5,12-Dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene.—To lithium phenylacetylide, made from 14.85 g (0.146 mol) of phenylacetylene and 2.80 g (0.122 mol) of lithium amide in 100 ml of dioxane, was added 15.7 g (0.061 mol) of 5,12-naphthacenequinone[4] in 150 ml of dioxane. The mixture was refluxed for 4 hr, then cooled and treated with 350 ml of 0.5 *M* aqueous ammonium chloride solution. Recrystallization of the product from benzene gave 15.95 g (57%) of colorless crystals, mp 216.5–218° dec. The infrared spectrum ($CHCl_3$) had a single peak at 3610 cm^{-1} for *trans* OH, and two peaks at 3550 and 3400 cm^{-1} corresponding to *cis*-hydrogen-bonded OH. The ratio of *cis* to *trans* was 4:1.

Anal. Calcd for $C_{34}H_{22}O_2$: C, 88.31; H, 4.77. Found: C, 87.97; H, 4.83.

5,12-Bis(phenylethynyl)naphthacene (IIb).—To 29 g of stannous chloride dihydrate in 200 ml of 50% aqueous acetic acid was slowly added 14.4 g of 5,12-dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene in 300 ml of dioxane. The mixture was stirred at room temperature for 2 hr, then diluted to a volume of 1500 ml with water. Recrystallization of the crude product from benzene gave 8.1 g (63%) of dark red-purple needles, mp 248° dec.

Anal. Calcd for $C_{34}H_{20}$: C, 95.33; H, 4.67. Found: C, 95.45; H, 4.78.

6,13-Dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene.—To lithium phenylacetylide, made from 10.20 g (0.10 mol) of phenylacetylene and 2.30 g (0.10 mol) of lithium amide in 100 ml of anhydrous dioxane, was added 3.08 g (0.01 mol) of 6,13-pentacenequinone[5] in 100 ml of dioxane. The mixture was refluxed for 4 hr, then treated with 600 ml of 0.5 *M* aqueous ammonium chloride solution. The crude product was washed with benzene, then washed with water. Recrystallization in chloroform gave 3.47 g (68%) of colorless solid, mp 230° dec. The infrared spectrum ($CHCl_3$) had a single peak at 3610 cm^{-1} for *trans* OH, and two peaks at 3550 and 3400 cm^{-1} corresponding to *cis*-hydrogen-bonded OH. The ratio of *cis* to *trans* was 1:1.

Anal. Calcd for $C_{38}H_{24}O_2$: C, 89.06; H, 4.69. Found: C, 89.32; H, 4.80.

6,13-Bis(phenylethynyl)pentacene (IIIb).—To 30 g of stannous chloride dihydrate in 25 ml of 50% aqueous acetic acid was added 1.38 g of 6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene in 90 ml of dioxane and the mixture was stirred at room temperature for 2 hr. Dilution with water gave 1.18 g of crude product. Recrystallization from xylene gave 0.91 g (63%) of deep blue crystals, which sublimed at 195°.

Anal. Calcd for $C_{38}H_{22}$: C, 95.39; H, 4.60. Found: C, 95.23; H, 4.75.

5,7,12,14-Tetrahydroxy-5,7,12,14-tetrakis(phenylethynyl)-5,-7,12,14-tetrahydropentacene.—A mixture of 10.20 g (0.10 mol) of phenylacetylene, 2.30 g (0.10 mol) of lithium amide and 75 ml of anhydrous dioxane was refluxed for 1 hr. More dioxane (100 ml) was added to the cooled mixture. 5,7,12,14-Pentacenediquinone[6] (1.69 g, 0.005 mol) was added all at once and the mixture was refluxed for 4.5 hr. Aqueous ammonium chloride solution (0.2 *N*, 400 ml) was added, followed by an addition of 200 ml of benzene. A tan solid, mp 400°, was collected after stirring the aqueous and benzene layers for 15 min. Recrystallization from chloroform gave 2.77 g (72%) of colorless crystals, infrared 3300 cm^{-1} (Nujol).

Anal. Calcd for $C_{54}H_{34}O_4$: C, 86.86; H, 4.56. Found: C, 87.16; H, 4.52.

5,7,12,14-Tetrakis(phenylethynyl)pentacene (IVb).—To a solution of 1.69 g (7.5 mmol) of stannous chloride dihydrate in 15 ml of 50% acetic acid was added 1.12 g (1.5 mmol) of the tetrol in 50 ml of dioxane. A dark green color formed as the mixture was stirred at room temperature for 5 hr. Filtration gave 0.98 g of solid which was insoluble in most organic solvents. Recrystallization from 1,2,4-trichlorobenzene gave dark green needles, mp >300°.

Anal. Calcd for $C_{54}H_{30}$: C, 95.58; H, 4.42. Found: C, 95.50; H, 4.28.

