

SYNTHESIS AND REACTIONS OF ORGANOLITHIUM AND -MAGNESIUM COMPOUNDS OF PERFLUORODIPHENYL ETHERS

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SUMMARY

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ and $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ have been prepared. Their stability, benzyne formation and reactions with water, carbon dioxide, cuprous chloride and oxygen, phosphorus tribromide, tin tetrachloride have been studied. Solvent effects of THF, diethyl ether and furan on the synthesis and subsequent reactions of $p\text{-C}_6\text{F}_5\text{-OC}_6\text{F}_4\text{Li}$ are reported.

INTRODUCTION

Lithium and magnesium perfluoroaromatic organometallics have been the subject of numerous investigations¹. These are versatile intermediates and serve as useful precursors in the preparation of functional² and multi-functional³ fluorinated aromatics. As synthetic intermediates, they have adequate nucleophilic properties to react with organometallic halides^{4,5}, or displace fluoride ion from fluorinated aromatics⁶, heterocyclics⁷, and olefins⁶.

The kinetic instability of the pentafluorophenyl organometallics, especially the lithium derivative, necessitates mild reaction conditions otherwise decomposition to a polyfluorophenylene polymer results⁸. This decomposition was demonstrated to be composed of two distinct pathways⁶, *e.g.*, nucleophilic reaction of one anion at the *para* position of another and tetrafluorobenzyne intervention^{9,10}.

We have recently disclosed¹¹ the synthesis of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) and are now reporting the synthesis and reactions of its organometallic derivatives.

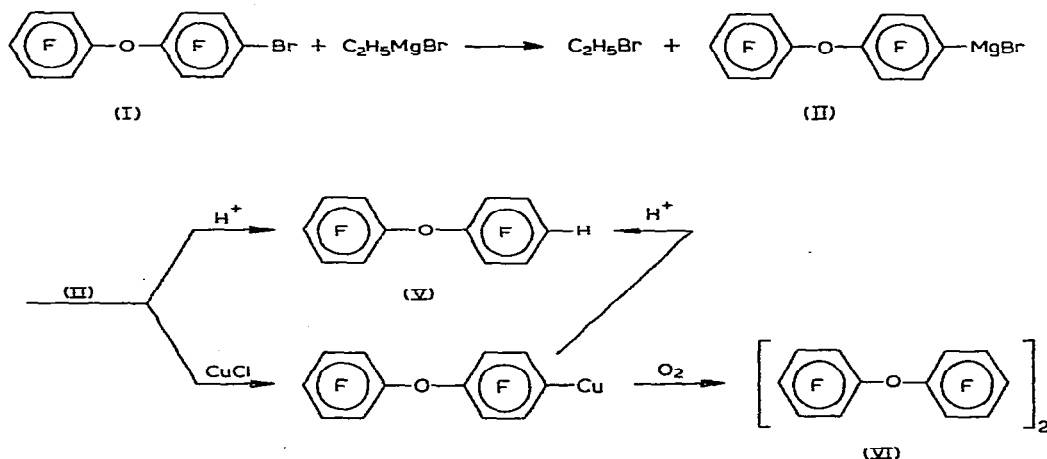
RESULTS AND DISCUSSION

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$

Reaction between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ and magnesium in tetrahydrofuran (THF) afforded an excellent yield of the Grignard reagent, $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (II). Derivatization via carbonation and reaction with phosphorus tribromide afforded the acid, $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{CO}_2\text{H}$ (III) and phosphine, $(p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4)_3\text{P}$ (IV) respectively.

The Grignard reagent (II) could be prepared more conveniently by halogen-metal interchange between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ and $\text{C}_2\text{H}_5\text{MgBr}$ ¹². Equilibration is

rapid and the position of equilibrium must be far to the right since ethylated products* are not detected even after several hours at room temperature. A THF solution of the Grignard prepared in this manner when hydrolyzed or treated with cuprous chloride and oxygen afforded $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) and the coupled product (VI), respectively.



