentafluorobiphenyl (0.380), 3'methyl-2,3,4,5,6-pentafluorobiphenyl (0.212)mmol), 4'-methyl-2,3,4,5,6pentafluorobiphenyl (0.183). o-Xylene. 0.19; 0.043; pentafluorobenzene (0.053), iodopentafluorobenzene (0.032 mmol), 2',3'-dimethyl-2,3,4,5,6-pentafluorobiphenyl (0.401), 3',4'-dimethyl-2,3,4,5,6-pentafluorobiphenyl (0.359). p-Xylene. 0.14; 0.019; pentafluorobenzene (0.031), iodopentafluorobenzene (0.060), 2',5'-dimethyl-2,3,4,5,6pentafluorobiphenyl (0.788). Isopropylbenzene. 0.17; 0.059; pentafluorobenzene (0.057), iodopentafluorobenzene (0.036), 2'-isopropyl-2,3,4,5,6-pentafluorobiphenyl (0.211), 3'isopropyl-2,3,4,5,6-pentafluorobiphenyl (0.239 mmol), 4'-isopropyl-2,3,4,5,6-pentafluorobiphenyl (0.193 mmol). tert-Butylbenzene. 0.17; 0.046 mmol; pentafluorobenzene (0.036), iodo-pentafluorobenzene (0.050), 2'-t-butyl-2,3,4,5,6-pentafluorobiphenyl (0.235 mmol), 3'-t-butyl-2,3,4,5,6-pentafluoro-biphenyl (0.291), 4'-t-butyl-2,3,4,5,6-pentafluoro-

biphenyl (0.206 mmol,). Chloro-benzene. 0.22; 0.073; pentafluorobenzene (0.006), iodopentafluorobenzene (0.104), 2'-chloro-2,3,4,5,6-pentafluorobiphenyl (0.277), 3'chloro-2,3,4,5,6-pentafluorobiphenyl (0.183), 4'-chloro-2,3,4,5,6-pentafluorobiphenyl (0.184). p-Dichlorobenzene. 0.56; 0.140; pentafluorobenzene (0.015), iodopentafluorobenzene (0.306), 2',5'-dichloro-2,3,4,5,6-pentafluorobiphenyl (0.430). Nitrobenzene. 0.62; 0.255; pentafluorobenzene (0.014), iodopentafluorobenzene (0.367), 2'-nitro-2,3,4,5,6-pentafluorobiphenyl (0.054), 3'-nitro-2,3,4,5,6-pentafluorobiphenyl (0.146), 4'nitro-2,3,4,5,6-pentafluorobiphenyl (0.039). Naphthalene. 0.06; 0.019; pentafluorobenzene (0.010), iodopentafluorobenzene (0.021), 1-(2,3,4,5,6-pentafluorophenyl)naphthalene(0.480),2-(2,3,4,5,6-pentafluorophenyl)naphthalene (0.275). 2.4.6-Trichloro-3,5-difluorobenzenediazonium hexafluorophosphate. Benzene 0.94; 0.032; 2,4,6-trichloro-3,5-difluorobenzene (0.119).2,4,6-trichloro-3,5-difluoroiodobenzene (0.861), 2,4,6-trichloro-3,5-difluorobiphenyl (0.002). Benzene (k₁ catalysis). Not determined; not determined; 2,4,6-trichloro-3,5-difluorobenzene (0.083), 2,4,6-trichloro-3,5-difluoroiodobenzene (0.242 mmol), 2,4,6-trichloro-3,5-difluorobiphenyl (0.658 mmol). Evaporation of the dichloromethane extracts followed by column chromatography on silica with CH2Cl2/hexane, recrystallization from ethanol and sublimation (0.3 torr) afforded 2,4,6-tchloro-3,5-difluorobiphenyl (153 mg, 52.2 %) as colorless needles, mp 61-62 °C. Naphthalene. 0.56; 0.141; 2,4,6-trichloro-3,5difluorobenzene (0.021), 2,4,6-trichloro-3,5-difluoroiodobenzene (0.100), 1-(2,4,6trichloro-3,5-difluorophenyl)-naphthalene (0.453), 2-(2,4,6-trichloro-3,5-difluorophenyl)naphthalene (0.125). 3,5-dinitrobenzenediazonium tetrafluoroborate. Benzene (KI catalysis) not determined; not determined; *m*-dinitrobenzene (0.001), 5-iodo-3,5dinitrobenzene (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, 63.7 %) as colorless flakes, mp 147-148 °C. **4-Nitrobenzenediazonium hexafluorophosphate.** *Benzene* (KI catalysis) not determined; not determined; nitrobenzene (0.005), 4-iodonitrobenzene (0.788), 4-nitrobiphenyl (0.181).