Fluorescence Measurements.—The techniques and instrumentation used for obtaining absolute emission intensities, spectra and quantum yields in the visible region have been described elsewhere.[11a] An instrument similar in design, but with sensitivity out to 1.0 μ, was constructed and used to obtain fluorescence data in the long-wavelength visible and near-infrared regions.[11b]

Registry No.—Ia, 120-12-7; Ib, 10075-85-1; Ic, 1499-10-1; Id, 10273-82-2; IIa, 92-24-0; *cis*-5,12-dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene, 18826-28-3; *trans*-5,12-dihydroxy-5,12-bis-(phenylethynyl)-5,12-dihydronaphthacene, 18826-65-8; IIb, 18826-29-4; IIIa, 135-48-8; *cis*-6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene, 18826-30-7; *trans*-6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene, 18826-66-9; IIIb, 18826-31-8; 5,7,12,14-tetrahydroxy-5,7,12,14-tetrakis(phenylethynyl)-5,7,12,14-tetrahydropentacene, 18841-60-6; IVb, 18826-38-5.

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(11) (a) B. G. Roberts and R. C. Hirt, *Appl. Spectr.*, **21**, 250 (1967); (b) M. M. Rauhut, B. G. Roberts, D. R. Maulding, W. Bergmark, and R. Coleman, submitted for publication.

Reactions of Pentafluorophenylcopper Reagent

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A pentafluorophenylcopper reagent containing magnesium halide was prepared from the reaction between pentafluorophenylmagnesium bromide and cuprous chloride. The reagent underwent reactions representative of both organocopper and perfluoroaryl organometallic compounds. Reactions with H_2O, CO_2, O_2, C_6H_5I, *p*-$C_6F_5OC_6F_4Br$, *p*-$CH_3OC_6F_4I$, $CF_2{=}CFI$, and $C_7F_{15}I$ have been studied. The effect of the magnesium halide content on the reactivity of the pentafluorophenylcopper reagent was examined.

The method for the preparation of decafluorobiphenyl from bromopentafluorobenzene and copper-bronze[1] suggests the intervention of a pentafluorophenylcopper intermediate. Reports have indicated that pentafluorophenylmercury,[2] zinc,[3] and cadmium[4] and more recently perfluoroalkylcopper compounds[5]

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(1) (a) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959); (b) W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Stand.*, *A*, *H*, **63**, 167 (1959); (c) J. M. Birchall, R. Hazard, R. N. Haszeldine, and W. W. Wakalski, *J. Chem. Soc.*, *C*, 47 (1967).

(2) R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *ibid.*, 4367 (1962).

(3) J. G. Noltes and J. W. G. Van den Hurk, *J. Organometal. Chem.*, **1**, 337 (1964).

(4) M. Schmeisser and M. Weidenbruch, *Chem. Ber.*, **100**, 2306 (1967).

(5) (a) I. M. White, J. Thrower, and V. C. R. McLoughlin, 4th International Fluorine Symposium, Estes Park, Colo., 1967; (b) J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Commun.*, 1259 (1967).

TABLE I

REACTIONS OF THE REAGENT PREPARED FROM C_6F_5MgBr + CuCl WITH RX[a]

RX	Solvent	Temp, °C	Time, hr	Products, % C_6F_5R	$(C_6F_5)_2$	C_6F_5X	Other, %
C_6F_5I	THF	66	10	74	74		
	DMAC	60	18	78	78		
p-$C_6F_5OC_6F_4Br$	DMAC	60	1.5	0	0	20	p-$C_6F_5OC_6F_4H$[b] (22) p-$C_6F_5OC_6F_4Br$ (30)
	THF	66	60	5	5	18	p-$C_6F_5OC_6F_4H$[b] (18) p-$C_6F_5OC_6F_4Br$ (50) p-$(C_6F_5OC_6F_4)_2$ (2)
p-$MeOC_6F_4I$	THF	66	20	70	12	~2	p-$MeOC_6F_4H$,[b] p-$(MeOC_6F_4)_2$
	Bu_2O	70	48	45	<1	0	
C_6H_5I	THF	66	168	71	0	0	
$CF_2{=}CFI$	THF	25–55	5	55	<1	<2	
$C_7F_{15}I$	DMAC	60	5	0	25	15	

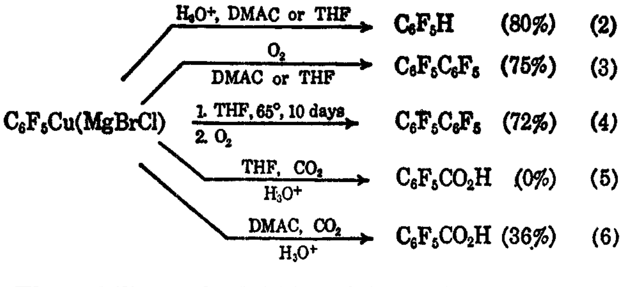
[a] The ratio of reactants was 1:1; the concentration of the organocopper species varied from *ca.* 0.2 to 0.3 mol/l. (see Experimental Section). [b] After aliquot hydrolysis.

are easily prepared and are more thermally stable than their corresponding hydrogen analogs. On this basis, attempts to prepare pentafluorophenylcopper[6] and study its reactions seemed feasible.

