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SYNTHESIS OF TRIFLUOROVINYLPOLYHALOARYL COMPOUNDS *via* POLYHALOARYLCOPPER COMPLEXES

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SUMMARY

The synthesis of some polyhaloarylcopper complexes (Ar_xCu; $Ar_x = C_6F_5$, p-HC_6F_4, p-BrC_6F_4, C_5NF_4, C_5NCl_4 and C_6Cl_5) and their reactions with $F_2C{=}CFI$ to yield the $F_2C{=}CFAr_x$ compounds are described. The copper coupling reaction between C_6F_5I and $F_2C{=}CFI$ as an alternate procedure for preparation of $F_2C{=}CFAr_x$ has also been studied.

INTRODUCTION

We have recently published[1] our preliminary results for a convenient synthesis of perfluorostyrene through the reaction between a perfluorophenylcopper compound and iodotrifluoroethylene. Because this method offers advantages over other published procedures for the synthesis of perfluorostyrene, it was of interest to explore it in greater detail for the preparation of other perhaloarylvinylic systems. This study is thus concerned with the reaction between various perhaloarylcopper complexes and iodotrifluoroethylene. Another method of synthesizing perfluorostyrene through an *in situ* copper coupling reaction will also be discussed.

RESULTS AND DISCUSSION

The synthesis of perhaloarylcopper compounds has recently been reported by various investigators[1–4]. In general, a perhaloaryl-lithium or perhaloarylmagnesium compound was allowed to react with a cuprous halide (Cl, Br or I) in diethyl ether or tetrahydrofuran (THF) to yield a perhaloarylcopper complex. No complete characterization of the perhaloarylcopper complexes has been reported as yet. Most of the reactions of perhaloarylcopper with various compounds have been carried out as the complexes of unknown composition. The products resulting from such reactions indicate that the reactive species may, for the sake of simplicity and convenience, be represented as "Ar_xCu" (Ar_x = poly or perhaloaryl group).

Cairncross and Sheppard[2] were the first to report the synthesis and isolation of pure pentafluorophenylcopper from the pentafluorophenylcopper complex. Complete characterization and certain reactions of pentafluorophenylcopper were also reported by these investigators.

Many of the reactions of perhaloarylcopper complexes or pure pentafluorophenylcopper are similar to those of the perhaloaryl-lithium or magnesium analogs. However, some reactions, as for example with iodotrifluoroethylene, are specific to the organocopper compounds and they show utility as useful intermediates for the synthesis of such compounds. As an example, "C_6F_5Cu" reacts with $F_2C{=}CFI$ to yield $C_6F_5CF{=}CF_2$. The pentafluorophenyl-lithium and magnesium compounds, however, react by another mechanism (addition–elimination at the ethylenic bond followed by nucleophilic substitution of the *para* fluorine) to yield a series of products[1].

$$(n+1)C_6F_5Li + F_2C{=}CFI \rightarrow C_6F_5(C_6F_4)_nCF{=}CFI \qquad (1)$$

In this study we have prepared other perhaloarylcopper complexes and found that they react similarly to the "C_6F_5Cu" in reactions with $F_2C{=}CFI$ to yield trifluorovinylperhaloaryl compounds in reasonable yields (see Table 1). The identification of other by-products in the reaction mixture, however, indicates that other competing reactions occur. The reasons for the competing reactions are not fully understood at this time. The chemical nature of the organocopper compounds undoubtedly plays an important role in controlling the rates of reactions and the product distribution. Our results indicate that at least three different type reactions take place (although not necessarily in the same reaction); (i) coupling reaction; (ii) metal–halogen exchange reaction and (iii) bis(polyhaloaryl)acetylene formation*. With the exception of the bis(polyhaloaryl)acetylene-forming reaction, the products of the various reactions between the perhaloarylcopper complexes and iodotrifluoroethylene can be accounted for by considering the following reactions.

$$Ar_xCu + F_2C{=}CFI \rightarrow Ar_xI + F_2C{=}CFCu \qquad (2)$$

$$Ar_xCu + F_2C{=}CFI \rightarrow CuI + Ar_xCF{=}CF_2 \qquad (3)$$

$$Ar_xCu + Ar_xI \rightarrow CuI + Ar_xAr_x \qquad (4)$$

$$F_2C{=}CFCu + Ar_xI \rightarrow CuI + Ar_xCF{=}CF_2 \qquad (5)$$

$$F_2C{=}CFCu + F_2C{=}CFI \rightarrow CuI + F_2C{=}CF\text{-}CF{=}CF_2 \qquad (6)$$

