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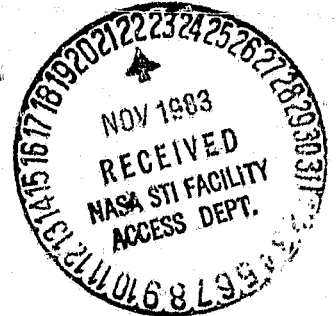
SYNTHESIS OF PERFLUOROALKYLENE DIANILINES

PREPARED BY:

K.L. Paciorek, T.I. Ito, D.H. Harris,
C.M. Beechan, J.H. Nakahara, and R.H. Kratzer



ULTRASYSTEMS, INCORPORATED
Irvine, California



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16. Abstract The objective of this contract was to optimize and scale-up the syntheses of 2,2-bis(4-aminophenyl)-hexafluoropropane and 1,3-bis(4-aminophenyl)hexafluoropropane, as well as to explore avenues to other perfluoroalkyl-bridged dianilines. Routes other than Friedel-Crafts reaction leading to 2,2-bis(4-aminophenyl)hexafluoropropane were investigated. The processes utilizing bisphenol-AF were all unsuccessful; reactions aimed at the production of 4-(hexafluoro-2-halo-isopropyl)aniline from the hydroxyl intermediate failed to yield the desired products. Tailoring the conditions of the Friedel-Crafts reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline, aniline, and aluminum chloride by using hydrochloride salts and selecting optimum reagent ratios, reaction times, and temperatures resulted in ~20% yield of pure crystallized 2,2-bis(4-aminophenyl)hexafluoropropane in 0.2 mole reaction batches. Yields up to ~40% were realized in small, ~0.01 mole, batches. The synthesis of 1,3-bis(4-aminophenyl)hexafluoropropane starting with perfluoroglutarimidine was reinvestigated. The yield of the 4-step reaction sequence giving 1,3-bis(4-acetamidophenyl)hexafluoropropane was raised to 44%. The yield of the subsequent hydrolysis process was improved by a factor of ~2. Approaches to prepare other perfluoroalkyl-bridged dianilines were unsuccessful. Reactions reported to proceed readily with trifluoromethyl substituents failed when longer chain perfluoroalkyl groups were employed.					
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FOREWORD

This Final Report describes the work performed by Ultrasystems, Inc. during the period 5 September 1980 through 5 November 1981 under Contract NAS3-22519, "Synthesis of Perfluoroalkylene Dianilines". The investigations were carried out by K. L. Paciorek, T. I. Ito, D. H. Harris, C. M. Beechan, J. H. Nakahara, and R. H. Kratzer, project manager, at the Chemicals and Materials Research Department, Irvine, California. The contract was administered by the NASA Lewis Research Center with Dr. Tito T. Serafini as the project manager.

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1. SUMMARY

This is the final report describing work performed by Ultrasystems, Inc. for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-22519.

The objective of this contract was to optimize and scale-up the syntheses of 2,2-bis(4-aminophenyl)hexafluoropropane and 1,3-bis(4-aminophenyl)hexafluoropropane, as well as to explore avenues to other perfluoroalkyl-bridged dianilines.

Routes other than Friedel-Crafts reaction leading to 2,2-bis(4-aminophenyl)hexafluoropropane were investigated. The processes utilizing bisphenol-AF were all unsuccessful; reactions aimed at the production of 4-(hexafluoro-2-halo-isopropyl)aniline from the hydroxyl intermediate failed to yield the desired products. Tailoring the conditions of the Friedel-Crafts reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline, aniline, and aluminum chloride by using hydrochloride salts and selecting optimum reagent ratios, reaction times, and temperatures resulted in ~20% yield of pure crystallized 2,2-bis(4-aminophenyl)hexafluoropropane in 0.2 mole reaction batches. Yields up to ~40% were realized in small, ~0.01 mole, batches. The synthesis of 1,3-bis(4-aminophenyl)hexafluoropropane starting with perfluoroglutarimidine was reinvestigated. The yield of the 4-step reaction sequence giving 1,3-bis(4-acetamidophenyl)hexafluoropropane was raised to 44%. The yield of the subsequent hydrolysis process was improved by a factor of ~2.

Approaches to prepare other perfluoroalkyl-bridged dianilines were unsuccessful. Reactions reported to proceed readily with trifluoromethyl substituents failed when longer chain perfluoroalkyl groups were employed.

2. INTRODUCTION

Polymers containing exclusively aromatic imides in the backbone exhibit high thermal and oxidative stabilities. However, such compositions are intractable and difficult to process. The incorporation of aliphatic segments linking some of the aromatic nuclei can increase solubility, processibility, and toughness, but this is frequently achieved only at the expense of lowered thermal, oxidative, and sometimes hydrolytic stabilities. It has been shown [ref. 1] that replacing aliphatic segments by their perfluorinated counterparts results in increased thermal, oxidative, and hydrolytic stability. Two bridging groups, $(CF_2)_3$ and $C(CF_3)_2$, were investigated. Unfortunately, the required dianilines could be synthesized in very low yields only. The current effort was directed at optimizing the synthesis of the two dianilines and to explore avenues to related perfluoroalkyl-substituted materials.

3. EXPERIMENTAL DETAILS AND PROCEDURES

General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (KBr oil No. 10 and Nujol) using Perkin-Elmer Corporation Infrared Spectrophotometers, Models 21 and 1330. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The mass spectrometric analyses were obtained employing a duPont 21-491B double focusing mass spectrometer attached to a Varian gas chromatograph Model 2700, equipped with a flame ionization detector, and a duPont 21-094 data acquisition and processing system. For general gas chromatographic analyses, Loenco Model 70 and Varian Model 3700 gas chromatographs were employed. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Reaction of bisphenol-AF with bis(trimethylsilyl)amine

Dropwise addition of an excess of bis(trimethylsilyl)amine (3.96 g, 18.96 mmol) to solid bisphenol-AF gave immediate exothermic reaction. After 24 hr of stirring at room temperature, the pale orange solution was refluxed for 1 hr. Cooling to ambient temperature, followed by removal in vacuo of the excess bis(trimethylsilyl)amine, gave a quantitative yield (7.14 g) of pure bis(trimethylphenoxysilane)-AF, $(\text{Me}_3\text{SiOC}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$. The mass spectrum (MS) is given in Table I.

Attempted reaction of bis(trimethylphenoxy)silane)-AF with bis(trimethylsilyl)amine

Refluxing a mixture of bis(trimethylphenoxy)silane)-AF (1.0 g, 2.08 mmol) and bis(trimethylsilyl)amine (3.83 g, 23.7 mmol) for 88 hr gave no visible indication of a reaction. Distillation to remove unreacted bis(trimethylsilyl)amine afforded a yellow liquid residue, identified by infrared spectral analysis and gas chromatography (GC) as the unreacted starting material, $(\text{Me}_3\text{SiOC}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$.

Reaction of bis(trimethylphenoxy)silane)-AF with chlorotrimethylsilane

A mixture of chlorotrimethylsilane (0.54 g, 5.0 mmol) and bis(trimethylphenoxy)silane)-AF (1.2 g, 2.5 mmol) was refluxed for 17 hr. Removal in vacuo of the volatiles resulted in quantitative recovery of bis(trimethylphenoxy)silane)-AF.