Isolation of the coupled product (VI) suggests the intervention of a perfluoroarylcopper intermediate. If the reaction between the $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ and cuprous chloride, leading to such an intermediate, were slow, one would expect to isolate an appreciable quantity of polymeric material from the competing decomposition of the $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (see below). The fact that polymeric material was not observed even after 5 days at 65° , indicates that the organocopper intermediate forms rapidly and is stable under these conditions. Subsequent hydrolysis of an aliquot from the reaction mixture produced a 78% yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$. Oxidation** of the remaining reaction mixture at room temperature produced a 71% yield of the coupled product (VI).

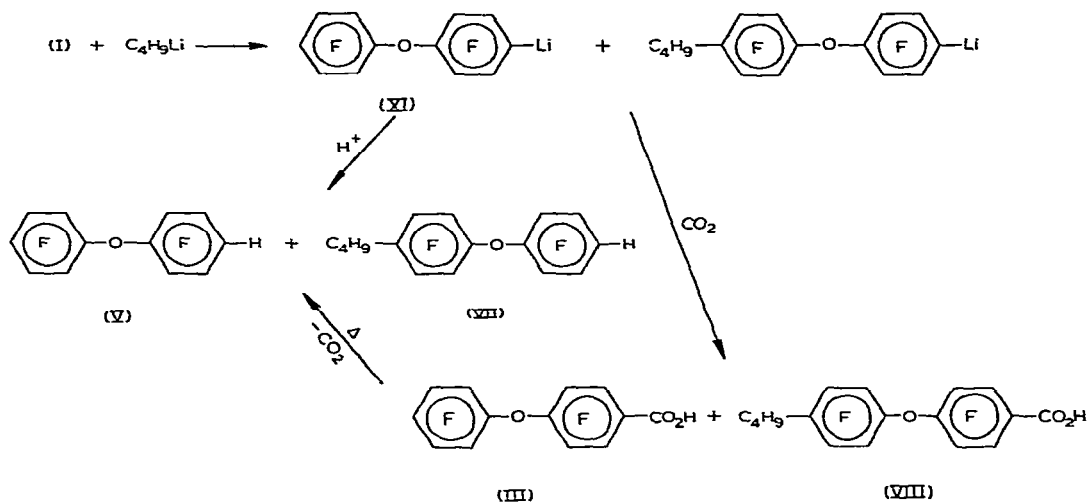
A THF solution of the Grignard reagent (II) (prepared by *Procedure A*, see *Experimental*) gradually decomposed at room temperature and rapidly (*ca.* 40% after 3 h) at the solvent reflux temperature (65°). Hydrolysis of the reaction mixture yielded a glassy, tractable, polymeric material.

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$

The addition of *n*-butyllithium to a THF solution of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ yielded two organometallic species. Analysis of a hydrolyzed aliquot by vapor phase chromatography (VPC) revealed the presence of three compounds in a 10/1/1 area ratio; $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$, $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$, and $p\text{-(4-}n\text{-C}_4\text{H}_9\text{C}_6\text{F}_4\text{O)C}_6\text{F}_4\text{H}$, respectively. Carbonation of the organometallic solution afforded two acids, (III) and (VIII).

* In this system small concentrations of ethylmagnesium bromide would be expected to irreversibly displace fluoride ion from either (I) or (II) producing (after hydrolysis) ethylated products.

