Palladium-Catalyzed Cross-Coupling of Perfluoroalkenylzinc Reagents with Aryl Iodides. A New, Simple Synthesis of α,β,β-Trifluorostyrenes and the Stereoselective Preparation of 1-Arylperfluoropropenes

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Perfluoroalkenylzinc reagents [$CF_2{=}CFZnX$ (1), (*Z*)-$CF_3CF{=}CFZnX$ (2), and (*E*)-$CF_3CF{=}CFZnX$ (3); X = perfluoroalkenyl group or I (Br or I for 1)] coupled with aryl iodides in the presence of $Pd(PPh_3)_4$ (1-3 mol %) to give the corresponding arylalkenes. A series of substituted α,β,β-trifluorostyrenes were prepared in good yields. This method provides ready availability of these fluorinated styrenes, which were previously obtained with difficulty. For the first time, 1-arylperfluoropropenes were prepared stereoselectively. Palladium-catalyzed reactions of 2 with aryl iodides gave stereospecific (*E*)-1-arylperfluoropropenes, and the same procedure with 3 gave stereoselective *Z*/*E* ratios ranging from 98/2 to 92/8.

Introduction

Palladium-catalyzed cross-coupling is a useful method for the formation of carbon-carbon bonds.[1] We recently reported preliminary results of our studies of the coupling of perfluoroalkenylzinc reagents with aryl iodides in the presence of $Pd(PPh_3)_4$.[2] (See Scheme I.)

We showed that a wide variety of substituents could be tolerated at any position on the aromatic ring, with only acidic functions excluded. The perfluoroalkenylzinc reagents were simple to prepare and thermally stable.[3] The generation of the zinc reagent and subsequent reaction with aryl iodide/$Pd(PPh_3)_4$ were all carried out in the same reaction flask to provide an expedient one-pot synthesis.

Scheme I

$$R_fCF{=}CFZnX + ArI \xrightarrow{Pd(PPh_3)_4} R_fCF{=}CFAr$$

1a: R_f = F; X = Br
1b: R_f = F; X = I
2: $R_f = CF_3$ *trans* to Zn; X = (*Z*)-$CF_3CF{=}CF$ or I
3: $R_f = CF_3$ *cis* to Zn; X = (*E*)-$CF_3CF{=}CF$ or I

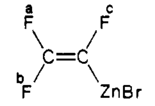
Experimental Section

Apparatus. Most reactions were carried out in an apparatus that consisted of a three-necked round-bottomed flask equipped with a water condenser topped with a glass tee. The extra necks were fitted with glass stoppers, or one was fitted with a rubber septum if no septum port was available. The glassware was assembled hot from the oven or flame-dried after assembly. The apparatus was flushed with and maintained under argon or nitrogen. A Teflon-coated magnetic stirbar was placed in the flask, and stirring was effected with a magnetic stirrer. All heating was done with an oil bath. In this section, the size of the flask shall be indicated for this standard glassware configuration unless a different apparatus was used.

Most products were isolated via flash chromatography. Preliminary tests of reaction mixtures were carried out on silica gel and alumina TLC plates (in hexane), and whichever type of material allowed the product spots to move the farthest was chosen as the column packing.

NMR spectra were generated on a JEOL FX90Q ($CDCl_3$, $CFCl_3$, or TMS internal references). IR spectra were obtained on a Beckman Acculab spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985 GC/MS system at 70 eV.

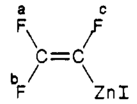
Generation of Trifluoroethylenylzinc Reagent in DMF (1a). A 100-mL three-necked round-bottomed flask containing a magnetic stirbar was fitted with a dry ice condenser. Into the flask were placed 4.6 g of activated zinc powder (71 mmol) and 50 mL of DMF. From a tared cylinder was added 16.1 g of $CF_2{=}CFBr$ (100 mmol) through the dry ice condenser (dry ice/isopropyl alcohol) inlet as the reaction mixture was stirred. An exotherm took place, and the mixture turned brown. The reaction mixture was stirred at room temperature for 3 h. The excess $CF_2{=}CFBr$ was removed in vacuo beginning at slightly reduced pressure and ending at 1 mmHg; then the mixture was heated to 60 °C until DMF began to distill. The zinc reagent was transferred to the standard apparatus equipped with a 100-mL flask. The yield was estimated to be 77% by ^{19}F NMR analysis vs benzotrifluoride ($PhCF_3$). The ^{19}F NMR spectrum shows the following:



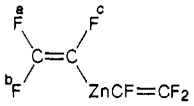
a, -96.3 ppm (dd)
b, -130.4 ppm (dd)
c, -194.7 ppm (dd)
J_{ab} = 93 Hz, J_{ac} = 33 Hz, J_{bc} = 105 Hz

The bis reagent, $Zn(CF{=}CF_2)_2$, is often detected as small shoulders on these peaks in the upfield direction. The ratio mono/bis is usually ~90/10 for this zinc reagent in DMF.

Preparation of $CF_2{=}CFZnI$ (1b) in THF. Into a standard apparatus equipped with a 20-mL flask were placed 1.5 g of activated zinc powder (22 mmol) and 10 mL of dry THF; then, 1.8 g of iodotrifluoroethylene (8.7 mmol) was added via syringe. The reaction mixture was stirred for 4 h, and ^{19}F NMR analysis showed that no vinyl iodide remained. The yield was determined to be 91% by ^{19}F NMR analysis (vs $PhCF_3$). The zinc reagent exhibited two sets of signals:



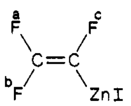
a, -94.1 ppm (dd)
b, -128.4 ppm (dd)
c, -194.8 ppm (dd)
J_{ab} = 87 Hz, J_{ac} = 33 Hz, J_{bc} = 106 Hz



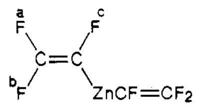
a, -94.5 ppm (dd)
b, -129.7 ppm (dd)
c, -195.9 ppm (dd)
J_{ab} = 89 Hz, J_{ac} = 34 Hz, J_{bc} = 105 Hz

mono/bis ≈ 70/30

This procedure is also applicable to formation of the zinc reagent in triglyme (TG). In TG, the ^{19}F NMR spectrum shows the following:



a, -96.0 ppm (dd)
b, -129.5 ppm (dd)
c, -194.5 ppm (dd)
J_{ab} = 91 Hz, J_{ac} = 33 Hz, J_{bc} = 106 Hz



a, -96.2 ppm (dd)
b, -130.7 ppm (dd)
c, -195.8 ppm (dd)
J_{ab} = 93 Hz, J_{ac} = 33 Hz, J_{bc} = 104 Hz

mono/bis ≈ 70/30

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[3] Hansen, S. W.; Spawn, T. S.; Burton, D. J. *J. Fluorine Chem.* **1987**, *35*, 415. Burton, D. J.; Hansen, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 4229.

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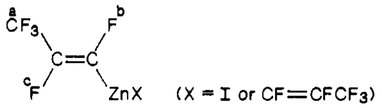
Generation of (*Z*)-$CF_3CF{=}CFZnI$ (2) in Triglyme. A dry 100-mL one-necked round-bottomed flask with septum port was charged with 5.0 g of activated zinc powder (76 mmol) and a magnetic stirbar. Dry TG (40 mL) was added via syringe, followed by 12.9 g of (*Z*)-$CF_3CF{=}CFI$ (50 mmol). The reaction mixture was stirred at room temperature for 1 h, during which time there was an exothermic reaction. The ^{19}F NMR yield of this reaction was typically >95%. The ^{19}F NMR spectrum shows the following:

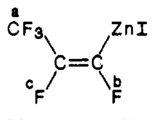


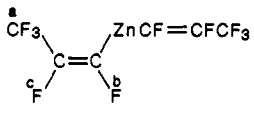
a, −67.6 ppm (2 overlapped dd)
b, −148.0 ppm (2 overlapped dq)
c, −180.8 ppm (2 overlapped dq)
mono/bis ≈ 70/30