Reaction of bis(trimethylphenoxy)silane)-AF with sodium amide

Sodium amide was prepared by dissolution of sodium metal (0.46 g, 20 mmol) in an excess of liquid ammonia at -78°C and in the presence of ferric chloride. Following the disappearance of the characteristic blue color of dissolved sodium and the formation of a gray suspension of sodium amide, a diethyl ether solution of bis(trimethylphenoxy)silane)-AF (4.3 g, 8.96 mmol) in ether (40 ml) was added over a period of 10 min. After the reaction mixture was warmed up to room temperature (~ 1.5 hr), ammonium chloride was added (to remove the excess of sodium amide). This was followed by addition of dilute hydrochloric acid and diethyl ether extraction. Work up of the aqueous portion by treatment with potassium hydroxide and ether extraction failed to result in the isolation of amine-containing products. Evaporation of the diethyl ether fraction afforded crystals (2.9 g, 96%)

shown by infrared analysis to consist of pure bisphenol-AF, $(\text{HOC}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$,

Preparation of 4-(hexafluoro-2-hydroxy-isopropyl)aniline

Under nitrogen by-pass in an apparatus equipped with a dry ice condenser (set on top of a water-cooled condenser) and an addition funnel, into aniline (96.5 g, 1.04 mol) at 190°C was added hexafluoroacetone sesquihydrate (203.3 g, 1.05 mol) over a 3.5 hr period. Heating was continued at $170\text{--}180^\circ\text{C}$ for an additional 11.5 hr. The solid mass obtained on cooling was taken up in diethyl ether and crystallized from diethyl ether-petroleum ether ($60\text{--}110^\circ\text{C}$) to afford the desired product, 183.2 g (68% yield), mp $150.5\text{--}151.3^\circ\text{C}$ [ref. 2, $149\text{--}150^\circ\text{C}$].

Reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with phosphorus pentabromide

a) At elevated temperature

Phosphorus pentabromide (1.10 g, 2.55 mmol) and 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.01 g, 3.90 mmol) were heated gradually from 22 to 124°C in the absence of solvent over a period of 3.75 hr. The temperature was then maintained at $124\text{--}128^\circ\text{C}$ for a further 2 hr. After cooling, neutralization with potassium hydroxide and ether extraction (4 x 10 ml) followed by evaporation gave 0.89 g of a brown sticky solid. Extraction and recrystallization from hot heptane afforded a solid (0.73 g) identified by combination gas chromatography and mass spectrometry (GC/MS) and infrared spectral analysis as the desired product, $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{Br})(\text{CF}_3)_2$, admixed with ring brominated alcohols and both ring and side chain brominated compounds. The mass spectral breakdown pattern is given in Table II.

b) At room temperature

To a solution of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.01 g,

3.90 mmol) in diethyl ether (2 ml) was added, dropwise, a solution of phosphorus pentabromide (1.79 g, 4.14 mmol) in benzene (5 ml). After stirring overnight at room temperature, the removal of volatiles in vacuo gave a solid residue which was treated first with aqueous base and then extracted with diethyl ether (4 x 15 ml). Removal of solvent in vacuo afforded a dark-red residue (0.24 g) which was shown by infrared analysis to be a mixture of ring-brominated fluoroalcohols.

Reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with thionyl bromide

A mixture of thionyl bromide (0.5 ml, 1.34 g, 6.45 mmol) and solid 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.07 g, 4.13 mmol) was heated at 140-145°C for 16 hr. This resulted in a yellow sublimate formed around the top of the flask and a black intractable solid at the bottom. Infrared and mass spectral analysis (Table III) of the yellow sublimate confirmed the presence of a dibrominated ring compound, $\text{H}_2\text{NC}_6\text{H}_2\text{Br}_2\text{C}(\text{OH})(\text{CF}_3)_2$ (0.41 g, 30.8% yield), mp 172-175°C, MW, 417 (mass spectrometry).

Reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with thionyl chloride

Thionyl chloride (1 ml, 1.67 g, 14.04 mmol) was added dropwise to solid 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.0 g, 3.86 mmol). The mixture was then heated overnight in inert atmosphere at 54°C. Subsequently, the volatiles were removed in vacuo. The residue, a pale yellow solid, was identified as unreacted starting material (0.85 g, 85% recovery).

Preparation of 4-(hexafluoro-2-hydroxy-isopropyl)aniline hydrochloride

A mixture of dry hydrogen chloride and nitrogen was passed through

an ethereal solution of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (20.0 g, 77.2 mmol) at 0°C for approximately 2 hr. Gradually, white solid precipitated out of solution. Removal of ether gave the desired product (22.4 g, 98.2%).

Reaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with aluminum trichloride

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (0.5 g, 1.93 mmol) and aluminum trichloride (0.26 g, 1.95 mmol) was heated at 134°C for 1.5 hr. Addition of water (~ 10 ml) gave an acidic solution which was neutralized with potassium hydroxide solution and extracted with diethyl ether (3 x 10 ml); the combined extracts were washed with water and dried over anhydrous magnesium sulfate. Removal of volatiles and drying in vacuo gave a brown solid (0.12 g) identified as unreacted starting material by infrared spectral analysis.

Typical small scale (~ 4 mmol) Friedel-Crafts reaction between 4-(hexafluoro-2-hydroxy-isopropyl)aniline, aniline, and aluminum trichloride

Dropwise addition of aniline (0.44 g, 4.72 mmol) to a solid mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.01 g, 3.90 mmol) and aluminum trichloride (0.58 g, 4.35 mmol) at 0°C gave an initial exothermic reaction. Heating at 160-165°C for 66 hr produced a black solid and white sublimate (0.02 g) identified by infrared spectral analysis as aniline hydrochloride. Extraction of the black solid with 5 N hydrochloric acid, followed by treatment with potassium hydroxide of the acid extract, gave a brown precipitate, which was then extracted with diethyl ether (3 x 25 ml). The combined ether extracts gave, after evaporation in vacuo, a black solid (0.88 g) shown by GC to contain 62% of the desired product, resulting in a 42% overall product yield.

Medium scale (~ 20 mmol) Friedel-Crafts reaction between 4-(hexafluoro-2-hydroxy-isopropyl)aniline hydrochloride, aniline, aniline hydrochloride, and aluminum trichloride

Aluminum trichloride (4.06 g, 30.45 mmol) was added slowly over 2 hr to a preheated (110-120°C) mixture of aniline (3.78 g, 40.6 mmol), aniline hydrochloride (2.63 g, 20.3 mmol) and 4-(hexafluoro-2-hydroxy-isopropyl)aniline hydrochloride (6.0 g, 20.3 mmol). A vigorous reaction ensued and after addition was completed, the temperature was raised to 165°C and maintained for 87 hr. A white sublimate (3.67 g) isolated at the end of the reaction was identified by infrared spectral analysis as a mixture of aniline hydrochloride and $\text{HCl} \cdot \text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{OH})(\text{CF}_3)_2$. Dilute acid extraction on the black solid residue, followed by treatment with potassium hydroxide solution (5 N), ether extraction (3 x 30 ml), water washing, drying, and volatiles removal gave a dark brown liquid/solid mixture (8.95 g). Steam distillation removed excess aniline and afforded a black residue (1.95 g) which was shown by GC to contain 65% of the desired product, which translated to a 20% overall product yield. Treatment with decolorizing carbon, followed by recrystallization from hot diethyl ether-hexane, afforded pure 2,2-bis(4-aminophenyl) hexafluoropropane (0.81 g, 12% overall yield).

Large scale (~ 200 mmol) Friedel-Crafts reaction between 4-(hexafluoro-2-hydroxy-isopropyl)aniline, aniline, and aluminum trichloride

In an inert atmosphere enclosure, aluminum trichloride (26 g, 195 mmol) was cautiously added to a stirred slurry of aniline (22 g, 236 mmol) and 4-(hexafluoro-2-hydroxy-isopropyl)aniline (50 g, 193 mmol). An initial vigorous reaction was observed which ceased after approximately 25% of the aluminum trichloride was added. The resultant mixture was

a solution of perfluoroglutaric acid (41.3 g, 0.172 mol) in 28 ml water was added freshly prepared silver oxide (obtained from 65.0 g, 0.383 mol of silver nitrate and 5 N sodium hydroxide); the resulting mixture was stirred at 55-60°C for 3.5 hr. Subsequently, the excess of silver oxide was filtered off. The filtrate, after concentration under reduced pressure and followed by drying over phosphorus pentoxide, afforded the silver salt (71.7 g, 91.8% yield).