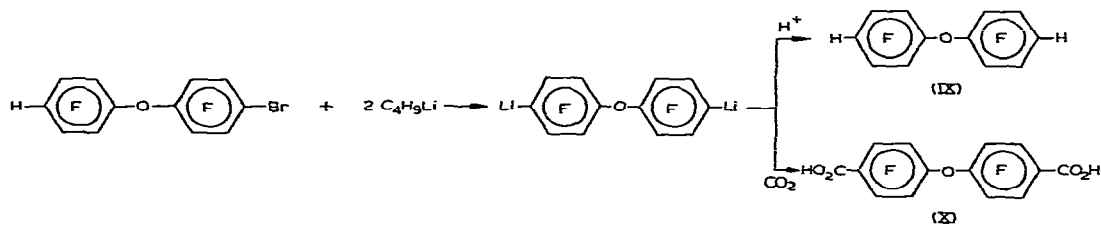
** Oxidation of organocopper compounds to yield coupled products is well documented in literature. We have recently shown¹⁵ that oxidation of " $\text{C}_6\text{F}_5\text{Cu}$ " produces a 72% yield of $(\text{C}_6\text{F}_5)_2$.



Analysis of the crude acid mixture [(III) and (VIII)] by VPC revealed the decarboxylated products (V) and (VII) in a 10/1 area ratio*. The butylated acid (VIII) was alternately prepared in a 47% yield, by the addition of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ to an excess of *n*-butyllithium followed by carbonation.

The presence of unreacted $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ in the above organometallic reaction mixture indicates that halogen-metal exchange and the alkylation reaction are competitive. Subsequent reruns of this reaction indicated that the ratio of metal-halogen exchange *vs.* alkylation never exceeded 10:1 respectively.

It is worthy to note that by substituting the 4'-fluorine in $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ by a hydrogen the resulting compound is not alkylated by *n*-butyllithium. Thus, the reaction between two equivalents of *n*-butyllithium and 4-bromo-2,2',3,3',5,5',6,6'-octafluorodiphenyl ether on hydrolysis gave only one volatile product, (IX).

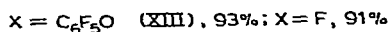
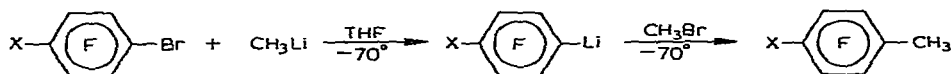


Carbonation of the organometallic solution afforded the diacid (X) in excellent yield.

The organolithium compound (XI) was also prepared by a metal-halogen interchange between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ and methylolithium at -70° in diethyl ether. Hydrolysis of the reaction mixture afforded a 95% yield of $p\text{-C}_6\text{F}_4\text{OC}_6\text{F}_4\text{H}$. Addition of tin tetrachloride to this organolithium reagent produced an 85% yield of $(p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4)_4\text{Sn}$ (XII). However, when (XI) was prepared in THF instead of diethyl ether, an interesting solvent effect was observed. Several minutes after the addition

* It has been previously reported¹¹ that (III) undergoes facile decarboxylation when subjected to VPC analysis (injection port 275°). This observation is quite general for a fluoroaromatic acid and will be elucidated in a subsequent communication.

of methyllithium, analysis of an aliquot sample (by VPC) revealed the presence of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ and $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{CH}_3$ (XIII), in an 8/2 area ratio, respectively. After an additional 30 min at -70° , a 1/10 area ratio of products was observed. Similar results were obtained when the experiment was repeated using $\text{C}_6\text{F}_5\text{Br}$.



Apparently $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ (or $\text{C}_6\text{F}_5\text{Li}$) is more nucleophilic in THF than in diethyl ether and effects displacement of a bromide ion from the methyl bromide present in the reaction mixture. Analogous solvent effects are not without precedence. $\text{C}_6\text{F}_5\text{MgBr}$ is reluctant to react with ethylene oxide¹³ or carbon dioxide in diethyl ether¹⁴ while in THF reactions go to completion.