Addition of ca. 50 mg of $ZnCl_2$ converted the mono/bis mixture to all-mono zinc reagent, and the ^{19}F NMR spectrum of mono reagent 2 is as follows:

a, −67.8 ppm (dd)
b, −148.4 ppm (dq)
c, −180.5 ppm (dq)
J_{ab} = 23 Hz, J_{ac} = 13 Hz, J_{bc} = 110 Hz

Preparation of (*E*)-$CF_3CF{=}CFZnI$ (3) in Triglyme. A dry 100-mL three-necked round-bottomed flask was equipped with the standard apparatus and charged with 5.3 g of activated zinc powder (81 mmol), 30 mL of dry TG, and 7.3 g of (*E*)-$CF_3CF{=}CFI$ (28 mmol). The reaction mixture was stirred at room temperature overnight; however, the reaction was essentially complete as soon as the exotherm subsided, which was usually less than 1 h. The ^{19}F NMR spectrum shows the following:





a, −69.5 ppm (dd)
b, −134.5 ppm (q)
c, −153.5 ppm (q)
J_{ab} = 9 Hz, J_{ac} = 16 Hz

a, −69.1 ppm (dd)
b, −133.7 ppm (q)
c, −153.8 ppm (q)
J_{ab} = 9 Hz, J_{ac} = 16 Hz

mono/bis ≈ 30/70

Yields of zinc reagent were typically greater than 90% as determined by ^{19}F NMR vs $PhCF_3$.

Preparation of $PhCF{=}CF_2$ (4). **1a** was prepared as previously described from 16.1 g of $CF_2{=}CFBr$ (100 mmol) and 4.6 g of activated zinc powder in 50 mL of DMF. The zinc reagent was transferred to a 200-mL flask; then 1.0 g of $Pd(PPh_3)_4$ (1.5 mol %) and 11.4 g of iodobenzene (55 mmol) were added, and the reaction mixture was stirred and heated at 65–75 °C for 3 h. The pot contents were flash distilled at <1 mmHg/room temperature, and approximately 15 mL of distillate was collected. The distillate was poured into 300 mL of ice water. After stirring with a glass rod, the upper aqueous layer was decanted and the organic layer was collected with a pipet. The organic material was dried over P_2O_5 and distilled through a 6-in. Vigreaux column at 59 °C/44 mmHg (ref 6: 68 °C/75 mm) to give 6.6 g of $PhCF{=}CF_2$, >96% pure by GLPC, for a 74% isolated yield. The ^{19}F NMR data is given in Table II. The ^1H NMR spectrum displays a broad singlet at 7.5 ppm. IR: $CF{=}CF_2$ stretch at 1750 (m), 1590 (s), 1495 (m), 1445 (m), 1280 (s), 1140 (s), 1100 (m), 1070 (m), 1035 (w), 980 (m), 910 (w), 750 (m), 680 cm^{-1} (m). Mass spectrum: $C_8F_3H_5^+$, 158 (100.0%); $C_7FH_5^+$, 108 (21.1); $C_7FH_4^+$, 107 (28.9). ^{13}C (ppm): $=CF_2$, 154.9 (ddd), J = 289.0, 281.9, and 50.7 Hz; $=CF$, 129.7 (ddd), J = 248.6, 45.5, and 19.4 Hz; *p*-C, 130.0 (s); *m*-C, 129.7 (s); Q-C, 127.9 (dd), J = 21.8 and 6.1 Hz; *o*-C, 125.4 (dd), J = 10.0 and 5.0 Hz.

Preparation of *o*-$NO_2C_6H_4CF{=}CF_2$ (5). **1a** was generated as usual from 15.8 g of $CF_2{=}CFBr$ (95 mmol) and 4.9 g of activated zinc powder in 75 mL of DMF. To the zinc reagent were added 12.5 g of *o*-nitroiodobenzene (50 mmol) and 1.4 g of $Pd(PPh_3)_4$ (2.4 mol %), and the reaction mixture was stirred at 65 °C overnight. Following cooling, the reaction mixture was dissolved in 200 mL of methylene chloride and washed with water (5 × 100 mL). The methylene chloride fractions were combined and evaporated. The brown tar that remained was dissolved in hexane and adsorbed onto 10 g of alumina (MCB, 80–200 mesh, neutral). The hexane was evaporated, and the alumina was loaded onto a flash chromatography column (2.3-cm o.d., 50-cm length, 6 in. of alumina) and eluted with 1 L of hexane in 100-mL fractions. The product was almost all in the second 100-mL fraction. Fractions 2–6 were shown to contain product by TLC. These combined fractions were evaporated to give 7.5 g (73% yield) of an orange oil, which was air-sensitive. Hydroquinone was added to inhibit polymerization. The ^1H NMR spectrum in acetone-d_6 shows unsymmetrical aromatic proton signals at 8.1 and 7.8 ppm. The ^{19}F NMR data is given in Table II. IR: 1780 ($CF{=}CF_2$, s), 1540 and 1355 (NO_2, s), 1300 (s), 1265 (m), 1160 (s), 1145 (s), 1100 (w), 995 (s), 860 (m), 795 (m), 760 cm^{-1} (m). Mass spectrum: $C_8F_3H_4NO_2^+$, 203 (19.7); $C_7FH_4NO_2^+$, 153 (100.0); $C_7F_3H_4^+$, 145 (84.4); $C_7FH_4NO^+$, 137 (43.4); $C_7F_2H_3^+$, 125 (27.9); $C_7F_2H^+$, 123 (42.6); $C_5H_3NO_2^+$, 109 (60.7); $C_7FH_4^+$, 107 (37.3); $C_3F_3H_2^+$, 95 (98.4); F_3NO^+, 87 (23.0); $C_2F_3^+$, 81 (32.8); $C_6H_3^+$, 75 (32.0). ^{13}C NMR (ppm): $=CF_2$, 154.3 (ddd), J = 288.9, 277.4, and 48.9 Hz; Ar C's, 148.6, 134.8, 133.3, 132.7, and 126.1 (all s); $=CF$, 126.6 (ddd), J = 231.2, 51.7, and 22.8 Hz; Q-C, 121.5 (dd), J = 16.2 and 4.0 Hz.

Table I. Isolated Yields of α,β,β-Trifluorostyrenes

$$CF_2{=}CFZnX + ArI \xrightarrow[\substack{1\text{–}3\ \text{mol}\ \%\\ 1\text{–}10\ \text{h},\ 60\text{–}80\ °\text{C}}]{Pd(PPh_3)_4} CF_2{=}CFAr$$

no.	α,β,β-trifluorostyrene	solvent	isolated yield, %
4	$C_6H_5CF{=}CF_2$	DMF	74
5	*o*-$NO_2C_6H_4CF{=}CF_2$	DMF	73
6	*p*-$MeOC_6H_4CF{=}CF_2$	THF	61
7	*o*-$(CH_3)_2CHC_6H_4CF{=}CF_2$	THF	70
8	2,5-$Cl_2C_6H_3CF{=}CF_2$	DMF	75
9	*o*-$CF_3C_6H_4CF{=}CF_2$	TG[a]	73
10	*m*-$NO_2C_6H_4CF{=}CF_2$	TG[a]	81
11	*p*-$ClC_6H_4CF{=}CF_2$	DMF	77
12	*p*-$CF_2{=}CFC_6H_4CF{=}CF_2$[b]	DMF	56

[a] TG = triglyme. [b] Room temperature for 2 days.