Preparation of 1,3-diiodohexafluoropropane

This reaction was performed in subdued light with a gentle flow of nitrogen through the apparatus to assist distillation of the product. To a hot (140-150°C oil bath), well-stirred mixture of FC-43 (42 ml) and iodine (65.3 g, 238 mmol) in a 250 ml three-neck flask equipped with a solids addition device and a distillation head (leading to a 0°C cooled receiver followed by a -78°C trap) was added silver perfluoroglutarate (20.7 g, 45.6 mmol) over a period of 16 min. Heating (oil bath 150-195°C) was continued for an additional 1 hr. The distillate consisted of two phases; cooling to -23°C and separating the two phases gave 12.3 g of the lower phase which, based on GC analysis consisted of 93% 1,3-diiodohexafluoropropane (62% yield). The two major impurities present were FC-43 and iodine. Iodine was subsequently removed by treatment with copper bronze.

Preparation of 1,3-bis(4-acetamidophenyl)hexafluoropropane

In an inert atmosphere enclosure, copper bronze (35.3 g, 556 mmol) was added to a solution of 4-iodoacetanilide (35.9 g, 138 mmol) and 1,3-diiodohexafluoropropane (27.8 g, 68.8 mmol) in dimethylsulfoxide (140 ml). The mixture was then stirred and heated under a nitrogen atmosphere for 14 hr at 120-133°C. The cooled mixture was filtered and the residue washed with dimethylsulfoxide (4 x 40 ml), followed by hot

methanol (4 x 50 ml). The combined dimethylsulfoxide filtrate was added slowly with vigorous stirring to water (3.0 l). The resulting precipitate was filtered and then extracted with boiling methanol (1.6 l). The concentrated methanol solution (all combined methanol washes) afforded 22.9 g (79.5% yield) of 1,3-bis(4-acetamidophenyl)hexafluoropropane, mp 247.5-248.0°C.

Attempted preparation of 1,3-bis(4-aminophenyl)hexafluoropropane

a) Via reduction with lithium aluminum hydride in tetrahydrofuran

A mixture of 1,3-bis(4-acetamidophenyl)hexafluoropropane (1.0 g, 2.4 mmol) and lithium aluminum hydride (0.5 g, 13.2 mmol) in tetrahydrofuran (20 ml) was refluxed for 7 hr. It should be noted that the addition of 1,3-bis(4-acetamidophenyl)hexafluoropropane to the lithium aluminum hydride-tetrahydrofuran mixture at room temperature resulted in an exothermal reaction. Subsequently, to the ice-cooled mixture was added an excess of water. The aqueous solution was then extracted with ether (2 x 25 ml) yielding 740 mg of an unidentified compound, not the desired 1,3-bis(4-aminophenyl)hexafluoropropane.

b) Via reduction with lithium aluminum hydride in ether

To a stirred mixture of lithium aluminum hydride (0.35 g, 9.2 mmol) in ether (20 ml), cooled in an ice/water bath, was slowly added 1,3-bis(4-acetamidophenyl)hexafluoropropane (0.4 g, 0.93 mmol). The resulting mixture was stirred vigorously at ambient temperature for 31 hr. Excess hydride was then destroyed by adding to the stirred mixture, cooled in ice-water, successively 0.35 ml water, 0.35 ml of 14% sodium hydroxide, and 1.05 ml water. Evaporation of the dried ethereal layer yielded 0.29 g of the same product as that obtained in the reduction performed in tetrahydrofuran.

c) Via hydrolysis with potassium hydroxide in methanol

A mixture of 1,3-bis(4-acetamidophenyl)hexafluoropropane (0.40 g, 0.96 mmol) and 5 ml of Claisen's alkali (prepared by dissolving 88.3 g of potassium hydroxide in 63.1 g of water, followed by dilution with methanol to a 250 ml volume) was stirred with refluxing in a nitrogen atmosphere for 16 min. Hot water (5 ml) was added and the stirred mixture was heated for an additional 16 min. After cooling, the bulk of the product was in the form of a solid globule. This was washed with cold (0-5°C) water (3 x 3 ml), then dissolved in ether and again washed with water. Evaporation of the dried ethereal solution gave as a major constituent an unidentified compound (M^+ , 382 ?).

d) Via hydrolysis with aqueous sulfuric acid

A well-stirred mixture of 1,3-bis(4-acetamidophenyl)hexafluoropropane (20.8 g, 49.6 mmol) and 187 ml of 70% sulfuric acid was heated under nitrogen by-pass at 99-103°C for 9.5 hr. The cool reaction mixture was then poured into ~ 1.3 l of water. Solid sodium bicarbonate was subsequently added very slowly with swirling until past the neutralization point. The mixture was extracted twice with ether (total 2.3 l). The ethereal solution was washed once with water (1500 ml), dried, and evaporated to give 17.6 g of crude product. This was dissolved in approximately 100 ml of 1:2 ether-hexane mixture. Nitrogen was passed over the solution at room temperature to evaporate ether and precipitate a solid impurity (2.3 g). The solid obtained on evaporation of the mother liquor was dissolved in ether (85 ml). Subsequently, hexane (400 ml) was slowly added with stirring to liberate the desired product. The material oiled out initially; thus, it was triturated with a spatula which caused it to solidify totally giving 9.6 g (58% yield) of 1,3-bis(4-aminophenyl)hexafluoropropane, mp 65-67°C. Further concentrations, without heat, afforded additional product (1.2 g) resulting in a total yield of 65%.

Preparation of perfluoro-*n*-octanoyl chloride

Following the procedure described earlier [ref. 4], a mixture of perfluoro-*n*-octanoic acid (100.05 g, 241.6 mmol) and isophthaloyl chloride (117.92 g, 580.8 mmol) was heated under nitrogen by-pass at 100-120°C for 3 hr. During this time, considerable amounts of hydrogen chloride were given off. Distillation gave crude perfluoro-*n*-octanoyl chloride (86.0 g, 82.3%), bp 60-65°C at 60 mm Hg. Redistillation afforded pure perfluoro-*n*-octanoyl chloride (68.84 g, 65.9%), bp 75-77°C at 110 mm Hg.

Reaction of acetanilide with perfluoro-*n*-octanoyl chloride and aluminum trichloride

The procedure used was essentially that utilized by Tamborski, et al. [ref. 5] for similar reactions. Perfluoro-*n*-octanoyl chloride (4.65 g, 10.75 mmol) was slowly (0.5 hr) added to a hot (50°C) mixture of aluminum trichloride (2.92 g, 21.89 mmol) and acetanilide (1.0 g, 7.39 mmol). Fumes of hydrogen chloride were observed and the mixture darkened. Heating was increased to maintain a temperature of 95°C for 15 hr. After cooling, volatiles were collected on a high vacuum line and identified as unreacted perfluoro-*n*-octanoyl chloride (1.97 g, 42% recovery). The purple-black residue was extracted with dilute hydrochloric acid which in turn was extracted with Freon-113 (3 x 20 ml). After filtration, followed by solvent removal, brown crystals (2.52 g) were obtained. These were identified by infrared spectral analysis and GC/MS as a mixture of $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$, $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$, and $\underline{n}\text{-C}_7\text{F}_{15}\text{COOH}$. This crude product was freed from the perfluorooctanoic acid by treatment of the ethereal solution with aqueous sodium bicarbonate (10%, 2 x 20 ml). Evaporation of the solvent afforded a yellow crystalline solid (1.17 g, 30% yield) which was a mixture of $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ and $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$.