Oxygen-Inhibited Reactions. Benzene. The amount of iodide required for complete evolution of nitrogen was 0.24 mmol. The following products were detected: pentafluorobenzene (0.006 mmol), iodopentafluorobenzene (0.053 mmol) and 2,3,4,5,6pentafluorobiphenyl (0.736 mmol). The experiment was repeated, but with 10 mL (0.4 mmol) of added O₂. The amount of iodide required for the complete evolution of nitrogen (1 mmol) was 0.38 mmol. The amount of the sodium thiosulfate solution used for the titration was 0.2 meq. The following products were detected: pentafluorobenzene (0.005 mmol), iodopentafluorobenzene (0.070 mmol) and 2.3,4,5,6-pentafluorobiphenvl (0.716 mmol). The other inhibited reactions were carried out under the same conditions, and the data is listed in serial form as follows: Inhibitor: mmol; mmol iodide consumed: mmols I₂ formed; products (mmol). Oxygen: 0.8; 0.47; 0. 15; pentafluorobenzene (0.006), iodopentafluorobenzene (0.097), 2,3,4,5,6-pentafluorobiphenyl (0.674). Iodine: 0.10; 0.22; not determined; pentafluorobenzene (0.002), iodopentafluorobenzene (0.111), 2,3,4,5,6-pentafluorobiphenyl (0.764). 0.50; 0.33; not determined; iodopentafluorobenzene (0.264 mmol, 26.4 %), 2,3,4,5,6-pentafluorobiphenyl (0.615). 1.0; 0.44; not determined; iodopentafluorobenzene (0.375), 2,3,4,5,6-pentafluorobiphenyl (0.552).

Diiodomethane. 8.0; 0.83; 0.05; iodopentafluorobenzene (0.70), 2,3,4,5,6-pentafluorobiphenyl (0.187). *Bromotrichloromethane*. 8.0; 0.24; not determined; pentafluorobenzene (0.005), bromopentafluorobenzene (0.050) iodopentafluorobenzene (0.056), 2,3,4,5,6-pentafluorobiphenyl (0.665).

IV. Products from the Charge-Transfer Arylations

The products for each reaction are listed in serial order as follows: Diazonium salt: Arene. products (mmol). Pentafluorobenzenediazonium tetrafluoroborate: Naphthalene. (1-(pentafluorophenyl)-naphthalene (0.42); 2-(pentafluorophenyl)naphthalene (0.24) p-Xylene. 2',5'-dimethyl-2,3,4,5,6-pentafluorobiphenyl (6) (0.62 mmol, 62%). 2,4,6-Trichloro-3,5-difluorobenzendiazonium hexafluorophosphate. Naphthalene. 2,4,6-trichloro-3,5-difluoro-benzene (0.35), 1-(2,4,6-trichloro-3,5-difluorophenyl)naphthalene (0.32); 2-(2,4,6-trichloro-3,5-difluorophenyl)naphthalene (0.11). 2-(2,4,6-Trichloro-3,5-difluorophenyl)-naphthalene was isolated from the residue after passing it through a short column of silica with ether-pentane and repeated recrystallization from ethanol, mp 98-99 °C; IR (KBr) 3046, 1437, 1415, 1400, 806, 787, 746, 726, 640 cm⁻¹; ¹H NMR (CDCl₃) & 7.51(m, 3H), 7.91(m, 4H). The amount of unreacted diazonium salt was determined to be <0.01 mmol, 1%. Mesitylene. 2,4,6trichloro-3,5-difluorobenzene (0.34); 2,4,6-trichloro-3,5-difluoro-2',4',6'-trimethylbiphenyl (0.60).⁵⁴ The amount of unreacted diazonium salt was <0.01 mmol, 1 %. The 3,5difluoro-2',4',6'-trimethylbiphenyl was isolated as colorless crystals (163 mg, 49 %) after passing the residue through a short column of silica with ether/pentane, recrystallization from methanol and sublimation at 0.3 torr.° 3,5-Dinitrobenzenediazonium tetrafluoroborate. Naphthalene: m-dinitrobenzene (0.01), 1-(3,5-dinitrophenyl)-