Synthesis and Reactions

A pentafluorophenylcopper reagent[7] containing halide ion was prepared by the reaction between pentafluorophenylmagnesium bromide and cuprous chloride in tetrahydrofuran (THF) (eq 1). Evaporation of the solvent *in vacuo* afforded a white solid that could be dissolved in most dipolar aprotic solvents. Reactions of the pentafluorophenylcopper species in THF [or N,N-dimethylacetamide (DMAC)] with oxygen and water yielded decafluorobiphenyl and pentafluorobenzene, respectively (eq 2–4). The yield of decafluorobiphenyl was not affected by refluxing the organometallic solution (THF) for 10 days prior to oxidation.[8] Carbonation of the THF solution of the reagent did not afford pentafluorobenzoic acid. When the same reaction was repeated and subsequently oxidized, the typical yield of decafluorobiphenyl was obtained. Carbonation of the same reagent in DMAC, however, afforded pentafluorobenzoic acid (eq 5 and 6).

$$C_6F_5MgBr + CuCl \xrightarrow[25°,\ 24\ hr]{THF} \text{“}C_6F_5Cu(MgBrCl)\text{”} \qquad (1)$$



The stability and solubility of the perfluoroarylcopper reagent seem characteristic for perfluorinated copper(I) compounds,[5] whereas its reactions (oxidation and hydrolysis) are characteristic of copper(I) organometallics in general.[9] The fact that the organometallic copper species can be carbonated in DMAC and not in THF presumably reflects the greater carbanion character in the more complexing solvent.

Results of the reactions of the organocopper reagent with various halogen compounds are presented in Table I. Apparently, this reagent reacts *via* two basic pathways; path I is representative of organocopper species,[10a] and path II is characteristic of perfluoroaryl organometallic species.[10b]

Variation of the solvent effects the course of reaction; *e.g.*, when the copper reagent is allowed to react with p-$C_6F_5OC_6F_4Br$ in DMAC, path II occurs specifically whereas in THF paths I and II are competitive. Similarly, p-$MeOC_6F_4I$ in dibutyl ether specifically reacts with the copper reagent by way of path I while in THF paths I and II are competitive.

The rates of reaction between the copper reagent and various substrates leading to coupled products (C_6F_5R, see Table I) qualitatively decrease in the series perfluoroaromatic ~ perfluoroolefin > aromatic > perfluoroalkyl halide with iodine being a more effective leaving group than bromine. Under our experimental conditions, reactions with perfluoroalkyl iodides failed to yield appreciable amounts of coupled products in either DMAC or THF.

A four-centered transition state where carbon–carbon bond making and carbon–halogen bond breaking are concerted has been proposed for the reactions of cuprous acetylides[11] or salts[12] with aryl halides. Our halogen mobilities are consistent with these proposals. However, the fact that perfluoroaromatics (and olefins) are more reactive toward the copper reagent than hydrocarbon aromatics may suggest that in the transition state of the former, carbon–carbon bond making may proceed to a greater extent than carbon–halogen bond breaking. This could conceivably lower the energy gap between fluoroaromatic ground and transition states by delocalization of negative charge throughout the fluoroaromatic ring. Quantitative data would be necessary to distinguish these possibilities.

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[6] Since our work began, the synthesis and certain reactions of pentafluorophenylcopper have been reported: see (a) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968); (b) S. S. Dua, A. E. Jukes, and H. Gilman, *J. Organometal. Chem.*, **12**, P24 (1968); (c) A. E. Jukes, S. S. Dua, and H. Gilman, *ibid.*, **12**, P44 (1968).

[7] Since the structure of this compound has not been determined as yet, the reagent will be designated by the general formula "$C_6F_5Cu(MgX_2)$." Qualitative analysis of the reagent indicated the presence of Cu, Mg and halide ions.

[8] Pentafluorophenylmagnesium bromide on the other hand decomposes to a hard, intractable "perfluorophenylene" under reflux conditions.

[9] G. M. Whitesides, J. San Filippo, Jr., C. P. Casey, and E. J. Panek, *J. Amer. Chem. Soc.*, **89**, 5302 (1967).

[10] (a) E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967); (b) R. J. De Pasquale *J. Organometal. Chem.*, **15**, 233 (1968).

[11] R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

[12] (a) R. G. R. Bacon and H. O. A. Hill, *J. Chem. Soc.*, 1097 (1964); (b) L. J. Belf, M. W. Buxton, and G. Fuller, *ibid.*, 3372 (1965).