Preparation of *p*-$CH_3OC_6H_4CF{=}CF_2$ (6). **1b** was prepared as usual from 13.5 g of $CF_2{=}CFI$ (65 mmol) and 5 g of activated zinc powder (85 mmol) in 40 mL of THF in the standard apparatus equipped with a 100-mL flask. This zinc reagent was transferred via a double-ended needle into a clean, dry 100-mL flask in a standard apparatus, 11.7 g of *p*-iodoanisole (50 mmol) and 1.1 g of $Pd(PPh_3)_4$ (1.8 mol %) were added, and the reaction mixture was stirred and heated at 60 °C for 1 h. The THF was removed in vacuo at room temperature/1 mmHg, the residue was washed with hexane (5 × 20 mL), and these portions were combined and rotary evaporated with 12 g of alumina. This alumina sample was loaded onto a 5 cm o.d. × 50 cm flash chromatography column that contained 6 in. of alumina. Hexane was the eluent, and 100-mL fractions were taken. The progress of the elution was monitored by TLC, and all the active fractions were combined and rotary evaporated to give 5.8 g, which was shown by GLPC analysis to be a 91:7:2 mixture of **6**, the dimer of **6**, and unidentified material for a combined yield of 61%. The ^{19}F NMR spectrum is reported in Table II. The ^1H NMR spectrum shows a singlet at 3.7 ppm (3 H) and an AB dd centered at 7.1 ppm (4 H). IR: 1750 ($CF{=}CF_2$, s), 1600 (s), 1570 (w), 1505 (s), 1455 (m), 1175 (s), 1140 (s), 1105 (s), 1030 (s), 1010 (m), 975 (s), 825 cm^{-1} (s). Mass spectrum: $C_9F_3H_7O^+$, 188 (9.2); $C_7F_3H_5^+$, 145 (100.0); 125 (64.9); 119 (26.0); 107 (31.3); 106 (29.0); 99 (67.2); 95 (53.4); 87 (26.0); 81 (35.1); 76 (26.7); 75 (97.7); 74 (40.5); 69 (96.9); 68 (50.4); 63 (34.4); 62 (34.4); 61 (26.0); 57 (34.4); 51 (38.2); 50 (68.7). ^{13}C NMR (ppm): *C*OMe, 161.4 (s); $=CF_2$, 154.6 (ddd), J = 287.5, 279.9, and 50.9 Hz; $=CF$, 130.0 (ddd), J = 225.4, 46.6, and 19.2 Hz; *o*-C, 127.1 (dd), J = 8.9 and 5.2 Hz; Q-C, 120.0 (dd), J = 22.6 and 6.3 Hz; *m*-C, 115.2 (s); CH_3O, 55.6 (s).

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(5) Dmowski, W. *J. Fluorine Chem.* **1981**, *18*, 25.
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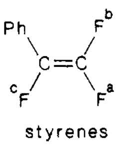
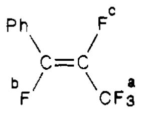
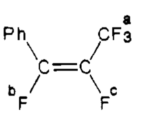
Table II. ^{19}F NMR Data of Isolated Compounds


styrenes


(*E*)-1-arylperfluoropropenes


(*Z*)-1-arylperfluoropropenes

		ppm			Hz		
no.	subst	a	b	c	J_{ab}	J_{ac}	J_{bc}
			Styrenes[a]				
4	H[b]	−101.4	−115.8	−176.0	73	32	110
5	o-NO_2[c]	−102.2	−117.8	−165.4	74	30	115
6	p-MeO[c]	−104.7	−119.1	−175.2	81	31	110
7	o-$(CH_3)_2CH$[d]	−104.8	−119.7	−156.6	79	29	118
8	2,5-Cl_2[d]	−101.6	−115.4	−165.6	70	29	116
9	o-CF_3[d,e]	−102.7	−117.8	−159.1	73	32	117
10	m-NO_2[c]	−98.4	−112.5	−178.0	66	33	110
11	p-Cl[b]	−100.2	−114.3	−176.6	72	33	110
12	p-$CF_2{=}CF$[b]	−87.9	−114.3	−178.4	70	33	108
			(*E*)-1-Arylperfluoropropenes[f]				
13	H[g]	−68.0	−145.7	−171.1	22	10	132
14	p-CH_3[g]	−67.7	−146.4	−172.4	22	12	130
15	p-Cl[g]	−67.8	−146.6	−169.9	22	9	132
16	m-NO_2[g]	−68.1	−146.7	−167.4	22	10	132
			(*Z*)-1-Arylperfluoropropenes[h]				
17	H[g]	−66.7	−108.1	−157.0	7.8	13.2	10.7
18	p-CH_3[g]	−66.6	−107.9	−157.2	7	12	12
19	p-Cl[b]	−65.8	−108.1	−154.9	8	13	9

[a] All signals are doublets of doublets unless otherwise indicated. [b] Acetone-d^6. [c] DMF. [d] THF. [e] o-CF_3 at −61.7 ppm (d), $J(o\text{-}CF_3\text{-}F_c)$ = 10 Hz, c is ddq. [f] a is dd, b is dq, c is dq. [g] TG. [h] a is dd, b is qd, c is qd.

Preparation of *o*-$(CH_3)_2CHC_6H_4CF{=}CF_2$ (7). **1b** was prepared as usual from 7.4 g of $CF_2{=}CFI$ (35 mmol) and 3.3 g of activated zinc (50 mmol) in 30 mL of THF in the standard apparatus equipped with a 50-mL flask. The reaction with 4.9 g of *o*-isopropyliodobenzene (20 mmol) was carried out with 0.57 g of $Pd(PPh_3)_4$ (2.5 mol %) at 80 °C overnight with stirring. The THF was removed under vacuum; however, TLC showed that product was present in the distillate. The distillate was recombined with the pot residue, and the reaction mixture was rotary evaporated with 50 mL of hexane and 8 g of silica gel (60–200 mesh). The evaporated material was loaded onto a 3.5 cm o.d. × 45 cm flash chromatography column with 6 in. of silica gel (60–200 mesh), and hexane was used as the eluent. The fraction that contained the product (by TLC) was evaporated to give 2.8 g 7 for a 70% yield (98% pure by GLPC). The ^{19}F NMR data is reported in Table II. ^1H NMR analysis showed signals at 1.24 [6 H, d, $J(CH_3\text{-}H)$ = 6.9 Hz], and 3.13 ppm [1 H, heptet of doublets, $J(H\text{-}CH_3)$ = 6.9 Hz, $J^5(H\text{-}F_c)$ = 2.4 Hz] and two multiplets centered at 7.4 ppm (4 H). IR: 1780 ($CF{=}CF_2$, s), 1465 (m), 1140 (s), 1100 (m), 1045 (m), 995 (s), 870 cm^{-1} (s). Mass spectrum: $C_{11}F_3H_{11}^+$, 200 (4.2); 165 (51.1); 164 (28.9); 151 (23.3); 145 (30.1); 133 (52.9); 129 (100.0); 128 (20.6); 116 (28.2); 115 (79.9); 107 (26.3); 81 (20.3); 75 (27.3); 69 (66.5); 63 (30.3); 51 (49.6); 50 (22.3).

Preparation of 2,5-$Cl_2C_6H_3CF{=}CF_2$ (8) in DMF. **1a** was prepared as usual from 22.2 g of $CF_2{=}CFBr$ (138 mmol) and 8.3 g of activated zinc (127 mmol) in 120 mL of DMF in a 250-mL flask with a dry ice/isopropyl alcohol condenser under a flow of nitrogen. The excess vinyl bromide and approximately 20 mL of DMF were removed in vacuo to give a solution that was approximately 1.3 M **1a**, and 104 mL of this reagent was used for this experiment. The zinc reagent was placed in a standard apparatus equipped with a 100-mL flask. Then 2,5-dichloroiodobenzene (10.9 g, 40 mmol) and $Pd(PPh_3)_4$ (0.86 g, 1.8 mol %) were added to the zinc reagent, and the mixture was heated at 75 °C for 2 days with stirring. The product was extracted from the reaction mixture with hexane (5 × 50 mL), and the hexane solution was washed with water (5 × 100 mL). The hexane solution was evaporated with 10 g of silica gel (Merck, grade 60) and chromatographed in the usual manner on 6 in. of silica gel (Merck, grade 60) in a 5 cm o.d. × 50 cm long flash chromatography column with hexane as eluent to give 6.8 g of product for a 75% yield. The ^{19}F NMR data is given in Table II. The ^1H NMR spectrum shows signals at 7.6 (2 H) and 7.7 ppm (1 H). IR: 1785 ($CF{=}CF_2$, m), 1480 (m), 1410 (m), 1335 (w), 1305 (s), 1265 (w), 1170 (s), 1115 (m), 1085 (m), 1020 (m), 905 (w), 835 (w), 820 cm^{-1} (w). Mass spectrum: $C_8F_3H_3Cl_2^+$, 226 (2.2); 156 (20.7); 141 (24.0); 106 (22.3); 105 (25.6); 99 (25.2); 87 (38.9); 86 (44.9); 85 (49.8); 80 (32.9); 75 (29.6); 74 (52.0); 73 (38.9); 69 (100.0); 62 (25.0); 61 (36.1); 60 (29.4); 56 (20.0); 50 (53.3). ^{13}C NMR (ppm): $=CF_2$, 154.4 (ddd), J = 290.4, 278.8, and 49.2 Hz; Ar C's, 133.7, 133.2, 132.4, and 132.2 (all s); $CCF{=}$, 127.9 (dd), J = 19.3 and 3.8 Hz; $CF{=}$, 126.1 (ddd), J = 232.5, 52.3, and 21.9 Hz.