(Ar_x = polyhaloaryl)

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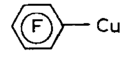
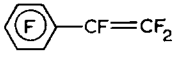
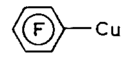
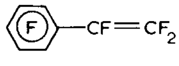
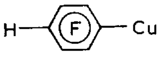
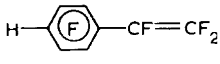
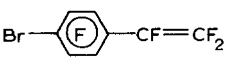
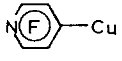
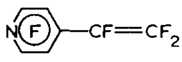
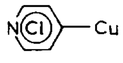
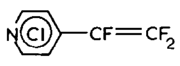
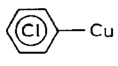
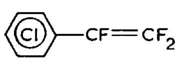
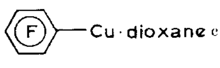
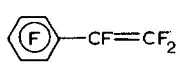
* Pentafluorophenylcopper, pentachlorophenylcopper and 2,3,5,6-tetrachloropyridylcopper have been reacted with various polyhaloethylenes (other than $F_2C{=}CFI$) and polyhaloethanes to yield bis(polyhaloaryl)acetylenes. In certain reactions the bis(acetylenes) were obtained as the principal product in yields up to 87%[5].

TABLE 1

PRODUCTS AND YIELDS FROM REACTIONS OF THE TYPE "Ar_xCu" + $F_2C{=}CFI$

"Ar_xCu"	Principal product [a] (Yield as determined by VPC)	By-products [b]
 [d]	 (55 %)	C_6F_5I, $(C_6F_5)_2$, $(F_2C{=}CF)_2$
 [c]	 (55 %)	C_6F_5I, $(C_6F_5)_2$, $C_6F_5C{\equiv}CC_6F_5$
 [c]	 (45 %)	p-HC_6F_4I, $(p$-$HC_6F_4)_2$, p-$HC_6F_4C{\equiv}CC_6F_4H$-p
 [c]	 (60 %)	HC_6F_4Br, $IC_6F_4CF{=}CF_2$, IC_6F_4Br, $(BrC_6F_4)_2$
 [c]	 (56 %)	NC_5F_4H, NC_5F_4I, $(NC_5F_4)_2$
 [d]	 (84 %)	NC_5Cl_4H, NC_5Cl_4I, $(NC_5Cl_4)_2$
 [d]	 (32 %)	C_6Cl_5H, $(C_6Cl_5)_2$
 [c]	 (88 %)	C_6F_5I, $(C_6F_5)_2$

[a] Products isolated by preparative VPC and characterized by elemental analysis (Table 4), NMR (Table 2) and mass spectrometry (Table 3).

[b] Products characterized by VPC retention time and GLC–mass spectrometry, in addition some of the new compounds were isolated by preparative VPC and further characterized by NMR spectroscopy.

[c] Prepared from the aryl Grignard.

[d] Prepared from the aryl-lithium.

The reaction between "C_6F_5Cu" and $F_2C{=}CFI$ was studied in greater detail than the other perhaloarylcopper reactions. The four products which were obtained, $C_6F_5CF{=}CF_2$, C_6F_5I, $(C_6F_5)_2$ and $(F_2C{=}CF)_2$, support the suggested metal–halogen exchange reactions and coupling reactions as described. The formation of a transient trifluorovinylcopper species is assumed. Additional evidence for the possible existence of such an intermediate will be presented later.

It was of interest to note that the "C_6F_5Cu" and "p-HC_6F_4Cu" complexes prepared from the Grignard (Ar_xMgX + CuX) yielded acetylenic compounds as one of the reaction products (see Table 1). The "C_6F_5Cu" prepared from the pentafluorophenyl-lithium (Ar_xLi + CuX) produced none of the acetylenic products. In order to account for the differences in products and product distribution, it appeared that the copper complexes must vary in reactivity and/or chemical structure depending on the mode of their synthesis. To test this hypothesis, pure C_6F_5Cu dioxanate, prepared as described by Cairncross and Sheppard[2], was allowed to react with $F_2C{=}CFI$. The reaction was exothermic, completed within 10 min and yielded the perfluorostyrene in 88% yield. No acetylenic compound was formed under these conditions. When equimolar quantities of C_6F_5Cu dioxanate and C_6F_5Li were allowed to react with $F_2C{=}CFI$, the rate of reaction was decreased, the yield of perfluorostyrene decreased to approximately 50% and no acetylenic compound was formed. However, when equimolar quantities of C_6F_5Cu dioxanate and C_6F_5MgBr were allowed to react with $F_2C{=}CFI$, the rate of reaction was decreased, the yield of perfluorostyrene was decreased to 50% and the acetylenic compound $C_6F_5C{\equiv}CC_6F_5$ was formed in 9% yield.