Path II (eq 8) is considerably more sensitive to the complexing ability of the solvent (DMAC > THF > Bu_2O) than path I (eq 7, X = Br, I). Since this type of equilibrium (path II) is characteristic of perfluoroaryllithium and magnesium reagents,[10b] suspicion is aroused regarding the nature of the organometallic involved in this process. To clarify this situation, hopefully magnesium halide was partially precipitated from the reagent with dioxane, and the reactions of the resulting reduced halide–organometallic solutions were investigated for comparison.[13]

$$C_6F_5Cu(MgBrCl) + RX \longrightarrow C_6F_5R + CuX(MgBrCl) \qquad (7)$$

$$\begin{array}{c} C_6F_5Cu(MgBrCl) + RX \rightleftharpoons C_6F_5X + RCu(MgBrCl) \qquad (8) \\ \downarrow O_2 \\ C_6F_5C_6F_5 + C_6F_5R + RR \end{array}$$

Reactivity of the Pentafluorophenylcopper Reagent *vs.* Magnesium Halide Content.—The halide-reduced organometallic solution was allowed to react with p-$MeOC_6F_4I$ and p-$C_6F_5OC_6F_4Br$ in the presence and the absence of an added equivalent of magnesium bromide. These results along with the reactions of the reagent prepared from $C_6F_5MgBr + CuCl$ are shown in Tables II and III.

Table II

Reactions of "RCu" with p-$C_6F_5OC_6F_4Br$ in DMAC at 60 ± 2° [a]

Reagent	RCu, initial concn,[b] mol/l.	Time, hr	Ratio of C_6F_5Br/ p-$C_6F_5OC_6F_4H$/ p-$C_6F_5OC_6F_4Br$	Starting material accounted for, %
$5.5C_6F_5Cu$–$MgBr_2$	0.22	0.08	4:7:10	
		3.0	3:6:2	95
C_6F_5Cu–$1.18MgBr_2$	0.22	0.08	1:1.8:15.5	
		3.0	1:1.4:1.2[c]	80
$C_6F_5MgBr + CuCl$	0.31	1.5	2:3:4[c]	79[d]

[a] Under these conditions, coupled products, *e.g.*, $(C_6F_5)_2$ or p-$C_6H_5OC_6F_4C_6H_5$, were not observed. [b] Obtained by determining C_6F_5H after aliquot hydrolysis. [c] Prior to oxidation. [d] After oxidation.

Table III

Reactions of "RCu" with p-$MeOC_6F_4I$ in THF at 66°

Reagent	RCu, initial concn,[a] mol/l.	Time, hr	Ratio of $(C_6F_5)_2$/ p-$C_6F_5C_6F_4OMe$	Completion,[b] %
$5.5C_6F_5Cu$–$MgBr_2$	0.22	3	1:3.5[c]	80
C_6F_5Cu–$1.18MgBr_2$	0.22	18	1:4.4[c]	80
$C_6F_5MgBr + CuCl$	0.24	20	1:6	85

[a] Obtained by determining C_6F_5H after aliquot hydrolysis. [b] Obtained from unreacted p-$MeOC_6F_4I$; further reaction time drove reactions to >90% completion. [c] Duplicate experiments.

From the data several points emerge; solutions studied containing various ratios of $MgBr_2$–arylcopper species undergo similar types of reactions, but with different rates and product distributions. The variation of the latter with $MgBr_2$ concentration strongly suggests that there is more than one reactive organocopper species present. Costa, *et al.*,[14] have recently discussed the various complexes formed in their synthesis of phenylcopper. Such complexes will vary in composition with change in stoichiometry and solvent.

It could be argued that a perfluoroaryl Grignard reagent is present from incomplete initial reaction (eq 1) or is formed by a reversible process inherent in the organocopper preparation. The perfluororarylmagnesium compound could then be the species responsible for the exchange process indicated by eq 8. This possibility, however, is inconsistent with the following observations. (a) Concerning the reversibility, the Grignard source could reasonably be formed from the complex given in eq 9. By mass law, added magnesium halide should enhance the Grignard concentration and thereby accelerate reactions involving this species. This reasoning, however, is not consistent with the results in Tables II and III, namely, that the halide-reduced copper reagent exchanges halogen at the faster rate. (b) Pentafluorophenylmagnesium compounds decompose after several hours at THF reflux temperature, affording a "perfluoropolyphenylene".[15] In contrast, the organocopper reagent prepared from $C_6F_5MgBr + CuCl$ is stable after 10 days at THF reflux temperature. (c) Pentafluorophenylmagnesium halides react irreversibly with CO_2[16] (THF) and N-methylformanilide[17] (Et_2O), whereas the copper reagent prepared above is not reactive in similar instances.

$$\text{“}C_6F_5Cu(MgX_2)\text{”} \rightleftharpoons C_6F_5MgX + CuX \qquad (9)$$

In view of these data, the reagent prepared from pentafluorophenylmagnesium bromide and cuprous halide seems to undergo reactions representative of a complexes pentafluorophenylcopper species. The variation of reaction rate with solvent (carbonation and rapid exchange in DMAC and not in THF; heterolytic decomposition in DMAC, see below) is probably typical of weakly ionized organometallics.[18] Even though the exact structure of the copper complexes prepared from the metathetical reaction of perfluoroaryl Grignards and cuprous halides is not known, the reagent is versatile and its modes of reaction are predictable.