naphthalene (0.75 mmol, 75 %),° 2-(3,5-dinitrophenyl)naphthalene (0.15 mmol, 15 %),° along with the excess naphthalene. 1-(3,5-Dinitrophenyl)naphthalene was isolated as yellow needles (154 mg, 53 %) after repeated recrystallization of the residue from a mixture of p-xylene and chloroform mixture. The combined aqueous phases were treated with a solution of potassium iodide (1.66 g, 10.0 mmol) and iodine (254 mg, 1.00 mmol) in water (20 mL) and kept overnight at room temperature. A thiosulfate solution was added to remove the excess iodine, and the resulting yellowish mixture was extracted with chloroform (3 x 20 mL). Found: 3,5-dinitroiodobenzene (0.05 mmol, 5 %), identified by the comparison with an authentic sample.^c The amount of 3.5dinitroiodobenzene thus determined was assumed to be equal to the amount of unreacted diazonium salt. With diiodomethane. Diiodomethane (268 mg, 80.5 µL, 1.00 mmol) was added to the reaction mixture prior to photolysis. 3,5-dinitroiodobenzene (0.08) and 1-(3,5-dinitrophenyl)naphthalene (0.02. The amount of unreacted diazonium salt was 0.90 mmol, 90 %. With carbon tetrabromide. Carbon tetrabromide (332 mg, 1.00 mmol) was added to the reaction mixture prior to photolysis. The reaction mixture was contained in an ice-water filled Dewar during the photolysis. 3,5-dinitrobromobenzene (0.13), 1-(3,5dinitrophenyl)naphthalene (0.25 mmol) and 2-(3,5-dinitrophenyl)naphthalene (0.06 mmol). The amount of unreacted diazonium salt was 0.49 mmol, 49 %. The reaction with 10 mmol of carbon tetrabromide was performed as in the previous experiment. 3.5dinitrobromobenzene (0.05) and 1-(3,5-dinitro-phenyl)naphthalene (0.02 mmol). The amount of unreacted diazonium salt was 0.90 mmol, 90 %. With Carbon Tetrachloride: Carbon tetrachloride (1.19 g, 746 µL, 10.0 mmol) was added to the reaction mixture prior

photolysis 1-(3,5-dinitro-phenyl)naphthalene (0.64) and 2-(3,5-dinitrophenyl)to naphthalene (0.11). The amount of unreacted diazonium salt was 0.18 mmol, 18 %. Mesitylene. m-dinitrobenzene (0.03); 2,4,6-trimethyl-3',5'-dinitrobiphenyl (0.70).^c The amount of unreacted diazonium salt was 0.25 mmol, 25 %. Removal of the solvent from the combined chloroform extracts left a yellow solid residue. 2,4,6-Trimethyl-3',5'dinitrobiphenyl (180 mg, 63 %) was repeatedly recrystallized from ethanol and sublimed at 0.3 torr, mp 162-163 °C (ethanol).° With diiodomethane. (268 mg, 1.00 mmol) 3,5dinitroiodobenzene (0.19);2,4,6-trimethyl-3',5'-dinitrobiphenyl(0.13); 2,4,6trimethyliodobenzene. The amount of unreacted diazonium salt was 0.62 mmol, 62 %. p-Dimethoxybenzene. m-dinitrobenzene (0.10 mmol, 0.10 %); 2,5-dimethoxyphenylacetonitrile (0.05), 2,5-dimethoxy-3',5'-dinitrobiphenyl (0.83).° The amount of unreacted diazonium salt was < 0.01 mmol, 1 %. Removal of the solvent from the combined chloroform extracts left an orange solid residue. With diiodomethane. (268 mg, 1.00 mmol) 3,5-dinitroiodobenzene (0.79); 2,5-dimethoxy-3',5'-dinitrobiphenyl (0.13). *m*-Xylene. m-dinitrobenzene (0.02), 2,6-dimethyl-3',5'-dinitrobiphenyl (0.25).° 2.4dimethyl-3',5'-dinitrobiphenyl (0.21). The amount of unreacted diazonium salt was 0.40 mmol, 40 %. 2,4-dimethyl-3',5'-dinitrobiphenyl was isolated as light yellow needles (27 mg, 10 %) after column chromatography of the residue on silica with ether/hexane and recrystallization from ethanol. The 2,4-isomer dimethyl-3',5'-dinitrobiphenyl was obtained in the form of a mixture with 25 % of as yellow needles from the enriched portions of the mother liquor left after the isolation of the previous isomer. 4-Nitrobenzenediazonium hexafluorophosphate. p-Dimethoxybenzene: nitrobenzene (0.08 mmol), 2,5-dimethoxy-phenylacetonitrile (0.04), 2,5-dimethoxy-4'-nitrobiphenyl (0.23).