Preparation of *o*-$CF_3C_6H_4CF{=}CF_2$ (9). **1b** was prepared as usual from 10.4 g of $CF_2{=}CFI$ (50 mmol) and 5.2 g of activated zinc (80 mmol) in 25 mL of TG in the standard apparatus equipped with a 50-mL flask. To the zinc reagent were added 10 g of *o*-iodobenzotrifluoride (36 mmol) and 1 g of $Pd(PPh_3)_4$ (2.4 mol %), and the mixture was stirred at 70 °C overnight. The reaction mixture was flash distilled at 2.5 mmHg/80 °C pot temperature to give 5.9 g of 98% pure (by GLPC) 9 for a 73% yield. The ^{19}F NMR data is listed in Table II. The ^1H NMR spectrum shows a multiplet at 7.9 ppm. IR: 1785 ($CF_2{=}CF$, m), 1325 (s), 1320 (s), 1275 (m), 1190 (s), 1160 (s), 1120 (m), 1080 (m), 1145 (m), 995 (m), 875 cm^{-1} (m). Mass spectrum: $C_9F_6H_4^+$, 226 (88.8); $C_9F_5H_4^+$, 207 (21.7); $C_8F_4H_4^+$, 176 (100.0); $C_8F_3H_4^+$, 157 (44.4); $C_7F_2H_4^+$, 126 (24.4); $C_7FH_4^+$, 107 (24.0). ^{13}C NMR (ppm): $=CF_2$, 154.4 (ddd), J = 289.0, 276.2, and 49.6 Hz; *m*-C, 133.6 (s); *o*-C to $CCF{=}CF_2$, 132.7 (d), J = 2.1 Hz; CCF_3, 131.0 (q), J = 30.9 Hz; *o*-C to CCF_3, 127.9 (q), J = 4.7 Hz; $=CF$, 126.8 (ddd), J = 233.7, 52.9, and 21.6 Hz; $CCF{=}CF_2$, 125.2 (d), J = 21.9 Hz; CF_3, 124.7 (q), J = 272.2 Hz.

Preparation of *m*-$NO_2C_6H_4CF{=}CF_2$ (10) in Triglyme. **1b** was prepared as usual from 17.1 g of $CF_2{=}CFI$ (82 mmol) and 10 g of activated zinc powder (153 mmol) in 70 mL of TG in a standard apparatus equipped with a 200-mL flask. Then, 17.4 g of *m*-nitroiodobenzene (70 mmol) and 0.9 g of $Pd(PPh_3)_4$ (1 mol %) were added to the reaction mixture, and the mixture was stirred overnight at room temperature. The ratio (^{19}F NMR) of styrene to zinc reagent was 46/54. The reaction mixture was then heated at 60 °C for 8 h, which effected completion of the reaction. The reaction mixture was poured into 150 mL of hexane and triturated. The hexane was decanted, and the trituration was repeated twice with fresh hexane. The combined hexane fractions were washed with water (5 × 100 mL) and then evaporated with 20 g of 60–200-mesh silica gel. On a 3 cm o.d. × 50 cm long flash chromatography column with 6 in. of 60–200-mesh silica gel, the product was eluted with 1 L of hexane in 100-mL fractions. The product eluted in five fractions, which were evaporated to give 11.5 g of **10**, >95% pure by GLPC, in 81% yield. The ^{19}F NMR data is found in Table II. The ^{1}H NMR spectrum shows an asymmetric multiplet centered at 8.0 ppm. IR: 1760 ($CF{=}CF_2$, s), 1540 and 1360 (NO_2, s), 1300 (s), 1285 (s), 1165 (s), 1110 (m), 1090 (m), 1030 (m), 1015 (m), 905 (w), 875 (w), 810 (w), 740 (m), 680 cm^{-1} (m). Mass spectrum: $C_8F_3H_4NO_2^+$, 203 (100.0); $C_8F_3H_4O^+$, 157 (57.9); $C_8F_2H_3^+$, 137 (88.2); $C_7FH_4^+$, 107 (36.0). ^{13}C NMR (ppm): $=CF_2$, 155.3 (ddd), J = 292.0, 284.0, and 49.2 Hz; CNO_2, 149.5 (s); C para to vinyl group, 131.4 (s); C ortho to both groups, 130.9 (dd), J = 11.3 and 5.5 Hz; $CCF{=}CF_2$, 129.7 (dd), J = 23.2 and 7.2 Hz; $=CF$, 128.6 (ddd), J = 226.5, 45.2, and 21.6 Hz; C meta to NO_2, 124.5 (s); C para to NO_2, 119.7 (dd), J = 11.2 and 6.9 Hz.

Preparation of *p*-$ClC_6H_4CF{=}CF_2$ (11). **1a** was prepared as usual from 35.3 g of $CF_2{=}CFBr$ (219 mmol) and 10 g of activated zinc (153 mmol) in 100 mL of DMF. Following removal of excess vinyl bromide in vacuo, the zinc reagent was transferred to a standard apparatus equipped with a 200-mL flask, 11.9 g of *p*-chloroiodobenzene (49.9 mmol) and 0.6 g of $Pd(PPh_3)_4$ (1 mol %) were added, and the reaction mixture was stirred and heated at 60–75 °C overnight. The reaction mixture was triturated with hexane (5 × 100 mL), and the combined hexane extracts were washed with water (5 × 100 mL). The organic solution was evaporated with 12 g of silica gel (60–200 mesh) and chromatographed on silica gel (Merck, grade 60) in a 3.5 cm o.d. × 50 cm long flash chromatography column with hexane as eluent to give, after evaporation, 9.6 g of **11** for a 77% yield, 96% pure by GLPC. The ^{19}F NMR data is given in Table II. The ^{1}H NMR spectrum shows a singlet at 7.4 ppm. IR: 1765 ($CF{=}CF_2$, vs), 1605 (m), 1505 (s), 1415 (m), 1345 (m), 1305 (vs), 1195 (m), 1165 (vs), 1135 (s), 1110 (s), 995 (s), 835 cm^{-1} (s). Mass spectrum: $C_8F_3H_4{}^{37}Cl^+$, 194 (33.0); $C_8F_3H_4{}^{35}Cl^+$, 192 (100.0); $C_8F_3H_4^+$, 157 (50.7); $C_8F_3H^+$, 137 (24.9); $C_7FH_4^+$, 107 (55.0). ^{13}C NMR (ppm): $=CF_2$, 154.7 (ddd), J = 289.4, 282.2, and 49.5 Hz; CCl, 135.6 (s); *m*-C's, 129.8 (s); $=CF$, 129.1 (ddd), J = 226.2, 45.2, and 20.3 Hz; *o*-C's, 126.7 (dd), J = 10.5 and 6.1 Hz; Q-C, 126.5 (dd), J = 22.9 and 7.0 Hz.