Stability of "$C_6F_5Cu(MgBrCl)$" in DMAC.—The decomposition (100°, DMAC) of the perfluoroarylcopper reagent was monitored by the decrease in pentafluorobenzene (formed on hydrolysis of aliquot samples) with time. After 8 hr, approximately 50% of the organometallic reagent had decomposed to an intractable material suspected to be a "perfluoropolyphenylene".[15] Products derived from the reaction of a copper species with DMAC were not observed. The decomposition was repeated in the presence of decafluorobiphenyl, and in another experiment with naphthalene. In the presence of decafluorobiphenyl, 62% of the organometallic reagent had decomposed after 1 hr yielding perfluoroterphenyl and perfluoroquaterphenyl along with the previously isolated "perfluoropolyphenylene." The decomposition of the organometallic was unaffected by the presence of naphthalene. Decafluorobiphenyl readily undergoes nucleo-

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(13) Halide-free pentafluorophenyl copper has been recently prepared, see ref 6a.

(14) G. Costa, A. Camus, L. Gatti, and N. Morsich, *J. Organometal. Chem.*, **5**, 568 (1966).

(15) This material was initially characterized by J. Thrower and M. A. White, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, 19K.

(16) R. J. Harper and C. Tamborski, *Chem. Ind.* (London), 1824 (1964).

(17) A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 808 (1961).

(18) A recent paper reported that the acid–base reaction between diethylcadmium and phenylacetylene is extremely solvent dependant: O. Yu. Okhlobystin and L. I. Zakharkin, *Zh. Obshch. Khim.*, **36**, 1734 (1966).

philic substitution reactions[19] and naphthalene is an effective radical scavenger.[20] Decafluorobiphenyl accelerated the decomposition of the organometallic whereas naphthalene did not afford a naphthylpentafluorophenyl adduct. These facts strongly suggest that under our conditions, the organocopper reagent is decomposing by a heterolytic rather than a homolytic mechanism.

Experimental Section

Fluoroaromatics used in this work were either purchased from Imperial Smelting (N. S. C) Ltd., Avonmouth, England, or prepared from published procedures. Solvents were purified and dried by conventional methods and distilled prior to use. Reactions involving organometallic reagents were carried out under dry nitrogen with the usual precautions for the rigorous exclusion of moisture and air. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected. The ^1H and ^{19}F nmr spectra were recorded on a Varian A 56-60 spectrometer in carbon tetrachloride as solvent; chemial shifts are reported in parts per million from internal tetramethylsilane or trichlorofluoromethane. Infrared spectra were run on a Perkin-Elmer "Infracord" spectrometer as KBr pellets (solids) of films (liquids.) Vpc analysis were performed on F & M Model 500 or 810 instruments using a 6 ft × 0.25 in. column, 20% Apiezon L (F & M Model 500) and a 11 ft × 0.25 in. column, 20% polyphenyl ether (six ring) on 60–80 mesh Chromosorb W (F & M Model 810). The mass spectral analysis were performed on a CEC-21-110B mass spectrometer.

A. Preparation of Pentafluorophenylcopper Reagent Containing Magnesium Halide.—Ethylmagnesium bromide (0.101 g, 80.0 ml in THF) was added to a stirred solution containing bromopentafluorobenzene (25.0 g, 0.101 mol) dissolved in THF (170 ml) containing *t*-butylbenzene (2.5 g) as an internal vpc standard.[21] The rate of addition was such that the temperature of the reaction did not exceed 30°. After the completion of addition, the reaction mixture was stirred for 0.5 hr at room temperature. On rapid addition of cuprous chloride (10.0 g, 0.101 mol), the reaction temperature rose to 35°. The resulting mixture was allowed to stir at room temperature for 18 hr. The precipitate was allowed to settle and an aliquot sample of the supernatant liquid was withdrawn, hydrolyzed, extracted with pentane and analyzed by vpc. The yields of pentafluorobenzene thus obtained ranged from 76 to 85%. Small amounts of decafluorobiphenyl[22] were detected in solution. The supernatant liquid showed little change after being stored for 2 weeks under nitrogen and was used for the following experiments.

Oxidation.—A 50-ml aliquot (0.015 mol) of the supernatant liquid prepared as described above was pipeted into a dry flask. Anhydrous oxygen was bubbled through the solution for 1.5 hr producing a dark mixture. An aliquot sample which was withdrawn and analyzed by vpc revealed that decafluorobipheny- (70–80%) was the major volatile product. From the reaction mixture, decafluorobiphenyl was isolated *via* alumina chromatography and its structure was verified by spectral comparisons with an authentic sample. The quantity of "C_6F_5Cu" in solution prepared as described above was estimated by averaging the yields of C_6F_5H and $(C_6F_5)_2$ obtained on hydrolysis and oxidation, respectively.

Carbonation.—A 50-ml aliquot (0.015 mol) was stirred at 25° for 2 hr while carbon dioxide was bubbled through the solution. Conventional work-up of the reaction mixture did not afford pentafluorobenzoic acid. The experiment was repeated and after carbonation the solution was oxidized by passing dry oxygen through the reaction mixture for 1.5 hr. Work-up of the reaction mixture afforded 2.5 g (75% yield) of decafluorobiphenyl.