Decomposition of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ (XI)

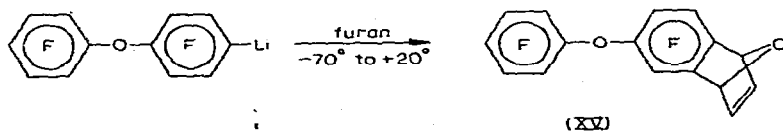
When a freshly prepared THF solution of (XI) was allowed to warm from -70° to room temperature, a tan, benzene-soluble, polymeric material (mol. wt. 4000 ± 100) resulted. The infrared spectrum of the polymer exhibited an Ar-O band at 8.7μ and was identical to that of the polymer obtained from a similar decomposition of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$. In order to gain insight into the mode of organometallic decomposition (via nucleophilic displacement, benzyne formation or both) a series of experiments was carried out.

(1). A THF solution of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ was allowed to remain at -70° for 4 h and subsequently hydrolyzed at -70° to produce a 72% yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$. In addition, a crystalline polymer, with an infrared spectrum similar to that of the previous experiment (-70° to room temperature decomposition), was obtained.

(2). The above experiment (1) was repeated in the presence of a ten-fold excess of anhydrous lithium iodide*. During the initial 4 h at -70° , aliquot samples were periodically withdrawn, hydrolyzed and analyzed by VPC. No products containing iodine were detected.

(3). The reaction mixture of (2) above was allowed to warm to room temperature. Analysis of the isolated, purified polymer had indicated incorporation of iodine into the polymeric structure.

(4). $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ was prepared at -70° in furan as the reaction medium**. As this reaction mixture was allowed to warm to room temperature, the organolithium compound decomposed to yield the benzyne-furan Diels-Alder adduct (XV).



* Reaction of tetrafluorobenzyne with lithium halides has been shown to be competitive with benzyne-pentafluorophenyllithium reactions under similar conditions⁶.

** Synthesis of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ in furan, in contrast to THF as the solvent, indicated no alkylation of the ring. This observation again indicates a greater nucleophilic character of the organolithium compound in THF as compared to furan.

(5). $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ was prepared as described in (4) above except that the reaction mixture was allowed to stand at -70° for 4 h and -30° for an additional hour. On hydrolysis of the reaction mixture, a quantitative yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ was obtained. [In contrast, using THF as a solvent, a 72% yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ plus polymer was obtained, see (1) above.]

The above observations suggest that at -70° in THF, decomposition of the organometallic compound occurs primarily (if not totally) by a nucleophilic displacement mechanism. If a benzyne intermediate had formed to any appreciable extent, its reaction with lithium iodide would lead to the detection of iodine-containing compounds. Iodine incorporation into the decomposed product (polymer), on warming the organometallic in the presence of lithium iodide, indicates that at some temperature between -70° and room temperature, formation of benzyne becomes competitive with nucleophilic displacement.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Solvents were purified and dried by conventional methods and distilled prior to use. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Chemical shifts are reported in ppm from the internal standard tetramethylsilane. The ^{19}F NMR spectra were recorded on a Varian V-4300-2-DP spectrometer at 40 MHz. Acetone was used as the solvent unless otherwise stated. Chemical shifts are reported in ppm from external trifluoroacetic acid. Infrared spectra were run on a Perkin-Elmer "Infracord" spectrometer as KBr pellets. VPC analyses were performed on an F & M Model 500 instrument using a helium flow of 60 cc/min, $6' \times 0.25''$ column, 20% Apiezon L on 60-80 mesh Chromosorb W and programmed from 100-275° (21°/min) after which it was held at 275°.

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (II)

Method A. $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) (1.00 g, 0.00243 mole) was added to magnesium turnings (0.243 g, 0.010 g-atom) in 15 ml of THF. The addition of 2 drops of ethylene bromide initiated the reaction. An additional quantity of (I) (2.0 g, 0.00486 mole) dissolved in 40 ml of THF was added dropwise at such a rate that the reaction mixture was maintained at *ca.* 35° . After completion of the addition, the reaction mixture was stirred for 2h. An aliquot was withdrawn from the reaction mixture, hydrolyzed with dil. HCl, extracted with petroleum ether (b.p. $30\text{--}60^\circ$) and analyzed by VPC. Analysis indicated only one major volatile product, $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) and a trace of unreacted (I).