Preparation of *p*-$CF_2{=}CFC_6H_4CF{=}CF_2$ (12). **1a** was prepared as usual from 35.6 g of $CF_2{=}CFBr$ (221 mmol) and 9.8 g of activated zinc powder (150 mmol) in 150 mL of DMF. Following removal of excess $CF_2{=}CFBr$ and ca. 20 mL of DMF in vacuo, 100 mL of this reagent (ca. 120 mmol) was transferred via double-ended needle into a standard apparatus equipped with a 200-mL flask; 9.9 g of *p*-diiodobenzene (30 mmol) and 0.19 g of $Pd(PPh_3)_4$ (0.6 mol %) were added. The reaction mixture was stirred at room temperature for 8 h. A 44/56 ratio of styrenes and zinc reagent was revealed by ^{19}F NMR analysis. The styrenes were presumably mono- and bissubstituted products. The reaction mixture was stirred for an additional $1^1/_2$ days. The reaction mixture was triturated with hexane (5 × 50 mL), and the hexane portions were combined and washed with water (5 × 100 mL). The hexane solution was evaporated with 10 g of silica gel (Merck, grade 60). Flash chromatography was effected on 6 in. of silica gel (Merck, grade 60) on a 5 cm o.d. × 50 cm long column. The fraction that showed only one spot by TLC was rotary evaporated to give 4 g of 94% pure *p*-bis(trifluorovinyl)benzene (56% yield). As soon as all data was obtained for the product, it was immediately redissolved in 50 mL of hexane to prevent dimerization. After 1 week at room temperature, no significant dimerization could be observed by ^{19}F NMR analysis. When the product was allowed to stand neat, it turned to a gel overnight. The ^{19}F NMR spectrum of *p*-$CF_2{=}CFC_6H_4CF{=}CF_2$ is given in Table II. The ^{1}H NMR spectrum shows a singlet at 7.3 ppm (acetone-d_6, TMS). IR: 1750 ($CF{=}CF_2$, s), 1420 (w), 1295 (s), 1165 (s), 1120 (s), 1035 (m), 995 (s), 850 cm^{-1} (m). Mass spectrum: $C_{10}F_6H_4^+$, 238 (49.7); $C_9F_4H_3^+$, 187 (39.6); $C_6F_3H_4^+$, 169 (100.0); CF_3^+, 69 (31.2).

Preparation of (*E*)-$C_6H_5CF{=}CFCF_3$ (13). **2** was prepared as usual from 12.9 g of (*Z*)-$CF_3CF{=}CFI$ (50 mmol) and 5.0 g of activated zinc powder (76 mmol) in 40 mL of TG in a 100-mL flask equipped with the standard apparatus. Iodobenzene (8.2 g, 40 mmol) was added via syringe followed by 0.3 g of $Pd(PPh_3)_4$ (0.5 mol %). The reaction mixture was heated at 75 °C for 4 h. The reaction mixture was flash distilled at >1 mmHg/oil bath temperature at 70 °C. The distillate was poured into 200 mL of ice/water. The organic material was removed with a pipet, washed twice with ice/water, and dried over P_2O_5. Distillation through a 6-in. Vigreaux column at 52–53 °C/15 mmHg (bp 148 °C, ref 5) gave 6.6 g of clear liquid, with a GLPC purity of >98%. The yield was 80% based on iodobenzene. The ^{19}F NMR data is given in Table II (cf. ref 5). The ^{1}H NMR spectrum shows a singlet at 7.6 ppm. IR: 1710 ($CF{=}CF$, w) (cf. ref 5), 1430 (w), 1340 (s), 1265 (m), 1160 (s), 1070 (s), 845 (w), 740 (w), 670 cm^{-1} (w). Mass spectrum: $C_9F_5H_5^+$, 208 (100.0); $C_9F_4H_5^+$, 189 (23.9); $C_9F_3H_4^+$, 169 (32.1); $C_8F_3H_5^+$, 158 (69.8); $C_8F_2H_5^+$, 139 (22.4); $C_8F_2H_4^+$, 138 (21.1); $C_8FH_4^+$, 119 (24.5).

Preparation of 2, Used To Prepare 14–16. **2** was generated in the usual manner from 21.0 g of (*Z*)-$CF_3CF{=}CFI$ (80 mmol) and 10.5 g of activated zinc powder (161 mmol) in 86 mL of TG in the standard apparatus equipped with a 200-mL flask. Aliquots of this 0.9 M zinc reagent were utilized in the next three preparations.

Preparation of (*E*)-*p*-$CH_3C_6H_4CF{=}CFCF_3$ (14). Approximately 30 mL of the 0.9 M solution of **2** was transferred to a standard apparatus equipped with a 50-mL flask. To this flask were added 7.6 g of *p*-iodotoluene (35 mmol) and 0.25 g of $Pd(PPh_3)_4$ (0.6 mol %). This reaction mixture was heated to 80 °C for 8 h with stirring. The reaction mixture was triturated with hexane (5 × 50 mL), and the hexane solution was washed with water (5 × 100 mL). The organic layer was evaporated with 12 g of silica gel (Merck, grade 60). The product was then chromatographed on 6 in. of silica gel (Merck, grade 60) in a 3 cm o.d. × 50 cm long flash chromatography column with 1 L of hexane. The fractions were collected in 25-mL test tubes, and fractions 2–7 contained product, which upon removal of hexane gave 5.1 g of liquid, which was 92% **14** by GLPC for a yield of 65%. The ^{19}F NMR data is given in Table II (cf. ref 5). ^{1}H NMR (ppm): s at 2.4 (3 H), AB dd at 7.5 (4 H). IR: 1705 ($CF{=}CF$, w) (cf. ref 5), 1375 (s), 1295 (m), 1215 (s), 1175 (s), 1155 (s), 1095 (m), 880 (w), 830 cm^{-1} (w). Mass spectrum: $C_{10}F_5H_7^+$, 222 (65.8); $C_9F_2H_7^+$, 153 (31.2); $C_9F_2H_5^+$, 151 (52.8); $C_9FH_6^+$, 133 (100.0); CF_3^+, 69 (27.2).

Preparation of (*E*)-*p*-$ClC_6H_4CF{=}CFCF_3$ (15). Approximately 25 mL of 0.9 M **2** was transferred to a standard apparatus equipped with a 100-mL flask, and 4.8 g of *p*-chloroiodobenzene (20 mmol) and 0.15 g of $Pd(PPh_3)_4$ (0.6 mol %) were added. The reaction mixture was stirred at 80 °C for 8 h. Flash chromatography in the same manner as described in the previous experiment gave 3.0 g of >96% (GLPC) product for a 61% yield. The ^{19}F NMR spectrum is given in Table II (cf. ref 5). The ^{1}H NMR spectrum shows an AB pattern centered at 8.2 ppm. IR: 1700 ($CF{=}CF$, w) (cf. ref 5, 1708), 1600 (w), 1495 (m), 1410 (m), 1365 (s), 1290 (m), 1190 (vs), 1100 (s), 1120 (w), 865 (m), 845 cm^{-1} (m). Mass spectrum: $C_9F_5H_4{}^{37}Cl^+$, 244 (21.7), M + 2; $C_9F_5H_4{}^{35}Cl^+$, 242 (75.7), M^+; $C_9F_4H_4^+$, 207 (41.3); 192 (32.5); $C_9F_4H_3^+$, 187 (56.8); $C_8F_3H_4^+$, 157 (30.9); $C_8F_2H_4^+$, 138 (61.8); $C_8H_3^+$, 99 (23.6); CF_3^+, 69 (100.0).