It is apparent, therefore, that although the perhaloarylcopper reagents as generally reported and used as intermediates, offer a means of introducing a perhaloaryl group, the rates of reaction and product distribution are strongly dependent on the mode of perhaloarylcopper synthesis.

Although the perhaloarylcopper compounds thus far appear to be the best intermediates for synthesizing perhaloaryltrifluorovinyl compounds, the copper coupling reaction* was also examined as another possible synthetic procedure for perfluorostyrene. This study was limited to the reactions between C_6F_5I, $F_2C{=}CFI$ and copper in dimethylacetamide solvent. The principal products from the reaction mixture were $C_6F_5CF{=}CF_2$ (47–55%) and $(C_6F_5)_2$ (46–50%) and a small yield of $F_2C{=}CF{-}CF{=}CF_2$. Under the same experimental conditions, $F_2C{=}CFI$ and copper in dimethylacetamide gave the coupled product $F_2C{=}CFCF{=}CF_2$.

In studies on the Ullmann reaction, it has been postulated that a transitory arylcopper intermediate may be formed which subsequently reacts with the aryl halide in solution to yield the coupling product. We have reported earlier[4] that "C_6F_5Cu" reacts with C_6F_5I to yield $(C_6F_5)_2$ while others have reported[7] that C_6F_5Br is coupled by metallic copper to give $(C_6F_5)_2$. From these observations, it would appear that in the copper coupling reactions there may exist a transient organocopper intermediate (in solution or on the copper surface), which in the presence of an active sp^2 carbon–iodine compound reacts rapidly to produce the observed coupled products. On the assumption that an active transient organo-

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* It was previously reported[6] that the reaction between C_6F_5I, $ClCF{=}CFI$ and copper bronze yielded a mixture of products; *cis*- and *trans*-$ClCF{=}CFC_6F_5$, three isomeric $ClCF{=}CFCF{=}CFCl$ and $(C_6F_5)_2$.

copper is formed, the following equations may explain the products observed in our study between the C_6F_5I, $F_2C{=}CFI$ and metallic copper

$$C_6F_5I + Cu \rightarrow \text{“}C_6F_5Cu\text{”} \quad (7)$$

$$F_2C{=}CFI + Cu \rightarrow \text{“}F_2C{=}CFCu\text{”} \quad (8)$$

The existence of "C_6F_5Cu" has already been established[1–4] and the possibility of "$F_2C{=}CFCu$" seems quite reasonable in view of the recent data[8] reported on the synthesis of "$C_7F_{15}Cu$" from the reaction between $C_7F_{15}I$ and metallic copper. In the synthesis of "$C_7F_{15}Cu$", however, this organometallic does not react with the sp^3 carbon–iodine bond of $C_7F_{15}I$ and thus is capable of isolation with a finite lifetime. On the other hand, "$F_2C{=}CFCu$" would react rapidly with the sp^2 carbon–iodine bond of $F_2C{=}CFI$ to form the observed $F_2C{=}CFCF{=}CF_2$ product. In addition, we have also shown[9] that "$C_7F_{15}Cu$" reacts with the sp^2 carbon–iodine bond of $F_2C{=}CFI$ to yield the $C_7F_{15}CF{=}CF_2$ olefin.

In the copper coupling reactions involving two different iodides ($R_fI + R'_fI$; cross-coupling reactions), the reaction products and yields will be dependent on the relative reaction rates. In the reactions between C_6F_5I and $F_2C{=}CFI$, approximately 50:50 mixtures of the coupled products $(C_6F_5)_2$ and cross-coupled product $C_6F_5CF{=}CF_2$ were found, indicating approximately equal reactivity ratios*. However, substitution of C_6F_5Br or C_6H_5I for C_6F_5I yielded no styrene products under the same experimental conditions. It would thus appear that the *in situ* cross-copper coupling reaction for sp^2 fluorocarbon iodides has limitations detracting from its broad synthetic applicability.