Removal of the solvent from the combined chloroform extracts left an orange solid residue. 2,5-Dimethoxy-4'-nitrobiphenyl was isolated as shiny yellow needles (51 mg, 20 %) after passing the residue through a short column of silica with chloroform/hexane, recrystallization from methanol and sublimation at 0.3 torr, mp 116-117 °C (MeOH: lit. mp 116.5 °C). 4-Nitroiodobenzene (0.56 mmol, 56 %) was identified by the comparison with an authentic sample. The amount of 4-nitroiodobenzene was assumed to be equal to the amount of unreacted diazonium salt. With diiodomethane (268 mg, 1.00 mmol): nitrobenzene (0.03), 4-nitroiodobenzene (0.42); 2,5-dimethoxy-4'-nitrobiphenyl (0.04). amount of unreacted diazonium salt was 0.45 mmol, 45 %. The 3-Nitrobenzenediazonium hexafluorophosphate. p-Dimethoxybenzene: nitrobenzene (0.11); 2,5-dimethoxyphenyl-acetonitrile (0.05); 2,5-dimethoxy-3'-nitrobiphenyl (0.20) mmol).° The amount of unreacted diazonium salt was 0.60 mmol, 60 %. Removal of the solvent from the combined chloroform extracts left an orange solid residue. 2,5dimethoxy-3'-nitrobiphenyl was isolated as pale yellow needles (51 mg, 20 %) after passing the residue through a short column of silica with chloroform/hexane, recrystallization from methanol and sublimation at 0.3 torr, mp 83-84 °C (MeOH; lit,° mp 83 °C). 3,5-Bis-(Trifluoromethyl)benzenediazonium. *p*-Dimethoxvbenzene 2.5dimethoxy-3',5'-bis-(trifluoromethyl)biphenyl (0.36).° The amount of unreacted diazonium salt was 0.60 mmol, 60 %. Removal of the solvent from the combined chloroform extracts left a yellowish solid residue. 2,5-Dimethoxy-3',5'-bis-(trifluoromethyl)biphenyl was isolated as colorless crystals showing a blue fluorescence (112 mg, 32 %), after passing the residue through a short column of silica with ether/pentane, recrystallization from methanol and sublimation at 0.3 torr, mp 67-68 °C.° With

11

3',5'-bis-(trifluoromethyl)iodobenzene (0.53); 2.5diiodomethane (1.00 mmol): The amount of unreacted dimethoxy-3'5'-bis-(trifluoromethyl)-biphenyl (0.26). 4-Bromobenzenediazonium. pdiazonium salt was 0.09 mmol, 9 %. Dimethoxybenzene: bromobenzene (0.11), 2,5-dimethoxy-phenylacetonitrile (0.06), 4bromo-2',5'-dimethoxybiphenyl (0.16). The amount of unreacted diazonium salt was 0.70 mmol, 70 %. With Diiodomethane (1.00 mmol): 4-bromoiodobenzene (0.22); 4-bromo-2',5'-dimethoxybiphenyl (0.07). The amount of unreacted diazonium salt was 0.63 mmol, 4-Ethoxycarbonyl)benzenediazonium hexafluorophosphate. 2.6-Di-tert-63 %. butylpyridine (1.00 mmol) was added to these reactions prior to photolysis. *p*-Dimethoxybenzene: ethyl benzoate (0.45 mmol, 45 %), 2,5-dimethoxyphenylacetonitrile (0.05 mmol, 5 %), 2,5-dimethoxy-4'-(ethoxycarbonyl)-biphenyl (0.09 mmol, 9 %).° The amount of unreacted diazonium salt was 0.40 mmol, 40 %. With diiodomethane: (1.00 mmol): ethyl 4-iodobenzoate (0.37). The amount of unreacted diazonium salt was 0.58 mmol, 58 %. Bis-3,5-(ethoxycarbonyl)benzene-diazonium hexafluorophosphate p-Dimethoxybenzene 2,6-Di-tert-butyl-4-methyl-pyridine (205 mg, 1.00 mmol) was added prior to photolysis. diethyl isophthalate (0.29), 2,5-dimethoxyphenylacetonitrile (0.04 mmol, 4 %), 2,5-dimethoxy-3',5'-bis-(ethoxycarbonyl)-biphenyl (0.62).° The amount of unreacted diazonium salt was 0.01 mmol, 1 %.

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