Preparation of (*E*)-*m*-$NO_2C_6H_4CF{=}CFCF_3$ (16). Approximately 25 mL of 0.9 M **2** was transferred to a standard apparatus equipped with a 50-mL flask, and 5.0 g of *m*-iodonitrobenzene (20 mmol) and $Pd(PPh_3)_4$ catalyst (0.19 g, 0.8 mol %) were added. The reaction mixture was stirred and heated at 80 °C for 8 h. The ^{19}F NMR spectrum showed a 53/47 ratio of product and zinc reagent, so an additional 0.5 g of catalyst was added and the reaction mixture was heated for an additional 8 h at 80 °C. After this interval, the conversion was complete, as evidenced by ^{19}F NMR analysis. The reaction mixture was triturated with hexane (5 × 50 mL), and the combined organic layers were washed with water (5 × 100 mL). The organic solution and 12 g of alumina were evaporated and loaded onto a 5 cm o.d. × 50 cm long flash chromatography column filled with 6 in. of alumina. The product was eluted with 1 L of hexane. Fractions 4–7 (25-mL test tubes) showed two spots by TLC. The other fractions (8–20) that gave one spot were combined and rotary evaporated to give 4.1 g of >95% pure product by GLPC for an 80% yield. The ^{19}F NMR data is given in Table II. The ^{1}H NMR spectrum shows a singlet at 8.6 ppm (1 H, isolated ortho hydrogen), two doublets, J = 8.4 Hz at 8.4 ppm (1 H) and J = 8.0 Hz at 8.0 ppm (1 H), and a triplet, J = 8.0 Hz at 7.7 ppm (1 H).

IR: 1710 (CF═CF, w), 1540 (m), 1370 (s), 1305 (m), 1285 (m), 1215 (s), 1195 (s), 1160 (s), 1095 (m), 940 (w), 920 (w), 865 (w), 835 (w), 750 (w), 685 cm^{-1} (w). Mass spectrum: $C_9F_5H_4NO_2^+$, 253 (33.1); $C_9F_4H_3^+$, 187 (100.0); $C_8F_2H_4^+$, 138 (52.3); CF_3^+, 69 (28.5).

Preparation of (*Z*)-PhCF═CFCF$_3$ (17). 3 was generated in the usual manner from 7.6 g of (*E*)-CF_3CF═CFI (30 mmol) and 3.9 g of activated zinc (60 mmol) in 20 mL of TG in a 50-mL flask equipped with the standard apparatus. To the zinc reagent were added 5.1 g of iodobenzene (25 mmol) and 0.39 g of Pd(PPh_3)$_4$ (1.4 mol %), and the reaction mixture was heated at 60 °C for an hour and then for 10 h at 40 °C. The reaction mixture was flash distilled at 80 °C oil bath temperature/0.05 mmHg. The distillate was poured into 150 mL of ice water, and the aqueous upper layer was decanted. The organic layer was washed with ice water (2 × 100 mL). The organic material was dried over P_2O_5 and distilled at 43 °C/14 mmHg (139 °C, ref 4) to give 4.1 g of liquid that was 96% pure by GLPC for a yield of 82%. The *Z*/*E* ratio was 97/3 (by ^{19}F NMR). ^{19}F NMR data is given in Table II (cf. ref 5). The ^{1}H NMR spectrum shows a singlet at 7.6 ppm. IR: 1720 (CF═CF, w) (ref 5, 1725), 1365 (s), 1305 (m), 1215 (s), 1155 (s), 1070 (s), 930 (m), 780 (m), 705 cm^{-1} (m). Mass spectrum: $C_9F_5H_5^+$, 208 (80.1); $C_9F_4H_5^+$, 189 (44.6); $C_9F_4H_3^+$, 187 (33.6); $C_9F_3H_4^+$, 169 (100.0); $C_8F_3H_5^+$, 158 (96.0); $C_8F_2H_5^+$, 139 (38.2); $C_8F_2H_4^+$, 138 (48.9); $C_8FH_5^+$, 120 (21.7); $C_8FH_4^+$, 119 (41.3); $C_8H_3^+$, 99 (41.0); $C_3F_2^+$, 74 (20.7); CF_3^+, 69 (65.7).

Preparation of (*Z*)-*p*-CH$_3$C$_6$H$_4$CF═CFCF$_3$ (18). 3 was generated as usual from 7.3 g of (*E*)-CF_3CF═CFI (28 mmol) and 5.3 g of activated zinc powder (81 mmol) in 30 mL of TG in a 50-mL flask equipped with the standard apparatus. To the zinc reagent were added 4.4 g of *p*-iodotoluene (20 mmol) and 0.2 g of Pd(PPh_3)$_4$ (1 mol %). The mixture was heated at 80 °C for 7 h with stirring. After cooling to room temperature, the reaction mixture was poured into a beaker and triturated with hexane (5 × 50 mL). The hexane fractions were combined and washed with water (3 × 200 mL). The organic layer was rotary evaporated with 12 g of silica gel (Merck, grade 60). The sample was chromatographed on 6 in. of silica gel (Merck, grade 60) in a 5 cm o.d. × 50 cm long flash chromatography column with hexane to give 3.1 g of material that was 93% 18 by GLPC. The ratio *Z*/*E* was 92/8 (by ^{19}F NMR analysis). The ^{19}F NMR spectrum is given in Table II (cf. ref 5). The ^{1}H NMR spectrum shows a doublet at 2.4 ppm [J^7 (H–F) = 2 Hz (3 H)] and an AB doublet of doublets centered at 8.0 ppm (4 H). IR: 1730 (CF═CF, w) (cf. ref 5), 1655 (w), 1375 (w), 1305 (s), 1220 (s), 1160 (s), 1070 (s), 935 (m), 835 (m), 750 cm^{-1} (w). Mass spectrum: $C_{10}F_5H_7^+$, 222 (36.0); $C_9F_2H_7^+$, 153 (24.1); $C_9F_2H_5^+$, 151 (37.6); $C_9FH_6^+$, 133 (100.0); CF_3^+, 69 (42.7).

Preparation of (*Z*)-*p*-ClC$_6$H$_4$CF═CFCF$_3$ (19). (*E*)-CF_3CF═CFZnI was prepared as usual from 12.1 g of (*E*)-CF_3CF═CFI (47 mmol) and 5.0 g of activated zinc (76 mmol) in 45 mL of TG in a 100-mL flask equipped with the standard apparatus, and 9.5 g of *p*-ClC_6H_4I (40 mmol) and 0.5 g of Pd(PPh_3)$_4$ (1 mol %) were added. The reaction mixture was stirred and heated at 70 °C for 13 h. The mixture was triturated with hexane (5 × 50 mL), and the combined organic layers were washed with water (5 × 100 mL). The hexane solution was evaporated with 12 g of silica gel (Merck, grade 60) and was loaded onto a 5 cm o.d. × 50 cm long flash chromatography column (silica gel, Merck, grade 60) and eluted with 1 L of hexane in 100–125-mL fractions. Fractions 2–4 were active by TLC and were combined and evaporated to give 7.2 g of 96% (by GLPC) pure 19 for a 74% yield. The product contained 3% (by GLPC) 15. The ^{19}F NMR data is given in Table II (cf. ref 5). The ^{1}H NMR spectrum shows a singlet at 7.6 ppm. IR: 1720 (CF═CF stretch, m) (cf. ref 5), 1600 (m), 1490 (m), 1360, 1300, 1210, 1160, 1100, 1060 (all s), 1020 (m), 930 (s), 720 cm^{-1} (m). Mass spectrum: M + 2, $C_9H_4F_5{}^{37}Cl^+$, 244 (32.3); M, $C_9H_4F_5{}^{35}Cl^+$, 242 (100.0); $C_9H_4F_5^+$, 207 (39.0); $C_8H_4F_3{}^{37}Cl^+$, 194 (9.8); $C_8H_4F_3{}^{35}Cl^+$, 192 (30.5); $C_9H_3F_4^+$, 187 (28.2); $C_8H_4F_3^+$, 157 (21.1); $C_8H_4F_2^+$, 138 (30.5).