EXPERIMENTAL

All organometallic reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freshly distilled from sodium. VPC analyses were carried out on an F&M Model 810 gas chromatograph using a 1.8 m × 6 mm column, 10% Apiezon on 60–80 mesh Chromosorb W. The mass spectral analyses were performed on a CEC–21–110B mass spectrometer (see Table 3). The ^{19}F NMR spectra were recorded on a Varian A56–60 spectrometer (see Table 2) and the chemical shifts are reported in ppm from internal trichlorofluoromethane.

Synthesis of perhaloarylmagnesium and -lithium intermediates

These intermediates were synthesized by established published procedures: C_6F_5MgBr[10], p-HC_6F_4MgBr[10], p-BrC_6F_4MgBr[10], 4-NC_5F_4MgBr[10], C_6F_5Li[11], C_6Cl_5Li[12], 4-NC_5Cl_4Li[13].

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* No attempt was made to quantitatively identify the third coupled product $(F_2C{=}CF)_2$ since under our experimental conditions this was not practical. The boiling point of $(F_2C{=}CF)_2$ is +7.5° and this prohibits convenient quantitative interpretation by our vapor-phase chromatographic procedures.

TABLE 2

NMR DATA

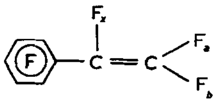
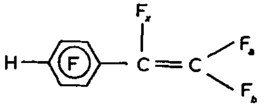
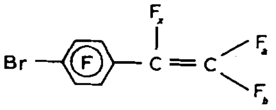
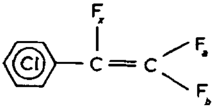
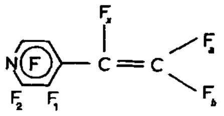
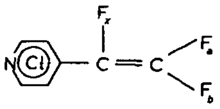
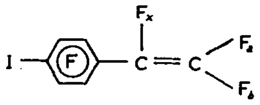
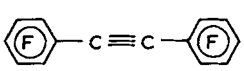
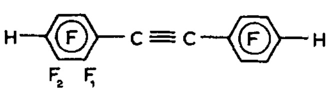
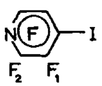
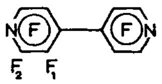
	o-F	*p*-F	*m*-F	F_x	F_a	F_b
	138	150	162	171	97	113
	138 H = 7.25 (multiplet)	—	138	172	96	112
	136	—	132	172	95	112
	—	—	—	168	99	114
	139 (F_1)	—	89 (F_2)	176	92	107
	—	—	—	171	97	110
	136	—	119	172	95	112
	135	150	162			
	136 H = 7.18 (multiplet)	—	139			
	124 (F_1)	—	90 (F_2)			
	139 (F_1)	—	87 (F_2)			

TABLE 3

MASS SPECTRAL ANALYSIS (MASS NUMBER, PROBABLE SPECIES) OF IONS OVER 10% OF BASE PEAK

$C_6F_5CF{=}CF_2$: (248, C_8F_8), (229, C_8F_7), (198, C_7F_6), (179, C_7F_5), (148, C_6F_4), (141, C_7F_3), (129, C_6F_3), (117, C_5F_3), (110, C_6F_2), (98, C_5F_2), (93, C_3F_3), (79, C_5F), (31, CF).

p-$BrC_6F_4CF{=}CF_2$: (308, C_8F_7Br), (239, C_7F_4Br), (229, C_8F_7), (210, C_8F_6), (179, C_7F_5), (160, C_7F_4), (141, C_7F_3), (129, C_6F_3), (110, C_6F_2), (93, C_3F_3).

4-$NC_5F_4CF{=}CF_2$: (231, NC_7F_7), (212, NC_7F_6), (200, NC_6F_6), (186, C_6F_6), (181, NC_6F_5), (162, NC_6F_4), (136, C_5F_4), (131, NC_5F_3), (124, C_4F_4), (117, C_5F_3), (112, NC_5F_2), (105, C_4F_3), (100, NC_4F_2), (98, C_5F_2), (93, NC_5F), (86, C_4F_2), (85, N_2F_3), (83, NCF_3), (81, NC_4F), (79, C_5F), (74, C_3F_2), (69, CF_3).