Method B. A THF solution of ethylmagnesium bromide (6.5 ml, 1.15 N, 0.0075 mole) was added dropwise to a 50 ml THF solution of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) (3.0 g, 0.0073 mole) at room temperature. After allowing the reaction mixture to stir for 15 min, an aliquot was withdrawn, worked-up as described above, and analyzed by VPC. Again the only major product was $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) with a trace of unreacted (I).

Carbonation of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (II)

Carbon dioxide was bubbled into a solution of (II) (prepared by Method A) maintained at 0° . After 30 min, the reaction mixture was warmed to room temperature with continuing carbonation. The mixture was concentrated leaving a grey residue which after triturating with 100 ml of petroleum ether (b.p. $30\text{--}60^\circ$), produced 2.8 g of a grey-white salt. The salt was added to 100 ml of hot water and acidified with dil. HCl. On cooling, the aqueous solution was extracted with 3–30 ml portions of diethyl ether. The combined diethyl ether extracts were dried (MgSO_4) and concentrated. Recrystallization of the crude material from petroleum ether (b.p. $90\text{--}120^\circ$) afforded 2.1 g (76%) of the acid (III), m.p. $163\text{--}165$ (lit.¹¹ m.p. $168\text{--}169^\circ$). Its infrared spectrum was identical with that of an authentic sample.

Reaction between cuprous chloride and $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (II)

Cuprous chloride (0.72 g, 0.0073 mole) was added to a THF solution of (II) (0.0073 mole, prepared by Method B). The reaction was initially exothermic and was stirred for an additional 16 h at room temperature. *tert*-Butylbenzene (0.5 g) was added as an internal standard and an aliquot was removed, hydrolyzed and analyzed by VPC. Analysis indicated $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) was present (80% yield). The reaction mixture was heated for 5 days (65°) after which another aliquot was removed, hydrolyzed and analyzed by VPC. At this time (V) was still present (78% yield). Through the cooled reaction mixture (25°), oxygen was bubbled for 1.25 h. VPC analysis of an aliquot indicated that 5% of (V) and another major component were the only volatile products. The reaction mixture was quenched with 5 ml of dil. HCl and phase separated. Methanol (10 ml) was added to the organic phase and the solid that settled was collected, washed (methanol) and dried, m.p. $163\text{--}166^\circ$, 1.3 g. From the filtrate another 0.4 g of material was obtained and combined with the previous, 1.7 g total (71%). Recrystallization from ethanol/benzene gave a sample, m.p. $169\text{--}170^\circ$ (lit.¹¹ m.p. $170\text{--}171^\circ$), whose infrared spectrum and VPC retention time were identical with ($p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4$)₂ (VI).

($p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4$)₃P (IV)

A THF solution (20 ml) of PBr_3 (3.52 g, 0.0130 mole) was added dropwise to $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ [prepared by Method A, 13.0 g, 0.0360 mole of (I) and 1.13 g, 0.0470 g-atoms Mg] cooled to 0° . At the completion of addition, the reaction mixture was allowed to warm to room temperature, stirred for 3 days, and hydrolyzed with 100 ml of 0.5 N HCl. The bulk of the solvent was removed by a rotary evaporation and the remaining aqueous mixture was extracted with 2×100 ml of CH_2Cl_2 . Concentration of the solution afforded 3.6 g (29%) of crude (IV), m.p. $110\text{--}115^\circ$. Recrystallization from isopropyl alcohol yielded an analytical sample, m.p. $125\text{--}128^\circ$. (Found: C, 42.44; P, 2.95. $\text{C}_{36}\text{F}_{27}\text{O}_3\text{P}$ calcd.: C, 42.41; P, 3.03%.)