The original acidic aqueous extract was made basic with potassium hydroxide and re-extracted with Freon-113 (3 x 20 ml). The organic layer, after solvent evaporation, gave white crystals (0.05 g, 5% recovery) of unreacted acetanilide.

Reaction of $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ and $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ mixture with LiAlH_4

Dropwise addition over 20 min of a solution of the fluorocarbon mixture (0.40 g) in diethyl ether (10 ml) to a diethyl ether (5 ml) slurry of lithium aluminum hydride (0.15 g, 3.95 mmol) under ambient conditions gave no discernible reaction. Heating at reflux temperature for 63 hr, followed by cooling and addition of water to destroy the excess of lithium aluminum hydride, gave two layers. Extraction with diethyl ether (3 x 20 ml), followed by solvent evaporation, afforded a yellow solid (0.3 g, 75% recovery) identified by GC/MS as predominantly $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ (see Table IV). No evidence was found for the presence of $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})-\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$.

Reaction of benzene with perfluoro-n-octanoyl chloride and aluminum trichloride

Dropwise addition of perfluoro-n-octanoyl chloride (10.0 g, 23.1 mmol) to a heated (50°C) slurry of benzene (20.0 g, 259.4 mmol) and aluminum trichloride (7.2 g, 54.0 mmol) gave an immediate exothermic reaction accompanied by evolution of hydrogen chloride. After heating at reflux temperature for 22 hr, no further hydrogen chloride evolution was observed. The resultant black reaction mixture was cautiously hydrolyzed and extracted with diethyl ether. Filtration through hydrophobic filter paper, followed by removal of ether, addition of Freon-113, and removal of all volatiles on water aspirator, gave a greenish liquid (6.91 g). Distillation (bp 62-65°C at 0.05 mm Hg) afforded pure phenyl perfluoro-n-

heptyl ketone (4.89 g, 45%), MW, 466 (Calcd., 474.17). The mass spectral breakdown pattern is given in Table V.

Reaction of $\text{H}_2\text{NC}_6\text{H}_4\text{C(O)-n-C}_7\text{F}_{15}$ with aniline and aniline hydrochloride

The procedure used was similar to that of Kray and Rosser [ref. 6]. A mixture of aniline (0.5 g, 5.4 mmol), aniline hydrochloride (0.13 g, 1.0 mmol), and $\text{H}_2\text{NC}_6\text{H}_4\text{C(O)-n-C}_7\text{F}_{15}$ (0.25 g, 0.51 mmol) was heated at reflux temperature for 64 hr. After cooling, the blue-black reaction mixture was extracted with diethyl ether and then benzene. Removal of the solvents from the combined organic extracts afforded a sticky, blue-black liquid-solid mixture. Steam distillation removed excess aniline and $\text{H}_2\text{NC}_6\text{H}_4\text{C(O)-n-C}_7\text{F}_{15}$. The GC/MS of the blue-black residue showed the presence of the compound to which the structure $(\text{H}_2\text{NC}_6\text{H}_4)_2\text{-CH(n-C}_7\text{F}_{15})$ was assigned (see Table VI) and the imine $\text{H}_2\text{NC}_6\text{H}_4\text{C(=NC}_6\text{H}_5\text{)-n-C}_7\text{F}_{15}$ (see Table VII).

Reaction of $\text{C}_6\text{H}_5\text{C(O)-n-C}_7\text{F}_{15}$ with aniline and aniline hydrochloride

A mixture of aniline (8.5 g, 91.3 mmol), aniline hydrochloride (3.6 g, 27.5 mmol), and $\text{C}_6\text{H}_5\text{C(O)-n-C}_7\text{F}_{15}$ (6.2 g, 13.1 mmol) was heated at 180°C for 23 hr, during which time two immiscible liquid layers were formed. Cooling to room temperature gave a black semi-solid mixture which was neutralized with aqueous bicarbonate (2.3 g, 27.5 mmol in 40 ml water). Steam distillation removed excess aniline and unreacted $\text{C}_6\text{H}_5\text{C(O)-n-C}_7\text{F}_{15}$. Extraction of the purple-red liquid residue with benzene (3 x 25 ml), followed by combination of the extracts, washing with water (2 x 20 ml), and removal of volatiles via a water aspirator, gave a brown liquid. Distillation afforded a pale yellow-green liquid,

bp 103-107°C at 0.001 mm Hg, which, based on GC/MS, consisted primarily of $C_6H_5C(=NC_6H_5)-n-C_7F_{15}$ admixed with traces of diphenylamine and aniline. Dissolution in benzene, followed by washing with dilute hydrochloric acid, successfully removed both of the amines to give, after drying over anhydrous magnesium sulfate and removal of benzene, pure $C_6H_5C(=NC_6H_5)-n-C_7F_{15}$ (3.91 g, 54%). Anal. Calcd. for $C_{20}H_{10}NF_{15}$: C, 43.73; H, 1.84; N, 2.55; F, 51.88; MW, 549.28. Found: C, 44.35; H, 2.08; N, 2.40; F, 51.46; MW, 540 (osmometry). For the mass spectral breakdown pattern, see Table VIII.

Reaction of $C_6H_5C(O)-n-C_7F_{15}$ with trifluoromethanesulfonic acid and aniline

Trifluoromethanesulfonic acid (2.4 g, 15.9 mmol) was slowly added to a mixture of $C_6H_5C(O)-n-C_7F_{15}$ (2.5 g, 5.3 mmol) and aniline (2.5 g, 26.8 mmol). Considerable heat was evolved initially and partial solidification was observed. After heating at 155-159°C for 20 hr, the reaction mixture was allowed to cool and was worked up by neutralization with aqueous bicarbonate and extraction with diethyl ether (3 x 25 ml); removal of volatiles via a water aspirator gave a red-brown liquid (4.55 g). Infrared spectral analysis and GC/MS indicated three major components: unreacted aniline and $C_6H_5C(O)-n-C_7F_{15}$ admixed with $C_6H_5(C=NC_6H_5)-n-C_7F_{15}$. Heating this mixture with more trifluoromethanesulfonic acid (2.4 g, 15.9 mmol) at 115°C for 64 hr failed to give exclusively the imine free from starting materials.

Reaction of the presumed " $H_2NC_6H_4C(OH)(C_6H_5)-n-C_7F_{15}$ " with aniline and aluminum trichloride

A mixture of aniline (1.3 g, 14.0 mmol) and " $H_2NC_6H_4C(OH)(C_6H_5)-n-C_7F_{15}$ " (0.8 g, 1.4 mmol) was slowly added to powdered aluminum trichloride (0.5 g, 3.8 mmol) at room temperature. Heating at 185°C for

21 hr gave a black solid and a pale yellow-green sublimate (1.0 g), the latter identified by infrared spectral analysis and GC/MS as a mixture of unreacted starting materials, diphenylamine, and aniline hydrochloride. Work up of the black residue gave only additional aniline.