Results

Aryl iodides reacted easily in less than 10 h at 60–80 °C with perfluoroalkenylzinc reagents in the presence of catalytic amounts of Pd(PPh_3)$_4$. It was desired in the case of α,β,β-trifluorostyrene synthesis to avoid high temperatures for extended periods of time because some of these styrenes would cyclodimerize.[4]

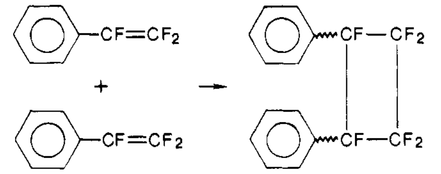


Table III. Isolated Yields of (*E*)-1-Arylperfluoropropenes and (*Z*)-1-Arylperfluoropropenes[a]

$$\underset{E\text{ or }Z}{CF_3CF{=}CFZnX} + ArI \xrightarrow[\substack{1\text{–}3\text{ mol \%}\\ 1\text{–}10\text{ h, }60\text{–}80\text{ °C}}]{Pd(PPh_3)_4} \underset{Z\text{ or }E}{CF_3CF{=}CFAr}$$

no.	1-arylperfluoropropene	isolated yield, %
13	(*E*)-C_6H_5CF═$CFCF_3$	80
14	(*E*)-*p*-$CH_3C_6H_4CF$═$CFCF_3$	65
15	(*E*)-*p*-ClC_6H_4CF═$CFCF_3$	61
16	(*E*)-*m*-$NO_2C_6H_4CF$═$CFCF_3$	80
17	(*Z*)-C_6H_5CF═$CFCF_3$[b]	82
18	(*Z*)-*p*-$CH_3C_6H_4CF$═$CFCF_3$[c]	70
19	(*Z*)-*p*-ClC_6H_4CF═$CFCF_3$[b]	74

[a] All preparations were conducted in triglyme with yellow Pd(PPh_3)$_4$ prepared in our laboratory. [b] *Z*/*E* = 97/3. [c] *Z*/*E* = 92/8.

Chromatographic procedures were also adopted to avoid extremes of heat in the workup. Styrenes with para substituents (*p*-MeO, *p*-Me, and *p*-Cl) were especially prone to dimerization and even when isolated in pure form would dimerize slowly at room temperature or below. The *p*-bis(trifluorovinyl)benzene would cyclodimerize into a gel at room temperature after 24 h, presumably cross-linking to form a polymer network connected with fluorinated cyclobutanes. See Table I for a summary of reaction conditions and yields of α,β,β-trifluorostyrenes.

The ^{19}F spectral data of all compounds reported here are summarized in Table II. Infrared and mass spectral data are given in the Experimental Section.

The synthesis of (*E*)-1-arylperfluoropropenes proceeded as easily as that of the styrenes. The stereochemistry of the products was 100% *E* isomer. In the synthesis of (*Z*)-1-arylperfluoropropenes, minor amounts of *E* isomers were isolated. See Table III for a summary of reaction conditions and yields of arylperfluoropropenes.

Discussion

Previously, the best general synthetic method to obtain α,β,β-trifluorostyrenes was reported by Dixon.[6] This procedure utilized the reaction of aryllithium reagents with tetrafluoroethylene and gave low yields of styrenes, due to competition of the styrenes with tetrafluoroethylene for the ArLi, which gave stilbenes. Our procedure offers significant advantages over previous methods. The zinc reagents are simple to prepare in triglyme, DMF, or tetrahydrofuran. Bromotrifluoroethylene does not react with zinc in triglyme, but 1a is formed easily in DMF, which allows for a cheaper, more readily available precursor.

Dmowski[5] synthesized 1-arylperfluoropropenes via reaction of aryl Grignard reagents with hexafluoropropene. A mixture of isomers was obtained, and there were limitations on aryl substituents; NO_2-substituted Grignard reagents were unreactive toward hexafluoropropene. Our method works well with many types of substituents, excluding only those that bear acidic hydrogens. Stereospecificity was observed in the formation of (*E*)-ArCF═$CFCF_3$, and stereoselectivity of no less than 92% was observed for (*Z*)-ArCF═$CFCF_3$.

We found the quality of the catalyst, Pd(PPh_3)$_4$, to be a critical factor. Most of our preliminary results were

Table IV. Electronic Effects Competition Reactions.[a] ^{19}F NMR Ratios

zinc reagent	electron-withdrawing substrate	electron-releasing substrate	electron withdrawing/electron releasing substituted product ratio
$CF_2{=}CFZnBr$ (DMF)[b]	p-ClC_6H_4I	p-$CH_3C_6H_4I$	68/32
(Z)-$CF_3CF{=}CFZnI$ (DMF)[b]	p-ClC_6H_4I	p-$CH_3C_6H_4I$	68/32
(E)-$CF_3CF{=}CFZnI$ (DMF)[b]	p-ClC_6H_4I	p-$CH_3C_6H_4I$	71/29
$CF_2{=}CFZnI$ (TG)[c]	p-$NO_2C_6H_4Br$	p-$CH_3OC_6H_4Br$	100/0
(Z)-$CF_3CF{=}CFZnI$ (TG)[c]	p-$NO_2C_6H_4Br$	p-$CH_3OC_6H_4Br$	100/0

[a] Conducted with 1 equiv of zinc reagent to 1 equiv each of substrate in an NMR tube. Approximately 5 mol % palladium catalyst was added. [b] Our own yellow $Pd(PPh_3)_4$ catalyst was used. [c] Alfa green phosphine palladium catalyst was used. NMR yields of p-$NO_2C_6H_4CF{=}CFR_f$'s were about 60%.

Table V. Zinc Reagent Competition Reactions with Aryl Iodides To Determine Relative Reactivities. ^{19}F NMR Tube Reactions[a]

$$\underset{1.0}{R_fZnX} + \underset{1.0}{R_f'ZnX} + \underset{1.0}{ArI} \rightarrow R_fAr + R_f'Ar$$

$$1.0 : 1.0 : 1.0$$

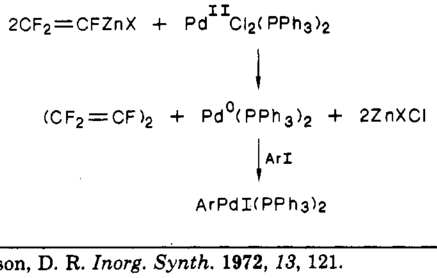
R_fZnX	$R_f'ZnX$	substrate	$R_fPh/R_f'Ph$
$CF_2{=}CFZnBr$ (DMF)[b]	(Z)-$CF_3CF{=}CFZnI$ (DMF)	PhI	72/28
(Z)-$CF_3CF{=}CFZnI$ (DMF)	(E)-$CF_3CF{=}CFZnI$ (DMF)	PhI	83/17
$CF_2{=}CFZnBr$ (TG)	(Z)-$CF_3CF{=}CFZnI$ (TG)	PhI	50/50
(Z)-$CF_3CF{=}CFZnI$ (TG)	(E)-$CF_3CF{=}CFZnI$ (TG)	o-$CF_3C_6H_4I$	69/31
(Z)-$CF_3CF{=}CFZnI$ (TG)	(E)-$CF_3CF{=}CFZnI$ (TG)	o-$CH_3C_6H_4I$	62/38
(Z)-$CF_3CF{=}CFZnI$ (TG)	(E)-$CF_3CF{=}CFZnI$ (TG)	o-PhC_6H_4I	64/36
(Z)-$CF_3CF{=}CFZnI$ (TG)	(E)-$CF_3CF{=}CFZnI$ (TG)	o-$(Me_2CH)C_6H_4I$	60/40

[a] A 0.5-mL volume of each zinc reagent was placed in an NMR tube with ca. 5 mol % catalyst. [b] Ratio of $CF_2{=}CFZnBr$ to (Z)-$CF_3CF{=}CFZnI$ was 65/35.

obtained with commercial catalyst obtained from Alfa (orange in color). Other lots we received were green. These samples of $Pd(PPh_3)_4$ gave unreliable results; in our preliminary report,[2] we made misleading statements based on results with these commercial catalysts, and we wish to take the opportunity to correct them here. For instance, we stated earlier that iodoarenes substituted with electron-releasing substituents reacted faster than electron-withdrawing-substituted iodoarenes. Competition experiments subsequently showed the reverse to be true (Table IV). We also reported that o-(trifluoromethyl)iodobenzene did not undergo Pd-catalyzed substitution. We have since found that this reaction proceeds in good yield (**9** in Table I, 73% isolated yield).