The ^{19}F NMR spectrum displayed typical pentafluorophenoxy absorptions at 80.0, 83.5 and 86.0 ppm. The remaining multiplets resonated at 53.6 (F_2 and F_6) and 79.0 ppm (F_3 and F_5).

 $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V)

The Grignard reagent, $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgCl}$, was prepared by the addition of $\text{C}_2\text{H}_5\text{MgCl}$ (22 ml of 2.9 N, 0.064 mole) to 200 ml of a diethyl ether solution of (I)

(25.0 g, 0.0610 mole) after 15 min the reaction mixture was hydrolyzed with dil. HCl, the organic layer phase separated, dried (MgSO_4) and concentrated leaving 19.9 g of a yellow liquid. This material was dissolved in petroleum ether (b.p. 30–60°) and eluted from a neutral grade Alumina column with petroleum ether (b.p. 30–60°). Concentration of the eluent left 18.4 g (90%) (V), m.p. 46–48° (lit.¹¹ m.p. 54–56°) whose infrared spectrum was identical with that of an authentic sample. The crude product (V) was further purified by sublimation (70°/0.4 mm), m.p. 54–55°.

Thermal stability of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{MgBr}$ (II)

The Grignard reagent (II) was prepared by *Method A*. Ethylbenzene (0.5 g) was added as an internal standard for VPC analysis. At intervals, aliquot samples were withdrawn, hydrolyzed and analyzed by VPC. After 24 h at room temperature, 5% decomposition of (II) was noticed. The reaction mixture was then refluxed gently. Analysis of subsequent samples showed 39% (3 h), 60% (25 h), 78% (70 h) and 99% (264 h) decomposition. Higher boiling products were detected in the aliquots withdrawn during the reflux period. Following work-up only a glassy-polymeric material was obtained.

Preparation and carbonation of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$

To a precooled (–70°), stirred solution of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) (3.0 g, 0.0073 mole) in 50 ml of THF was added *n*-butyllithium (0.0073 mole, 5 ml of a hexane solution) at such a rate that the temperature did not exceed –65°. Fifteen min after the completion of the addition, an aliquot was withdrawn, acidified and analyzed by VPC. Two major components in a 10/1 area ratio plus unreacted (I) (~5%) were found. The major component was determined as $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) while the minor component was found to be $p\text{-(4-}n\text{-C}_4\text{H}_9\text{C}_6\text{F}_4\text{O)C}_6\text{F}_4\text{H}$ (VII). The reaction mixture was then carbonated for 15 min at –70° and warmed to room temperature with continued carbonation. Usual work-up of the reaction mixture afforded 2.3 g of a material, m.p. 138–143°. VPC analysis of this acid mixture revealed the decarboxylated* products (V) and (VII) in a 10/1 area ratio. Recrystallization of this acid mixture from petroleum ether (90–120°) afforded 2.1 g (73%) of the acid $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{CO}_2\text{H}$ (III), m.p. 163–165°.

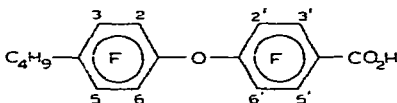
Preparation of $p\text{-(4-}n\text{-C}_4\text{H}_9\text{C}_6\text{F}_4\text{O)C}_6\text{F}_4\text{CO}_2\text{H}$ (VII)

A THF solution (25 ml) of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) (3.0 g, 0.0073 mole) was added to a precooled (–70°) solution of *n*-butyllithium (0.023 mole, 15 ml of a hexane solution). After 15 min, the reaction mixture was carbonated and worked up as previously described. Recrystallization from petroleum ether (60–90°) afforded 1.4 g (47%) of the acid (VII). (Found: C, 49.38; H, 2.40; F, 36.40. $\text{C}_{17}\text{H}_{10}\text{F}_8\text{O}_3$ calcd.: C, 49.26; H, 2.41; F, 36.71%) VPC analysis of this acid showed that it was identical by retention time to the minor acid component in the previous experiment.