Reaction of $C_6H_5C(O)-n-C_7F_{15}$ with acetanilide and aluminum trichloride

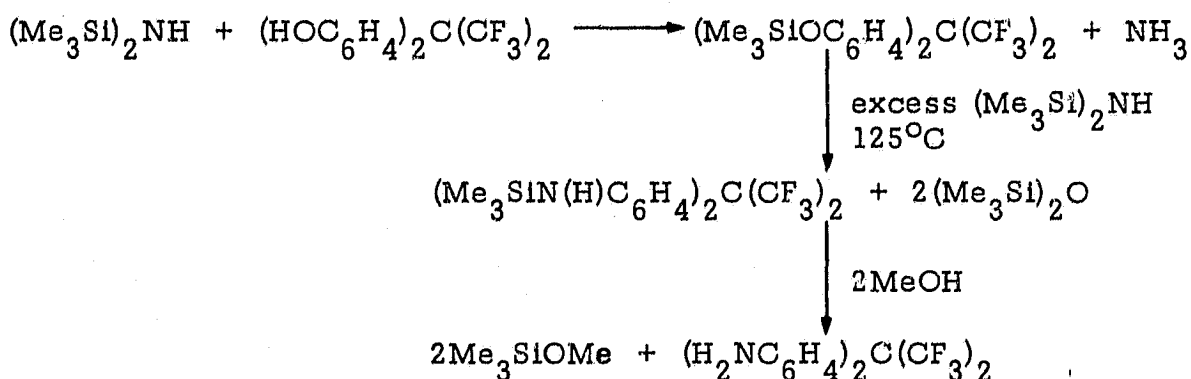
A mixture of $C_6H_5C(O)-n-C_7F_{15}$ (1.37 g, 2.89 mmol), acetanilide (0.78 g, 5.78 mmol), and aluminum trichloride (1.16 g, 8.67 mmol) was heated at 165°C for 24 hr. After cooling, the reaction mixture consisted of a black solid with a colorless liquid above it. This was pipetted out and identified by its infrared spectrum as unreacted $C_6H_5C(O)-n-C_7F_{15}$ (0.65 g, 47% recovery). Work up of the black solid by neutralization with aqueous sodium bicarbonate and extraction with diethyl ether (3 x 25 ml), followed by evaporation of the solvent, gave a yellow crystalline solid (0.75 g), identified by infrared spectral analysis as a mixture of unreacted acetanilide and $C_6H_5C(O)-n-C_7F_{15}$.

4. TECHNICAL DISCUSSION

The major objective of this contract was to optimize the syntheses of 2,2-bis(4-aminophenyl)hexafluoropropane and 1,3-bis(aminophenyl)-hexafluoropropane and to provide sufficient quantities of these compounds for NASA for laminate evaluations. In addition, synthesis of other dianilines, wherein the methylene group in methylene-dianiline is replaced by perfluoroalkyl linkages, were to be explored.

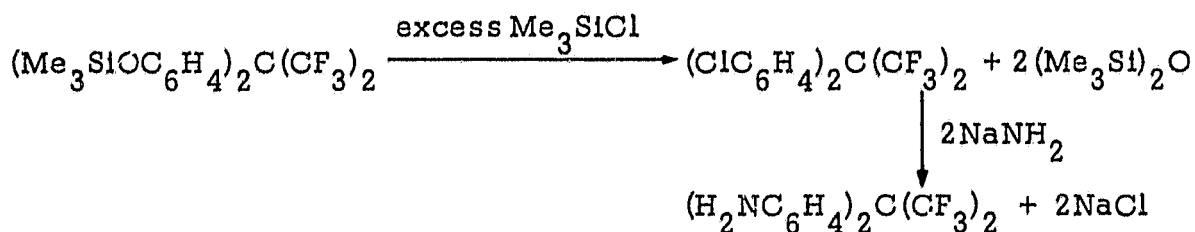
4.1 Synthesis of 2,2-bis(4-aminophenyl)hexafluoropropane

2,2-Bis(4-aminophenyl)hexafluoropropane was obtained in a low yield [ref. 1] by interaction of aluminum chloride, aniline, and 4-(hexafluoro-2-hydroxy-isopropyl)aniline at elevated temperatures. In view of the very low yield (10%), based on gas chromatographic analysis and the difficulty in isolating the pure product, which would be expected to decrease the final yield below 10%, the initial efforts under this program were concentrated on exploring alternate, more promising routes. The ideal starting material would be bisphenol-AF since it is commercially available. A reaction sequence involving the interaction of hexamethyldisilazane with bisphenol-AF looked particularly attractive, i.e.:

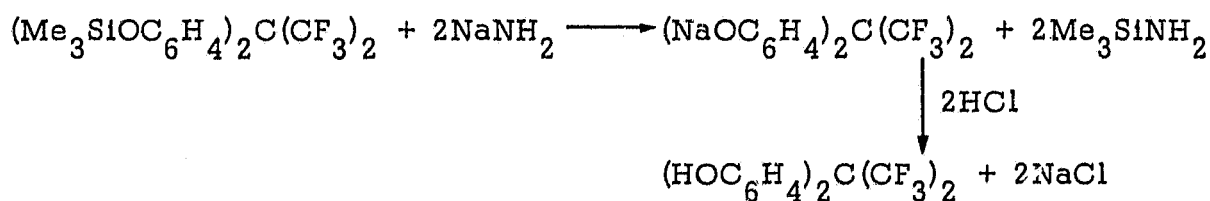


The exothermic reaction between hexamethyldisilazane and bisphenol-AF, $(\text{HO-C}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$, in the absence of solvent, gave the trimethyl-

silyl ether in a quantitative yield. Further reaction by heating with an excess of hexamethyldisilazane at 125°C for 88 hr failed to form the amine derivative, $(\text{Me}_3\text{SiN(H)C}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$, which based on literature data [ref. 7] would have been readily hydrolyzed with methanol to the desired 2,2-bis(4-aminophenyl)hexafluoropropane. Similarly, an excess of trimethylchlorosilane at reflux temperature failed to cleave the carbon-oxygen bond to give 2,2-bis(4-chlorophenyl)hexafluoropropane. The latter compound would be expected to form on treatment with sodium amide 2,2-bis(4-aminophenyl)hexafluoropropane, e.g.:

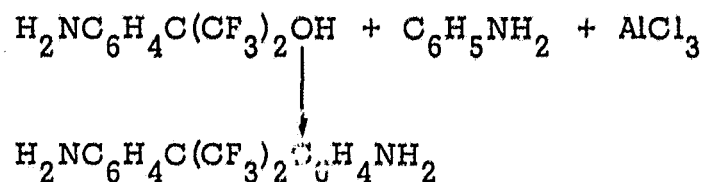


The direct reaction of sodium amide (both prepared in situ and commercial material [R.O.C./R.I.C.]) with the trimethylsilyl ether of bisphenol-AF also failed to cleave the C-O bond; instead the Si-O bond was cleaved preferentially, reforming bisphenol-AF during work-up acidification:



The relatively ready coupling of perfluoroalkyl halides with iodoaromatic compounds was reported [ref. 8, 9] and was utilized in the synthesis of 1,3-bis(4-aminophenyl)hexafluoropropane [ref. 1]. Thus, transformation of 4-(hexafluoro-2-hydroxy-isopropyl)aniline to 4-(hexafluoro-2-bromo-isopropyl)aniline followed by copper coupling offered an alternate synthesis route to 2,2-bis(4-aminophenyl)hexafluoropropane, i.e.:

effort was devoted to optimize the Friedel-Crafts process:



The parameters evaluated were the reagent ratios, temperatures, reaction times, use of amine hydrochlorides instead of the free amines, modes of mixing and addition. The experiments carried out are summarized in Tables X and XI. It is apparent from this listing that the best yield of the pure isolated product achieved was 20% with respect to the fluorinated alcohol employed. This is significantly better than the 10% gas chromatographic yield reported previously. From the data given in Tables X and XI, it is apparent that at low temperatures ($\sim 80^\circ\text{C}$) no reaction occurs (Test No. 6, Table X). Using no free amines, only amine hydrochlorides, gave a low yield of the desired product, showing that the complexation of aluminum chloride with the amino group is advantageous (Test No. 3, Table XI). It would seem that the quantity of aluminum chloride, at least in the reactions conducted below 165°C , should be at least equimolar with respect to the alcohol (Test Nos. 7 and 8, Table X). In the absence of aluminum chloride, the process does not proceed as shown by interaction of the alcohol with aniline and aniline hydrochloride (Test No. 12A, Table X) where only a trace of 2,2-bis(4-aminophenyl)hexafluoropropane was found to be present by gas chromatography; the major product was diphenylamine. This finding is not really surprising since the interaction of aniline with aniline hydrochloride at elevated temperature is known to produce diphenylamine [ref. 10]. Parallel results were obtained when substituting the fluorinated alcohol by its hydrochloride (Test No. 5, Table XI). It is believed that yields of $\sim 30\text{-}40\%$ can be achieved in small scale reactions starting with only

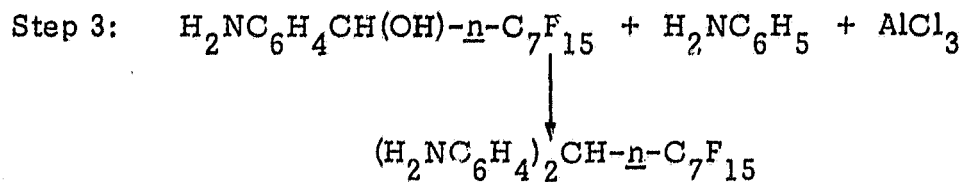
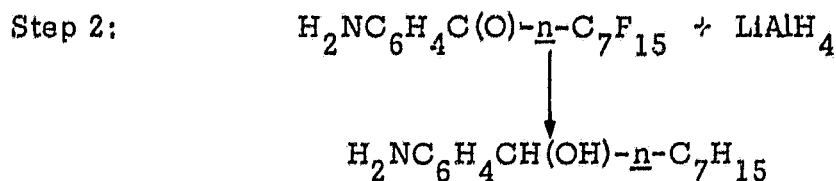
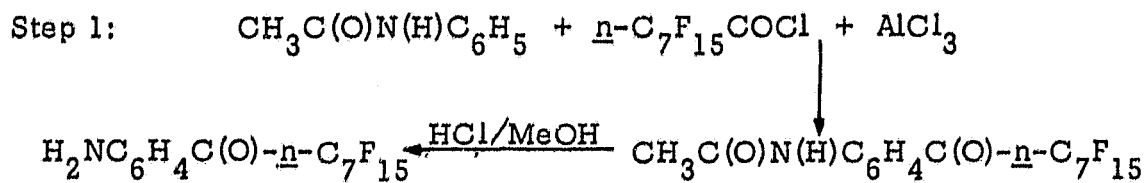
~ 1 g fluorinated alcohol. Scale-up was found to be associated with reduced yields most likely due to local overheating of the non-homogeneous mixture. It was also observed that using longer reaction times (87 hr at 150-160°C instead of e.g. 50 hr) facilitates product isolation by eliminating the presence of unreacted starting material without impairing the overall yield.

4.2 Synthesis of 1,3-bis(4-aminophenyl)hexafluoropropane

1,3-Bis(4-aminophenyl)hexafluoropropane was synthesized previously [ref. 1], the yield, however, in the final hydrolysis step was very low. The four-step process starting with perfluoroglutarimidine was repeated under the current program resulting in an overall 43% yield of 1,3-bis(4-acetamidophenyl)hexafluoropropane. The final hydrolysis reaction to remove the NH₂-protecting acetyl group was performed in aqueous sulfuric acid, not in methanolic hydrogen chloride and the final purification was carried out using a diethyl ether-hexane mixture. The yield of the pure free amine using this approach was 65% which was a significant improvement over the 35% yield realized previously in the hydrolysis step. Furthermore, the purification itself was much less tedious. Alternate procedures to obtain the free amine from 1,3-bis(4-acetamidophenyl)hexafluoropropane, namely lithium aluminum hydride reduction, both in ether and tetrahydrofuran, and alcoholic potassium hydroxide hydrolysis resulted in products other than 1,3-bis(4-aminophenyl)hexafluoropropane. These have not been identified. Based on the literature [ref. 11,12], lithium aluminum hydride reductions of amides can lead either to C-N cleavage derived (the desired path) amines or the ethyl-substituted amines. The mass spectrum of the product did not support the formation of either one of these compounds.

4.3 Other perfluoroalkyl-bridged dianilines

The ultimate purpose of this program is to provide dianilines which can be employed in PMR polyimides [ref. 13] either replacing 4,4-methylene-dianiline or in conjunction with it. It is probable that the properties imparted by the perfluoroalkyl bridging group will not be impaired if only one of the hydrogens of the bridging methylene group is replaced by a fluorocarbon side chain. To prepare this type of a system, a three-step reaction sequence, delineated below, was visualized, e.g.:



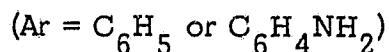
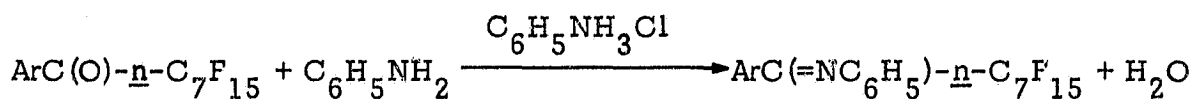
The first step was found to give ~ 36% yield of a mixture of $\text{H}_2\text{NC}_6\text{H}_4\text{C(O)-n-C}_7\text{F}_{15}$ and $\text{CH}_3\text{C(O)N(H)C}_6\text{H}_4\text{C(O)-n-C}_7\text{F}_{15}$. Friedel-Crafts reactions between perfluoro-acid chlorides and aromatic compounds appear to proceed smoothly at mild temperatures [ref. 5]; however, more vigorous

conditions (90-100°C, 15-20 hr) seem to be required for acetanilide to react with the long chain n-perfluorooctanoyl chloride. It should be noted that what appeared to be two isomeric forms of $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ were obtained. A possible by-product in the reaction sequence could be $\text{C}_6\text{H}_5\text{N}(\text{H})\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ which would have the same molecular weight (489) as the required product $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$. To determine if one of the two isomer peaks in the GC spectrum (molecular ion, 489) was due to $\text{C}_6\text{H}_5\text{N}(\text{H})\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$, a sample was taken and hydrolyzed with concentrated hydrochloric acid and methanol. Analysis of the reaction mixture indicated the presence of aniline, however, both peaks associated with the molecular ion 489 were still present. This would imply that the Friedel-Crafts reaction resulted in the production of at least two position isomers.

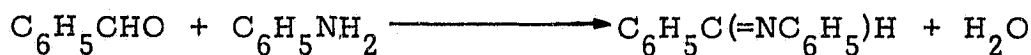
The second step in the three-stage synthesis of $(\text{H}_2\text{NC}_6\text{H}_4)_2\text{CH}-\underline{n}\text{-C}_7\text{F}_{15}$ involves reduction of the carbonyl group to an alcohol by lithium aluminum hydride. Since the lithium aluminum hydride reduction process would be expected to cleave the acetyl protecting group, no hydrolysis of $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ to $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ was carried out prior to attempting the reduction step. It was found that in diethyl ether even after prolonged periods at reflux temperature, no desired product could be identified by GC/MS analysis. Instead, a fairly clean conversion from $\text{CH}_3\text{C}(\text{O})\text{N}(\text{H})\text{C}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ to $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})-\underline{n}\text{-C}_7\text{F}_{15}$ was observed. The relative intensities of the two major peaks in the gas chromatogram, which showed the 489 m/e ion, were unchanged by the reaction. On the basis that prolonged reaction times at high temperatures were needed for the first step in the reaction sequence, it does not seem unreasonable that a higher temperature may be necessary also for the lithium aluminum hydride reduction.