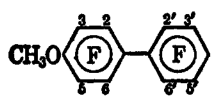
Another 50-ml aliquot (0.015 mol) of the THF solution was concentrated *in vacuo* producing a white residue which was then dissolved in 50 ml of dimethylacetamide (DMAC). The solution was carbonated as described above and yielded 1.5 g of pentafluorobenzoic acid (36% yield).

Reaction with Iodopentafluorobenzene.—Iodopentafluorobenzene (2.5 g, 8.6 mmol) was added to 25 ml of the THF solution of pentafluorophenylcopper reagent (8.6 mmol). The reaction mixture was heated at 66° for 10 hr. The precipitate that formed was filtered under nitrogen and the filtrate was quenched with 25 ml of water. The resulting mixture was extracted with two 25-ml portions of petroleum ether (bp 30–60°). The petroleum ether solution was concentrated leaving 3.3 g of an oil which solidified on standing. Recrystallization of this material from methanol afforded 2.1 g (74% yield) of decafluorobiphenyl. The above reaction was repeated in DMAC with similar results.

Reaction with 4-Pentafluorophenoxybromotetrafluorobenzene. DMAC Solvent.—A 50-ml quantity of the THF solution containing pentafluorophenylcopper reagent (0.015 mol) was concentrated to remove all the THF. To this solid was added 50 ml of DMAC and 4-pentafluorophenoxybromotetrafluorobenzene (6.30 g, 0.015 mol). After heating this solution at 60° for 1.5 hr, an aliquot sample was removed, worked up as previously described and analyzed by vpc. The analysis indicated C_6F_5Br, *p*-$C_6F_5OC_6F_4H$, *p*-$C_6F_5OC_6F_4Br$ in a 2:3:4 area ratio, respectively.[23] The reaction mixture was then oxidized by passing dry oxygen throgh the mixture for 3 hr at 60°. The reaction was hydrolyzed and analyzed by vpc indicating six compounds: C_6F_5Br (20%), $(C_6F_5)_2$ (6%), *p*-$C_6F_5OC_6F_4H$ (6%), *p*-$C_6F_5OC_6F_4Br$ (30%), *p*-$C_6F_5OC_6F_4C_6F_5$ (8%), and *p*-$(C_6F_5OC_6F_4)_2$ (9%).

THF Solvent.—4-Pentafluorophenoxybromotetrafluorobenzene (6.30 g, 0.015 mol) was added to 50 ml of a THF solution of pentafluorophenylcopper reagent (0.015 mol), the reaction mixture heated at 66° for 1.5 hr and a sample was removed for vpc analysis. At this time, no appreciable reaction had occurred so the reaction was allowed to proceed for an additional 20 hr. Analysis by vpc indicated the following compounds: C_6F_5Br, $(C_6F_5)_2$, *p*-$C_6F_5OC_6F_4H$, *p*-$C_6F_5OC_6F_4Br$ and *p*-$C_6F_5OC_6F_4C_6F_5$ in 1:1:1:-20:1 are a ratio, respectively. After 2.5 days of additional heating at 66°, an additional product appeared, *p*-$(C_6F_5OC_6F_4)_2$. The products identified in increasing vpc retention time were C_6F_5Br (18%), $(C_6F_5)_2$ (5%), *p*-$C_6F_5OC_6F_4H$ (18%), *p*-$C_6F_5OC_6F_4Br$ (50%), *p*-$C_6F_5OC_6F_4C_6F_5$ (5%) and *p*-$(C_6F_5OC_6F_4)_2$ (2%).

Reaction with 4-Methoxyiodotetrafluorobenzene. THF Solvent.—4-Methoxyiodotetrafluorobenzene (3.7 g, 0.012 mol) was added to 50 ml of the THF solution of pentafluorophenylcopper reagent (0.012 mol). The reaction mixture was stirred and heated at 66° for 20 hr. Analysis of the reaction mixture by vpc and mass spectroscopy indicated four products, *p*-$CH_3OC_6F_4H$, $(C_6F_5)_2$, *p*-$CH_3OC_6F_4C_6F_5$ (70% yield), and *p*-$(CH_3OC_6F_4)_2$ in a 1:1:6:1 area ratio, respectively. Mass spectral analysis provided the parent ion peaks *m/e* 180, 334, 346 and 358, respectively. The major product, *p*-$CH_3OC_6F_4C_6F_5$, was isolated by preparative vpc in a 70% yield, mp 58–60°, *m/e* 346. Its ^1H nmr spectrum exhibited a triplet (J = 2 Hz) at 4.2 ppm. The ^{19}F nmr spectrum indicated five regions: +137.6 (m, 2), +139.6 (m, 2), +150.9 (t of t, 1, $J_{4'5'}$ = 21 Hz, $J_{4'6'}$ = 1.5 Hz), +156.9 (one-half AA′XX′, 2), +160.9 (m, 2). These were assigned the fluorine atoms at the 2–6 (or 2′–6′), 4′, 3–5, and 3′–5′ positions, respectively.