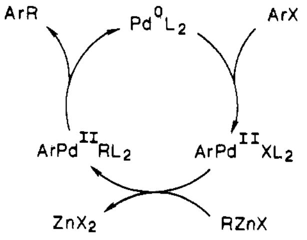
We obtained the best results with $Pd(PPh_3)_4$ prepared in our laboratory according to Coulson.[7] We have made one modification of Coulson's procedure in that we dried the catalyst under vacuum for at least 8 h, instead of using a slow stream of nitrogen. In our laboratory, catalyst dried under a stream of nitrogen turned green and had unreliable activity.

We found that aryl iodides gave the most consistent results. Aryl bromides often did not give any reaction, and although this may depend upon the quality of catalyst, we did not pursue this aspect any further. $Pd(PPh_3)_4$ was the only catalyst found to give good results. $Ni(PPh_3)_4$, Pd_2(dibenzylideneacetone)$_3$, and $Ni[P(OEt)_3]_3$ were also tried and did not give any catalytic activity. However, in one experiment, $PdCl_2(PPh_3)_2$ gave a 75% ^{19}F NMR yield of $PhCF{=}CF_2$ in TG from **1b** and PhBr. Small amounts of $(CF_2{=}CF)_2$ were observed, presumably because the zinc reagent reduced the Pd(II) compound, to give $Pd(PPh_3)_2$.



$$2CF_2{=}CFZnX + Pd^{II}Cl_2(PPh_3)_2 \longrightarrow (CF_2{=}CF)_2 + Pd^{0}(PPh_3)_2 + 2ZnXCl \xrightarrow{ArI} ArPdI(PPh_3)_2$$

The palladium catalysis is generally understood to involve the following cycle:[1]



The mechanism of the palladium(0)-catalyzed coupling involves the oxidative addition of the substrate to palladium to give a palladium(II) intermediate ($ArPdIL_2$). Arylpalladium iodides are easily synthesized,[8] and we found that they reacted directly with **1a** to give styrenes. No $ArPdCF{=}CF_2$ was observed by ^{19}F NMR; therefore, such a species must be very short-lived. We obtained direct evidence for this mechanism in the following manner: 1 equiv of zinc reagent was allowed to react with $^1/_2$ equiv of phenylpalladium iodide, and the reaction mixture was examined by ^{19}F NMR. Only styrene and zinc reagent were observed. This result showed that the zinc reagent reacted with the palladium(II) species and gave styrene directly with no observable $ArPdCF{=}CF_2$ species. $ArPdCF{=}CF_2$ is postulated to be a short-lived intermediate. Because an excess of zinc reagent was used, all of the ArPdI was presumed to be consumed; therefore, all Pd was present as Pd(0). If the reaction required a Pd(IV) intermediate such as $Ar_2PdI(CF{=}CF_2)$ before collapse to $ArCF{=}CF_2$, we should have been able to observe $ArPdCF{=}CF_2$, since there was no ArI present to "push" $ArCF{=}CF_2$ from palladium. If zinc reagent reacted with $ArPdCF{=}CF_2$ to a significant extent, we would also expect to see $(CF_2{=}CF)_2$, which we know is possible from experiments with $PdCl_2(PPh_3)_2$. We observed no diene in this experiment. When an excess of ArI was added to the reaction mixture, the remainder of the zinc reagent was consumed and styrene was formed. Since we started with

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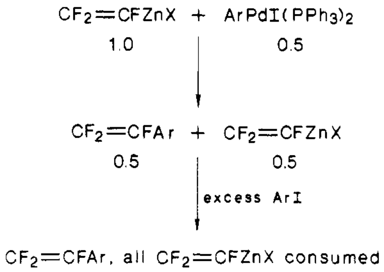
[7] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

[8] Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6.

a Pd(II) species, these results suggested that Pd(0) had been regenerated, thus allowing subsequent formation of ArPdI. This experiment is summarized in the following equations:



The order of reactivity of the zinc reagents was found to be **1** ≈ **2** > **3** via competition reactions (See Table V). It is interesting to note that when **2**(*Z*) competed with **3**(*E*) for PhI, the ratio **13**/**16** (*E*/*Z* products) was 83/17. However, when these propenylzinc reagents competed for ortho-substituted iodoarenes, the average ratios were approximately 60/40. It is not obvious whether these results are due to steric or electronic effects. At any rate, an ortho substituent does not noticeably hamper the reaction.

As mentioned previously, aryl iodides with electron-withdrawing substituents were found to be more reactive than aryl iodides with electron-releasing substituents (Table IV). This behavior parallels the electronic-effect profile found for the formation of arylpalladium iodides[9] and suggests that withdrawal of electron density from the palladium enhances the reactivity of ArPdI toward the zinc reagent.

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Registry No. **4**, 447-14-3; **5**, 105436-16-6; **6**, 82907-00-4; **7**, 105436-18-8; **8**, 105436-20-2; **9**, 105417-07-0; **10**, 105436-15-5; **11**, 82907-01-5; **12**, 113268-53-4; **13**, 41500-48-5; **14**, 72926-84-2; **15**, 79796-49-9; **16**, 114199-15-4; **17**, 41424-70-8; **18**, 72926-85-3; **19**, 79796-48-8; $CF_2{=}CFBr$, 598-73-2; (*Z*)-$CF_3CF{=}CFI$, 102682-81-5; (*E*)-$CF_3CF{=}CFI$, 102682-82-6; iodotrifluoroethylene, 359-37-5; iodobenzene, 591-50-4; *o*-nitroiodobenzene, 609-73-4; *p*-iodoanisole, 696-62-8; *o*-isopropyliodobenzene, 19099-54-8; 2,5-dichloroiodobenzene, 29682-41-5; *o*-iodobenzotrifluoride, 444-29-1; *m*-nitroiodobenzene, 645-00-1; *p*-chloroiodobenzene, 637-87-6; *p*-diiodobenzene, 624-38-4; *p*-iodotoluene, 624-31-7.

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[9] Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

Aryne Cycloaddition to the Aromatic Ring of Mesitylmagnesium Bromide. An Anion-Assisted Diels–Alder Reaction?

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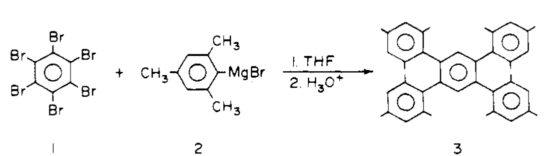
Hexabromobenzene and excess mesitylmagnesium bromide give, after an aqueous quench, a 20% yield of the diaryne adduct 4 (in addition to 30–55% of 1,2,4,5-tetramesitylbenzene). The aryne cycloadditions that lead to 4 occur across the 2,5-positions of the aromatic ring of the Grignard reagent. Competition experiments show that the aryl ring of mesitylmagnesium bromide is considerably more reactive as a diene than is the aryl ring of mesitylene itself.

Introduction

We describe here a reaction in which the capacity of a benzenoid ring to function as the diene in a [4 + 2] cycloaddition is enhanced through conversion to a Grignard reagent. The reaction was discovered accidentally in the following way.

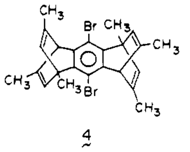
The reaction of hexabromobenzene with excess mesitylmagnesium bromide was shown recently[1] to give after aqueous quench 1,2,4,5-tetramesitylbenzene (**3**) in 30–55% yield. In scaling this reaction up, another product was isolated, whose structure and mode of formation form the basis of this paper.



1 2 3

Results and Discussion

Treatment of hexabromobenzene with 8 equiv of mesitylmagnesium bromide in THF at room temperature for 12 h followed by aqueous quench gave, after workup (see Experimental Section for details), a white powder, mp 306–308 °C dec, in 20% yield, in addition to >30% of the more soluble **3** (mp 258–259 °C). Structure **4** is assigned to the new product.[2] The mass spectrum of **4** showed the presence of two bromine atoms (M^+ at m/e 470, 472, and 474). The ^1H HMR spectrum showed four vinyl methyl groups (δ 1.89), two bridgehead methyls (δ 2.12), two



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[1] Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.

[2] In fact, the NMR spectrum indicated the presence of two products with nearly identical NMR spectra. We presume that the minor product (only a few percent) is the C_{2v} regioisomer of 4.

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