$C_6H_5NH_2$, and $C_6H_5NH_3Cl$ was carried out on a small scale and GC/MS analysis performed on the reaction mixture. Even after 64 hr at reflux temperature (aniline as solvent), substantial amounts of unreacted starting materials were present, together with an unexpected compound, $(H_2NC_6H_4)_2C(H)-n-C_7F_{15}$. A small quantity of what appeared to be the intermediate carbinol, $(H_2NC_6H_4)_2C(OH)-n-C_7F_{15}$ was identified in the mixture based on the mass spectrum which was similar to that of the presumed $H_2NC_6H_4C(OH)(C_6H_5)-n-C_7F_{15}$ (compare Tables VII and VIII). No molecular ions were present, only $[M-H_2O]^+$; the base peak was formed by the loss of the C_7F_{15} fragment. Subsequent investigations revealed that these compounds were not the carbinols but the imine derivatives $ArC(=NC_6H_5)R_f$. This was fully verified by molecular weight determination, elemental analysis, and, most importantly, the comparison of the infrared spectrum of $C_6H_5C(=NC_6H_5)-n-C_7F_{15}$ with that of the benzylidene aniline, $C_6H_5CH=NC_6H_5$. In agreement with its structure, this material was recovered unchanged on treatment with aniline and aluminum trichloride.

The reaction pathway proposed for the formation of the substituted benzylidene is as follows:



This parallels the preparation of benzylidene aniline from benzaldehyde and aniline:



It is difficult to comprehend why substitution of the aldehydic proton by a CF_3 group causes the reaction pathway to follow the carbinol route whereas

substitution by $\underline{n}\text{-C}_7\text{F}_{15}$ appears to favor the benzylidene aniline condensation. To further complicate matters, whereas only one major product was observed in the reaction of $\text{C}_6\text{H}_5\text{C(O)-}\underline{n}\text{-C}_7\text{F}_{15}$ with aniline and aniline hydrochloride, in the case of $\text{H}_2\text{NC}_6\text{H}_4\text{C(O)-}\underline{n}\text{-C}_7\text{F}_{15}$, even after extended periods of time in refluxing aniline in the presence of aniline hydrochloride, only partial reaction took place. The GC/MS analysis of the resulting reaction mixture indicated unreacted starting materials admixed with two major products, one corresponding to $\text{H}_2\text{NC}_6\text{H}_4\text{C(=NC}_6\text{H}_5)\text{-}\underline{n}\text{-C}_7\text{F}_{15}$ (Table VII), the other consistent with the structure $(\text{H}_2\text{NC}_6\text{H}_4)_2\text{C(H)-}\underline{n}\text{-C}_7\text{F}_{15}$ (Table VI).

Published work by Kray and Rosser [ref. 6] has shown that the outcome of the condensation reactions is often influenced by the acid catalyst. Consequently, the reaction of the phenyl \underline{n} -perfluoroheptyl ketone with aniline was repeated in the presence of trifluoromethanesulphonic acid, $\text{CF}_3\text{SO}_3\text{H}$, as catalyst instead of $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$. Under these conditions, it was found that only partial reaction occurred resulting in the same imine. Using more forcing conditions (3 days at 165°C) failed to give 100% conversion. No evidence was found in the gas chromatogram that any carbinol-type compound or $\text{C}_6\text{H}_5\text{C(C}_6\text{H}_4\text{NH}_2)_2\text{C}_7\text{F}_{15}$ was formed. It therefore appears that aniline hydrochloride is a more efficient catalyst than trifluoromethanesulphonic acid in these reactions, however, the desired type of compound is not produced. The use of a \underline{n} -substituted aniline should prevent formation of the imine-type product and thus lead to the desired carbinol intermediate. Consequently, the reaction of $\text{C}_6\text{H}_5\text{C(O)-}\underline{n}\text{-C}_7\text{F}_{15}$ with acetanilide in the presence of a non-protonated acid, aluminum trichloride, was attempted. After 24 hr at 165°C , work up gave only unreacted starting materials. This result adds further weight to the hypothesis that the imine-type product is the only species formed when the \underline{n} -perfluoroheptyl group is attached to the carbonyl carbon atom.

5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are conclusions and recommendations reached during the current investigations of synthetic approaches to perfluoroalkyl-bridged dianilines.

- 1) Synthesis of 2,2-bis(4-aminophenyl)hexafluoropropane using the Friedel-Crafts reaction was optimized to yield 20% of pure product. It does not appear that using this process the yield in large batch reactions can be significantly improved.
- 2) The yield in the synthesis of 1,3-bis(4-aminophenyl)hexafluoropropane was improved by a factor of ~ 2 and the purification method in the last hydrolysis step was greatly simplified.
- 3) Preparation of other perfluoroalkyl-bridged dianilines was unsuccessful. Further investigation of synthetic approaches to these type of compositions using 4-aminophenyl perfluoroheptyl ketone or related compounds as the starting material would seem to offer a definite promise.

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TABLE I
 ION FRAGMENTS AND INTENSITIES RELATIVE TO
 BASE PEAK OF $(\text{Me}_3\text{SiOC}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$ ^a

m/e		m/e		m/e	
45	21.0	226	41.5	461	11.2
73	64.3	315	22.5	465	34.1
74	19.3	352	14.8	466	18.2
75	16.9	411	90.7	480	<u>100.</u>
77	18.7	412	67.8	481	69.2
150	10.3	413	26.2	482	26.3
191	10.8	414	11.3	483	10.8

a) Peaks having intensities less than 10% of the base peak are not reported.

TABLE II
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF REACTION MIXTURE AFTER PHOSPHORUS PENTABROMIDE
TREATMENT OF 4-(HEXAFLUORO-2-HYDROXY-ISOPROPYL)ANILINE^a

m/e		m/e		m/e	
124	11.0	239	15.3	332	19.2
125	15.3	240	13.2	334	12.5
142	14.4	241	13.9	337	50.8
143	14.8	242	47.0	338	14.8
144	11.9	243	27.7	339	47.6
145	13.7	250	19.7	340	12.2
150	12.1	251	13.3	346	23.7
151	12.1	252	36.3	348	43.6
152	13.0	253	11.7	350	38.9
153	13.2	254	17.8	352	12.4
169	13.0	259	24.8	379	15.5
170	24.5	267	10.4	381	31.9
171	30.9	268	49.7	383	15.2
172	19.5	269	17.4	397	59.7
173	21.1	270	47.5	399	<u>100.</u>
174	15.0	271	13.6	401	47.4
188	11.5	276	11.9	402	53.6
189	19.5	278	14.9	403	32.3
190	16.6	280	12.3	409	10.4
192	10.7	298	10.6	411	10.0
193	12.2	300	13.4	414	10.0
198	43.7	301	32.2	415	21.5
199	11.9	302	12.8	417	37.0
200	43.7	303	32.3	419	17.6
201	12.0	318	11.0	476	26.5
202	12.0	319	24.9	478	52.1
219	11.6	320	42.0	479	11.8
220	15.1	321	42.4	480	51.8
221	11.5	322	38.8	481	12.6
222	11.5	323	28.4	482	27.3
223	20.9	330	13.0	484	13.0
232	13.0	331	12.7		

a) Peaks having intensities less than 10% of the base peak are not reported.