$(n\text{-}C_4H_9)_2O$ Solvent.—A 50-ml aliquot of pentafluorophenylcopper reagent (0.015 mol)–THF solution was heated *in vacuo* to dryness. To this solid was added *n*-dibutyl ether (70 ml) and the reaction mixture was stirred and heated at 70° for 2 days. Analysis of the reaction mixture by vpc indicated *p*-$CH_3OC_6F_4C_6F_5$ (45%) as a major reaction product with *p*-$CH_3OC_6F_4I$ (50%) remaining unreacted. Only a trace of $(C_6F_5)_2$ was formed.

Reaction with Iodobenzene.—Iodobenzene (1.6 g, 7.9 mmol) was added to 25 ml of the THF solution of pentafluorophenylcopper reagent (7.9 mmol) and the reaction mixture was heated at 66°. The reaction was monitored by vpc analysis which indicated that the reaction proceeded very slowly. After 7 days at 66°, vpc analysis indicated $C_6F_5C_6F_5$ (71%) as the only reaction product. There was no $(C_6H_5)_2$ or $(C_6F_5)_2$ present. The

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[19] (a) R. J. De Pasquale and C. Tamborski, *J. Org. Chem.*, **32**, 3163 (1967); (b) J. Thrower and M. A. White, private communication, May 1964.

[20] D. H. Heg and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

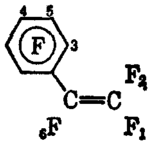
[21] The yields were obtained by the vpc method using an internal standard unless otherwise stated.

[22] In the reactions where decafluorobiphenyl was the reaction product, the yield of decafluorobiphenyl was determined by subtracting the initial concentration formed during the preparation of pentafluorophenylcopper reagent (blank) from the observed value.

[23] Pentafluorobenzene, the other product of this reaction, was not determined in the vpc analysis.

reaction mixture was hydrolyzed and the crude product (1.6 g) was recrystallized from the CH_3OH/C_6H_6 mixture, mp 109–111°, with an infrared spectrum identical with that of an authentic sample.

Reaction with Iodotrifluoroethylene.—Freshly distilled iodotrifluoroethylene (8.7 g, 0.042 mol) was added to 150 ml of the THF solution of pentafluorophenylcopper reagent (0.042 mol). The reaction flask, equipped with a methanol-ice condenser, was heated gradually from 25 to 55°. After 5 hr at 55°, the reaction mixture was cooled and analyzed by vpc. Analysis indicated the presence of two products, $C_6F_5CF{=}CF_2$[24] and C_6F_5I, in a 20:1 area ratio, respectively. The solution was decanted from the precipitate, hydrolyzed with water (5 ml), filtered, dried ($CaCl_2$) and distilled. The fraction with bp 124–125° was further analyzed by vpc and indicated a purity of 98%. The perfluorostyrene had a characteristic C=C absorption in the infrared spectrum at 5.65 μ. Its ^{19}F nmr spectrum shown multiplets at +97, +113, +138, +150, +162 and +171 ppm which were assigned the F_1–F_6, respectively. The experimentally derived coupling constants were $J_{1,2} = 63$, $J_{1,6} = 36$, $J_{1,3} = 2.5$, $J_{1,4} = 1$, $J_{2,6} = 117$, $J_{2,3} = 10.5$, $J_{2,4} = 1.5$, $J_{4,5} = 20$ Hz.



Reaction with Perfluoroheptyl Iodide.—*n*-Perfluoroheptyl iodide (6.6 g, 0.013 mol) was added to 50 ml of the supernatant THF solution of pentafluorophenylcopper reagent (0.013 mol). The resulting solution was stirred at 25° for 3 hr. Analysis by vpc indicated the formation of two products $(C_6F_5)_2$ (4%) and C_6F_5I (3%). The reaction mixture was then heated to 60° for 5 hr. The two products increased in concentration to 25 and 15%, respectively. After hydrolysis of the reaction mixture, C_6F_5H (47%) was also observed. None of the desired product perfluoro-*n*-heptylbenzene[25] was detected. When the reaction was repeated in DMAC as the solvent, analogous results were obtained.

B. Preparation of Halide-Reduced Pentafluorophenylcopper Reagent.—The organocopper reagent was prepared as described above from pentafluorophenylmagnesium bromide (0.101 mol in 250 ml of THF) and cuprous bromide (14.5 g, 0.10 mol). After the reaction mixture was stirred overnight, 10.0 ml of anhydrous dioxane was added and the precipitate was filtered under dry nitrogen. A 1-ml aliquot was removed from the filtrate and analyzed for bromide ion by quenching in 3 ml of 3 *N* HNO_3 and titrating the resulting solution potentiometrically with silver nitrate. The concentration of bromide ion in solution was determined as 0.33 mequiv/ml. The filtered THF solution of pentafluorophenylcopper reagent was used in the following experiments.