4-$NC_5{}^{35}Cl_4CF{=}CF_2$: (295, $NC_7Cl_4F_3$), (260, $NC_7Cl_3F_3$), (225, $NC_7Cl_2F_3$), (210, NC_6Cl_3F), (199, $C_6Cl_2F_3$), (149, C_5Cl_2F), (140, NC_6ClF), (118, C_4Cl_2), (114, C_5ClF), (109, NC_5Cl), (105, NC_6F), (85, NC_3Cl), (79, C_5F).

$C_6Cl_5CF{=}CF_2$: (328, $C_8Cl_5F_3$), (293, $C_8Cl_4F_3$), (258, $C_8Cl_3F_3$).

p-$HC_6F_4CF{=}CF_2$: (230, C_8F_7H), (211, C_8F_6H), (180, C_7F_5H), (161, C_7F_4H), (141, C_7F_3), (130, C_6F_3H), (117, C_5F_3H), (111, C_6F_2H), (99, C_5F_2H), (93, C_3F_3H), (80, C_5FH), (31, CF).

p-IC_6F_4Br: (354, C_6F_4BrI), (227, C_6F_4Br), (179, C_2F_4Br) (148, C_6F_4), (129, C_6F_3) (117, C_5F_3), (110, C_6F_2), (98, C_5F_2), (93, C_3F_3), (86, C_4F_2), (79, C_5F).

p-$IC_6F_4CF{=}CF_2$: (356, C_8F_7I), (229, C_8F_7), (210, C_8F_6), (179, C_7F_5), (160, C_7F_4), (148, C_6F_4), (141, C_7F_3), (129, C_6F_3), (122, C_7F_2), (117, C_5F_3), (110, C_6F_2), (98, C_5F_2), (93, C_3F_3).

p-$HC_6F_4C{\equiv}CC_6F_4H$-*p*: (322, $C_{14}H_2F_8$), (253, $C_{13}H_2F_5$), (222, $C_{12}H_2F_4$), (161, C_7HF_4), (141, C_7F_3), (128, C_9HF), (123, C_7HF_2), (117, C_5F_3), (111, C_6HF_2), (99, C_5HF_2), (93, C_3F_3), (92, C_6HF).

$C_6F_5C{\equiv}CC_6F_5$: (358, $C_{14}F_{10}$), (339, $C_{14}F_9$), (327, $C_{13}F_9$), (320, $C_{14}F_8$), (308, $C_{13}F_8$), (296, $C_{12}F_8$), (289, $C_{13}F_7$), (282, $C_{14}F_6$), (277, $C_{12}F_7$), (270, $C_{13}F_6$), (258, $C_{12}F_6$), (251, $C_{13}F_5$), (234, $C_{10}F_6$), (227, $C_{11}F_5$), (179, C_7F_5), (165, C_9F_3), (141, C_7F_3), (93, C_3F_3).

$(C_6Cl_5)_2$: (494, $C_{12}Cl_{10}$), (459, $C_{12}Cl_9$), (424, $C_{12}Cl_8$), (389, $C_{12}Cl_7$), (354, $C_{12}Cl_6$), (319, $C_{12}Cl_5$), (284, $C_{12}Cl_4$), (247, C_6Cl_5), (212, C_6Cl_4), (177, C_6Cl_3).

$(4\text{-}NC_5Cl_4)_2$: (428, $C_{10}Cl_8N_2$), (393, $C_{10}Cl_7N_2$), (358, $C_{10}Cl_6N_2$), (288, $C_{10}Cl_4N_2$), (214, C_5Cl_4N), (179, C_5Cl_3N), (167, C_4Cl_3N), (132, C_4Cl_2N), (118, C_4Cl_2), (109, C_5ClN).

$(4\text{-}NC_5F_4)_2$: (300, $C_{10}F_8N_2$), remaining peaks were less than 10% of base M^+. (281, $C_{10}F_7N_2$), (262, $C_{10}F_6N_2$), (255, C_9F_7N), (231, C_9F_5N), (224, C_8F_6N), (205, C_8F_5N), (200, C_6F_6N), (193, C_7F_5N), (186, C_8F_4N), (155, C_7F_3N), (150, C_5F_4N), (141, C_7F_3), (131, C_5F_3N), (129, C_6F_3), (124, C_4F_4), (117, C_5F_3), (112, C_3F_4), (100, C_2F_4), (93, C_3F_3), (69, CF_3).