The infrared spectrum of this acid showed a broad OH band at 3.4 μ and a C=O band at 5.84 μ . Its ^1H NMR (acetone- d_6) spectrum exhibited a carboxylic proton resonance at 9.56 ppm and a typical butyl group resonance at 2.8 (area 2), 1.1–2.0 (area 4) and 0.93 (area 3) ppm.

* See footnote p. 275.

The ^{19}F NMR spectrum exhibited basically 2 AA'XX' patterns. The first pattern halves were centered at 63.2 and 80.3 ppm while the second pattern halves were centered at 68.4 and 81.6 ppm. These patterns confirmed the 4,4'-orientation. The resonances were assigned to the 3',5'-; 2',6'-; 3,5- and 2,6-fluorine atoms respectively. The 3,5-fluorine atoms were broadened by the H-F coupling thus distinguishing them from the 3',5'-fluorine atoms. Extra lines appeared in the 80.3 and 81.6 ppm multiplets due to the 2',2-fluorine coupling. These assignments were substantiated by decoupling techniques.



Reactions between $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ and CH_3Li

A. $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ solvent. Methyl lithium in diethyl ether (3.0 ml, 1.6 N, 0.0049 mole) was slowly added (3 min) to a diethyl ether solution (25 ml) of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Br}$ (I) (2.0 g, 0.0049 mole) precooled to -70° . tert-Butylbenzene was used as an internal standard. The reaction mixture was homogeneous at this temperature and stirring was continued for an additional 15 min. VPC of an aliquot sample after hydrolysis indicated a 95% yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V). A by-product of the reaction $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{CH}_3$ (XIII) (3%) was also identified as well as unreacted (I) (2%).

B. THF solvent. The above experiment was repeated except that THF (25 ml) was substituted for the diethyl ether. Five minutes after the completion of addition of methyl lithium, an aliquot sample was hydrolyzed and analyzed by VPC. Analysis indicated two products $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) and $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{CH}_3$ (XIII) in a 8/2 area ratio respectively. After 30 min another aliquot was withdrawn, hydrolyzed, analyzed by VPC and indicated an area ratio of 1/10 [(V)/(XIII)]. This corresponds to a 93% yield of (XIII). The reaction mixture was then hydrolyzed with dil. HCl and extracted with 3–30 ml portions of petroleum ether (b.p. $30\text{--}60^\circ$). The combined organic layers were dried and concentrated leaving 2.2 g of oily material. The oil was dissolved in 10 ml of methanol, cooled to -70° and the crystals which formed were filtered. Recrystallization from methanol afforded 0.5 g of an analytical sample of (XIII), m.p. $52\text{--}53^\circ$. (Found: C, 45.28; H, 0.89; F, 49.36. $\text{C}_{13}\text{H}_3\text{F}_9\text{O}$ calcd.: C, 45.08; H, 0.88; F, 49.2%) The ^1H NMR spectrum of (XIII) showed a triplet at 2.32 ppm (J 2 Hz).

By following procedure B above using $\text{C}_6\text{F}_5\text{Br}$ as substrate, a 91% yield of $\text{C}_6\text{F}_5\text{CH}_3$ was obtained.

$(p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4)_4\text{Sn}$ (XII)

$p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ was prepared as described above ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ solvent) from (I) (30 g, 0.073 mole) and methyl lithium (45 ml, 1.6 N, 0.072 mole). To this solution precooled to -70° , was added tin tetrachloride (4.8 g, 0.018 mole) in 30 ml of hexane. The reaction mixture which became cloudy was stirred at -70° for 6 h and then allowed to attain room temperature. The reaction mixture was filtered and the precipitate was triturated with 100 ml of boiling methanol. The methanol mixture was filtered yielding 22.4 g of the product (XII), m.p. $255\text{--}257^\circ$. (Found: C, 39.73;

F, 47.40; Sn, 7.85. $C_{48}F_{36}O_4Sn$ calcd.: C, 39.94; F, 47.41; Sn, 8.23 %.