Reaction with 4-Pentafluorophenoxybromotetrafluorobenzene.—A 50-ml sample of the above THF solution was gently heated to dryness *in vacuo*. To this dry residue was added 50 ml of DMAC and cumene (0.40 g) as an internal standard. An aliquot sample was removed, hydrolyzed and analyzed for pentafluorobenzene in order to determine the concentration of the pentafluorophenylcopper reagent. The DMAC solution was divided into two equal fractions (A and B). To fraction A was added p-$C_6F_5OC_6F_4Br$ (2.24 g, 5.45 mmol) and the mixture was heated to 60 ± 2°. After 5 min, an aliquot sample was removed, worked up and indicated the products C_6F_5Br–p-$C_6F_5OC_6F_4H$–p-$C_6F_5OC_6F_4Br$ in a 4:7:10 area ratio, respectively; after 3 hr, the ratio of products was 3:6:2 with *ca.* 95% of the material accounted for. To fraction B was added an ether solution (2.30 ml, 5.45 mmol) of magnesium bromide and p-$C_6F_5OC_6F_4Br$ (2.24 g, 5.45 mmol). The reaction mixture was stirred and heated at 60 ± 2°. After 5 min, an aliquot was worked up, analyzed and indicated the products C_6F_5Br–p-$C_6F_5OC_6F_4H$–p-$C_6F_5OC_6F_4Br$ in a 1:1.8:15.5 area ratio, respectively; after 3 hr, the ratio of products was 1:1.4:1.2 with *ca.* 80% of the material accounted for.

Reaction with 4-Methoxyiodotetrafluorobenzene.—A 25-ml sample (5.5 mmol) of the above THF solution was allowed to react with p-$CH_3OC_6F_4I$ (1.7 g, 5.5 mmol) at 66°. After 3 hr, the reaction was 80% complete and analysis of the reaction mixture indicated two major components, $(C_6F_5)_2$ and p-$CH_3OC_6F_4$-C_6F_5, in a 1:3.5 area ratio. After 4 hr, the reaction was nearly completed. To another 25-ml sample (5.5 mmol) of the above THF solution was added an ether solution of magnesium bromide (2.3 ml, 5.5 mmol) and p-$CH_3OC_6F_4I$ (1.7 g, 5.5 mmol). The reaction was heated at 66° and after 18 hr (80% completion), the ratio of $(C_6F_5)_2$-p-$CH_3OC_6F_4C_6F_5$ was 1:4.4.

C. Thermal Stability of Pentafluorophenylcopper Reagent. THF Solution.—A THF solution of pentafluorophenylcopper reagent (prepared as described in A above) was hydrolyzed and analyzed by vpc, indicating a 74% yield of C_6F_5H. The supernatant solution was then heated at 66° for 10 days, cooled to room temperature and oxidized yielding decafluorobiphenyl (74%).

DMAC Solution.—A 25-ml aliquot of the supernatant THF solution was heated *in vacuo* until dryness. The solid residue was dissolved in DMAC (25 ml) and heated to 100°. At intervals, samples were witdrawn and analyzed by vpc for C_6F_5H. From the decrease of C_6F_5H with time, the per cent decomposition of the organocopper reagent was determined (2 hr, 22%; 4.5 hr, 38%; 8 hr, 47%). After 8 hr, the reaction mixture was hydrolyzed with 3 *N* HCl (20 ml). The residue was filtered and triturated with hot THF, dried and yielded 0.25 g of a solid, mp >400°. The infrared spectrum of this material was identical with that of perfluoropolyphenylene.

DMAC and Decafluorobiphenyl.—The above experiment was repeated in the presence of 0.5 mol quantity of decafluorobiphenyl. After 1 hr, 62% of the organocopper reagent had decomposed (38% of decafluorobiphenyl remained). Also detected by the vpc analysis were two other components in a 4:1 area ratio. The molecular weights of these compounds, *m/e* 482 and 630, and their vpc retention time suggest the compounds perfluorotriphenyl and perfluoroquaterphenyl, respectively.

DMAC and Naphthalene.—The above experiment was repeated in the presence of naphthalene (*ca.* 4 mol quantity). Analysis of aliquot samples indicated a per cent decomposition of the organocopper reagent: 1 hr, 12%; 5.5 hr, 40%. There was no perfluorotriphenyl-, perfluoroquaterphenyl- or pentafluorophenylnaphthalene found in vpc analysis of the reaction mixture. Within the experimental error, no naphthalene was consumed during the course of the reaction.

Registry No.—Iodopentafluorobenzene, 827-15-6; 4-pentafluorophenoxybromotetrafluorobenzene, 14055-44-8; 4-methoxyiodotetrafluorobenzene, 1744-45-2; iodobenzene, 591-50-4; iodotrifluoroethylene, 359-37-5; perfluoroheptyl iodide, 335-58-0.

Acknowledgment.—We wish to express our appreciation to Lee D. Smithson of the Air Force Materials Laboratory for performing the mass spectral analysis.

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[24] (a) J. M. Antonucci and L. A. Wall, *SPE Trans.*, **3**, 225 (1963); (b) B. R. Letchford, C. R. Patrick, M. Stacey, and J. C. Tatlow, *Chem. Ind.* (London), 1472 (1962).

[25] C. Tamborski, G. Moore and R. J. De Pasquale, unpublished studies.