Synthesis of perhaloarylcopper compounds

To the perhaloaryl-lithium (at —70°) (x mole) or perhaloarylmagnesium bromide (at 0°) (x mole) in tetrahydrofuran was added an equivalent of CuCl (x mole). The reaction mixture was stirred for approximately 20 h and then allowed to warm up to room temperature.

General procedure for reaction of perhaloarylcopper and $F_2C{=}CFI$

To the above described perhaloarylcopper compounds (*x* mole) at room temperature was added dropwise freshly distilled $F_2C{=}CFI$ (*x* mole) and an internal standard, *e.g.* n-octane or n-decane. A slight exotherm of 3–4° was observed. The reaction mixture was heated between 50–60° and maintained at this temperature for a period of up to 20 h. The progress of the reaction was followed by removing samples periodically and analysis by VPC. When the $F_2C{=}CFI$ was consumed, as indicated by VPC, the reaction mixture was cooled, hydrolyzed with 6 *N* HCl and extracted with diethyl ether. After drying over $MgSO_4$, the solution was concentrated on a rotary evaporator. VPC analysis of the concentrate yielded the product ratios and/or yields. The products were separated by preparative VPC. In most experiments the concentrate prior to separation was also subjected to a VPC–mass spectrometric analysis. The products of reaction were characterized by ^{19}F and ^{1}H NMR, mass spectrometric analysis (on isolated compounds) and VPC retention times.

Synthesis of C_6F_5Cu dioxanate

C_6F_5MgBr was prepared as described previously from C_6F_5Br (54.8 g; 0.22 mole) and magnesium (5.4 g; 0.22 mole) in 200 ml of diethyl ether. To this Grignard solution, cooled to 0°, was added CuBr (57.4 g; 0.40 mole) and the reaction mixture was stirred for 3 h. To this mixture was added an additional 600 ml of dry diethyl ether and 100 ml of dry dioxan. After stirring at 0° for 30 min, the mixture was filtered under nitrogen and the filtrate was concentrated leaving a light yellow solid. The solid was washed under nitrogen several times with dry hexane and concentrated in a rotary evaporator yielding 39.5 g of a white free-flowing powder which gave a negative halide test with $AgNO_3$ solution. The white powder (C_6F_5Cu dioxanate[2]) was dissolved in 400 ml of anhydrous THF. This stock solution was standardized by VPC using an internal n-dodecane standard and was then used for subsequent reactions.

Reaction between C_6F_5Cu dioxanate and $F_2C{=}CFI$

To C_6F_5Cu dioxanate/THF solution (0.015 mole) at 0° was added $F_2C{=}CFI$ (0.03 mole). An exotherm of a few degrees was noted. Within 10 min a white precipitate formed and VPC analysis of a hydrolyzed sample showed the absence of C_6F_5H, indicating complete consumption of the organocopper compound. The reaction mixture was hydrolyzed with 6 *N* HCl, extracted with diethyl ether and the diethyl ether layer washed several times with 6 *N* HCl to remove the residual THF. VPC analysis of the diethyl ether solution indicated $C_6F_5CF{=}CF_2$ (88%) and small amounts of C_6F_5I and $(C_6F_5)_2$.

Reaction between C_6F_5Cu dioxanate, C_6F_5Li and $F_2C{=}CFI$

C_6F_5Li (0.03 mole) was prepared as described previously[11] from C_6F_5H and n-C_4H_9Li at −70° in THF. To this solution was added C_6F_5Cu dioxanate/THF solution (0.03 mole). After stirring for 40 min at −70°, $F_2C{=}CFI$ (0.06 mole) was added. No exotherm was noted. The reaction was allowed to warm to room temperature, and after 1 h the reaction mixture was hydrolyzed with 6 *N* HCl, extracted with diethyl ether and the diethyl ether extracted several times with 6 *N* HCl. VPC analysis of the dried diethyl ether solution indicated $C_6F_5CF{=}CF_2$ (50%), C_6F_5I and $(C_6F_5)_2$.

Reaction between C_6F_5Cu dioxanate, C_6F_5MgBr and $F_2C{=}CFI$

C_6F_5MgBr (0.03 mole) was prepared as described previously[10] from C_6F_5Br (0.033 mole) and C_2H_5MgBr (0.03 mole). To this solution was added C_6F_5Cu dioxanate/THF solution (0.03 mole). The resulting mixture was stirred at room temperature for 30 min. No exotherm was noted when $F_2C{=}CFI$ (0.06 mole) was added. After one additional hour there was no apparent reaction (no precipitate, copper salts). After refluxing for *ca.* 18 h, a white precipitate formed, the reaction was hydrolyzed with 6 *N* HCl and worked up as described above. VPC analysis of the dried diethyl ether solution indicated $C_6F_5CF{=}CF_2$ (50%), $C_6F_5C{\equiv}CC_6F_5$ (9.0%), C_6F_5I and $(C_6F_5)_2$.