Preparation and carbonation of $(p\text{-LiC}_6\text{F}_4)_2\text{O}$

n-Butyllithium (10.1 ml, 1.5 N, 0.0152 mole) in pentane solution was added dropwise to a THF solution (50 ml) of *p*-(4-BrC₆F₄O)C₆F₄H (3.0 g, 0.0076 mole) precooled to -70° . After 15 min, an aliquot sample was hydrolyzed, analyzed by VPC and found to contain only one volatile product (*p*-HC₆F₄)₂O. The reaction mixture was carbonated at -70° for 30 min and allowed to warm to room temperature with continued carbonation. The solvent was aspirated and the remaining salt was dissolved in hot water. On acidification, a precipitate formed, was filtered, washed and dried, m.p. 255–262°. One recrystallization from *o*-dichlorobenzene yielded 2.8 g (81 %) of an analytical sample of (X), m.p. 270–272° (Found: C, 41.89; H, 0.44; F, 37.87; $C_{14}H_2F_8O_5$ calcd.: C, 41.81; H, 0.50; F, 37.80 %). Infrared analysis exhibited a broad OH band at 3.4 μ and a C=O band at 5.85 μ .

Stability of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{Li}$ (XI)

(a). The organolithium compound (XI) was prepared according to the previously described procedure. Analysis of an aliquot by VPC indicated a major component, *p*-C₆F₅OC₆F₄H (V) (90 %) and two minor components (VII) and unreacted (I) accounting for the remaining 10 %. The reaction mixture was kept at -70° for 4 h after which another aliquot was withdrawn and analyzed by VPC. A 72 % yield of (V) was found indicating that 20 % of the original organolithium compound (XI) decomposed after 4 h at -70° .

The organolithium was allowed to attain room temperature and then stirred for an additional 8 h. Hydrolysis and work-up of the reaction mixture afforded a brittle polymer. A portion of the polymer was dissolved in benzene and precipitated with methanol. The precipitated polymer had a softening point of 120° and a mol. wt. of 4000 ± 100 (vapor phase osmometry). The ¹⁹F NMR spectrum of the polymer exhibited multiplets at 51.8, 59.0, 64.8, 79.1 and 80.1 ppm (area 1/7/1/5/1).

(b) An equimolar quantity of anhydrous lithium iodide was added to a THF solution of *p*-C₆F₅OC₆F₄Li prepared as described previously. The reaction mixture was kept at -70° . Aliquot samples were removed periodically and analyzed by VPC. No iodinated diphenyl ether compounds were found. The reaction mixture was then allowed to attain room temperature and held at this temperature for 18 h. Hydrolysis and work-up of the mixture produced a polymeric material (softening point 125°) containing 5.2 % iodine.

(c). The organolithium compound (XI) was prepared as described previously except that furan was the solvent instead of THF. After the reaction mixture attained room temperature it was hydrolyzed, and worked-up by the usual procedure. The crude material obtained was recrystallized from methanol (3 times) affording the benzyne-furan adduct (XV) (63 %), m.p. 90–92°. (Found: C, 50.69; H, 1.38; F, 40.12. $C_{16}H_4F_8O$ calcd.: C, 50.53; H, 1.05; F, 40.00 %.) The ¹H NMR spectrum showed a broad bridge head singlet at 5.9 ppm and an olefinic triplet at 7.05 ppm (*J* 1 Hz) with a relative area of 1 : 1.

(d). The organolithium compound (XI) was prepared in furan as described in (c) above. The reaction mixture was kept at -70° for 4 h and then warmed to -30° for an additional hour. On hydrolysis of the reaction mixture, a quantitative

yield of $p\text{-C}_6\text{F}_5\text{OC}_6\text{F}_4\text{H}$ (V) was obtained.

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