In situ *synthesis of $F_2C{=}CF{-}CF{=}CF_2$*

Into a three-necked flask equipped with a stirrer, thermometer and a water condenser was added $F_2C{=}CFI$ (20.0 g; 0.10 mole), copper powder (19.1 g; 0.30 g atom) (U.S. Bronze Powders Inc., natural fine copper No. 44F), n-$C_{12}H_{26}$ (10.0 g, internal standard) and freshly distilled dry dimethylacetamide (150 ml). The outlet of the condenser was connected to a trap cooled in a Dry Ice–alcohol bath. The reaction mixture was heated at 60° for 3 h and cooled to room temperature; a sample removed for VPC analysis indicated that 73% of $F_2C{=}CFI$ still remained unreacted. The trap contained a colorless liquid which was subjected to ^{19}F NMR and mass spectral analysis. The ^{19}F NMR indicated a mixture of $F_2C{=}CFI$ and $F_2C{=}CF{-}CF{=}CF_2$ in a 1.8:1 ratio. Mass spectral analysis of the mixture indicated the presence of $F_2C{=}CFI$, $F_2C{=}CF{-}CF{=}CF_2$ and a trace of $F_2C{=}CFH$.

In situ *synthesis of $C_6F_5CF{=}CF_2$*

Into an apparatus, as described above, was added C_6F_5I (29.4 g; 0.10 mole), copper powder (19.1 g; 0.30 g atom), $F_2C{=}CFI$ (20.8 g; 0.10 mole), n-$C_{12}H_{26}$ (10.0 g; internal standard) and freshly distilled dry dimethylacetamide (150 ml). The reaction mixture was heated at 60° for 18 h, cooled, hydrolyzed with 6 *N* HCl, extracted with pentane and dried ($MgSO_4$). VPC analysis of the reaction mixture indicated $C_6F_5CF{=}CF_2$ (47%), $(C_6F_5)_2$ (46%) and a trace of C_6F_5H. The cold trap contained a colorless liquid whose ^{19}F NMR analysis indicated a mixture of $F_2C{=}CFI$ and $F_2C{=}CF{-}CF{=}CF_2$ in a 4:1 ratio.

TABLE 4

ANALYSES OF COMPOUNDS

	C (%)		H (%)		Other (%)		M.p.[a]
	Calc.	Found	Calc.	Found	Calc.	Found	(°C)
$C_6F_5CF{=}CF_2$	38.7	38.6	0.0	0.0	—	—	
p-$HC_6F_4CF{=}CF_2$ (nc)	41.7	41.5	0.43	0.51	—	—	
p-$BrC_6F_4CF{=}CF_2$ (nc)	31.1	31.0	0.0	0.0	Br 25.8	25.2	
4-$NC_5F_4CF{=}CF_2$ (nc)	36.4	36.6	0.0	0.0	N 6.06	5.98	
4-$NC_5Cl_4CF{=}CF_2$ (nc)	28.3	28.4	0.0	0.0	Cl 47.8	47.7	
$C_6Cl_5CF{=}CF_2$ (nc)	29.1	29.0	0.0	0.0	Cl 53.7	53.9	45–47
$C_6F_5C{\equiv}CC_6F_5$	46.9	46.9	0.0	0.0	—	—	121.5–123[b]
$HC_6F_4C{\equiv}CC_6F_4$-H (nc)	52.2	51.9	0.62	0.71	F 47.2	47.0	130.5–132
p-HC_6F_4I (nc)	26.1	26.0	0.37	0.35	I 46.0	45.2	
$(C_6Cl_5)_2$	28.9	29.0	0.0	0.0	Cl 71.1	71.2	306–308[c]
(4-$NC_5Cl_4)_2$							222–224[d]
(4-$NC_5F_4)_2$	40.0	40.3	0.0	0.0	N 9.33	9.33	81–83[e]

[a] Corrected melting points.

[b] Lit.[14] 123.5°.

[c] Lit.[15] 309°.

[d] Lit.[16] 226–228°.

[e] Lit.[17] 81–82°.

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