TABLE III
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $\text{H}_2\text{NC}_6\text{H}_2\text{Br}_2\text{C}(\text{OH})(\text{CF}_3)_2$ ^a

m/e		m/e		m/e	
17	10.5	80	<u>100.</u>	276	15.6
18	50.5	81	57.6	278	30.5
36	10.7	82	97.8	280	17.0
39	11.4	90	19.9	346	46.3
40	11.1	91	10.6	348	80.4
52	14.1	139	13.3	349	12.2
62	11.8	170	11.0	350	51.2
63	15.5	198	14.0	415	39.7
69	25.9	200	14.4	417	67.1
79	62.8	251	13.2	419	38.3

a) Peaks having intensities less than 10% of the base peak are not reported.

TABLE IV
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{O})\text{C}_7\text{F}_{15}$ ^a

m/e		m/e		m/e	
20	6.7	66	6.4	119	27.1
28	9.1	69	28.7	120	50.6
31	7.5	76	7.8	121	23.8
38	7.3	77	40.6	131	16.2
39	19.9	78	15.3	169	16.2
50	9.3	91	17.6	181	5.6
51	20.0	92	43.3	470	31.1
52	7.2	93	18.4	471	10.9
63	11.3	94	13.5	488	6.9
64	15.7	100	12.9	489	<u>100.</u>
65	29.2	109	5.1	490	26.8

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE V
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $C_6H_5C(O)C_7F_{15}$ ^a

m/e		m/e		m/e	
50	9.8	105	<u>100.</u>	154	8.4
51	21.8	106	46.0	158	10.6
69	13.7	107	6.4	169	11.0
76	9.2	119	14.0	181	6.6
77	76.0	123	8.3	427	17.4
78	15.5	127	6.1	455	34.6
100	13.2	131	19.0	456	11.4
104	6.7				

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE VI
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $(H_2NC_6H_4)_2C(H)C_7F_{15}$ ^a

m/e		m/e		m/e	
20	6.6	152	5.7	198	46.8
65	4.1	153	5.3	199	8.3
69	7.9	154	4.4	228	6.5
72	5.2	155	15.5	246	4.7
84	8.8	167	7.7	283	7.0
85	6.0	168	13.9	392	7.4
90	5.5	169	8.0	454	4.6
93	6.1	180	18.4	547	38.2
98	37.0	181	10.3	548	13.4
99	46.7	182	5.0	565	22.8
100	4.8	195	22.8	566	94.2
142	5.2	196	44.9	567	49.6
151	4.0	197	<u>100.</u>	568	10.5

a) Peaks having intensities less than 4% of the base peak are not reported.

TABLE VII
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{=NC}_6\text{H}_5)\text{-n-C}_7\text{F}_{15}$ ^a

m/e		m/e		m/e	
20	4.2	78	4.0	194	8.5
28	9.2	91	4.7	195	<u>100.</u>
39	5.9	92	14.5	196	21.2
51	16.9	98	6.5	207	6.1
65	7.8	118	28.1	545	4.3
69	7.7	119	8.8	564	18.4
77	44.0				

a) Peaks having intensities less than 4% of the base peak are not reported.

TABLE VIII
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $\text{C}_6\text{H}_5\text{C}(\text{=NC}_6\text{H}_5)\text{-n-C}_7\text{F}_{15}$ ^a

m/e		m/e		m/e	
20	6.7	100	12.6	180	<u>100.</u>
27	7.3	103	17.1	181	64.2
31	8.0	104	8.5	182	18.2
39	9.7	119	18.5	198	7.1
50	15.7	127	7.5	199	7.1
51	33.1	131	14.5	211	11.6
52	8.2	139	7.1	228	6.6
63	7.4	151	11.0	229	12.0
69	27.1	152	14.1	265	5.7
74	5.3	153	9.3	452	11.3
75	8.7	158	6.6	472	7.0
76	18.4	168	5.7	530	54.6
77	62.1	169	21.2	531	19.2
78	22.6	170	5.2	547	5.0
81	7.7	177	7.1	549	90.1
89	5.3	178	13.4	550	56.7
90	14.4	179	24.4	551	14.3
91	5.2				

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE IX

SUMMARY OF REACTIONS OF
4-(HEXAFLUORO-2-HYDROXY-ISOPROPYL)ANILINE
WITH PHOSPHORUS PENTABROMIDE

Test No.	Reaction Conditions ^a		Product g.	Remarks
	Temp, °C	Time, hr		
1	123-124	4	1.49	mainly ring (both mono and di-) bromination, some alcohol substitution
2	25-124	2.25	0.88	~ 25% alcohol substitution, ring poly-bromination
	124-136	18		
3	25-124	3.75	0.90	alcohol substitution and ring poly-bromination
4	25	12	0.24	ring bromination

a) In each test, 1 g of the alcohol was treated with an equimolar quantity of phosphorus pentabromide in the absence of solvent.

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TABLE X
FRIEDEL-CRAFTS REACTIONS OF ANILINE AND/OR ANILINE HYDROCHLORIDE
AND 4-(HEXAFLUORO-2-HYDROXY-ISOPROPYL) ANILINE

Test No. ^a	Mole Ratio ^b				Temp °C	Time hr	Crude Product g	Yield ^c	
	Alcohol	Aniline	Aniline Hydro- chloride	AlCl ₃				H ₂ NΦC(CF ₃) ₂ ΦNH ₂ %	(%)
1	1	4	-	1	185-196	70	0.9	16	(25)
2	1	4	-	1	185-196	70	0.8	19	(33)
3	1	2	-	1	183-198	70	0.6	26	(53)
4	1	4	-	0.5	183-197	70	1.52	34	(29)
5	1	2	-	1	154-160	24	0.61	25	(53)
6	1	2	-	1	78-80	30	0.87	none ^d	
7	1	1	-	0.5	150-154	17	0.66	8	(16)
8	1	2	-	0.5	160-165	24	1.24	8	(8)
9	1	1	-	1	165	66	0.9	42	(62)
10	1	1.5	-	1.5	160-163	63	0.6	27	(62)
11	1	2	-	1	148-150	24	0.8	24	(39)
12	1	-	1	1	155-160	66	0.9	25 ^a	(38)
12A	1 (2.0)	7	1.5	-	175-180	117	5.1	T ^f	(T)
13	1 (10.24)	1	-	1	165-170	50	2.63 ^g	20	(100)
14	1 (16.0)	1.5	-	1.5	150-160	87	3.99 ^g	19.5	(100)
15	1 (10.0)	2	1	1.5	160-175	48	5.30	20	(49)
16	1 (50.0)	1	1	1	156-165	64	9.82 ^g	15	(100)
17	1 (50.0)	1	-	1	160-170	88	11.61 ^g	18	(100)

a) In Test Nos. 1-5 and 12A, aniline was added to the other reagents at room temperature; in all the other tests, with the exceptions of experiments 15, 16, and 17, this addition was carried out with ice-cooling. In Test No. 15 the fluorinated alcohol, aniline hydrochloride, and aluminum trichloride were stirred and heated to 100°C; aniline was then added slowly to the brown reaction mixture. In Test No. 16 to the mixture of aniline and aniline hydrochloride at 30°C was added slowly (45 min) aluminum trichloride; this was followed by the introduction of the fluorinated alcohol. In Test No. 17 aluminum trichloride was added to the aniline-fluorinated alcohol mixture.

b) In Test Nos. 1-12, a 1 g portion of the alcohol was reacted in the denoted mole ratio with aniline and aluminum chloride; in all the other tests the quantity of alcohol used is given in parentheses.

c) The yield has been determined by gas chromatography on the crude product and is based on the alcohol used; the value in the brackets corresponds to the percent of the fluorinated di-aniline in the isolated solid.

d) The isolated solid was composed of starting material only.

e) If one bases the yield on aniline hydrochloride employed and allows for the recovered sublimed aniline hydrochloride, the actual yield becomes 44%.

f) Trace.

g) This is the weight of pure crystallized 4-(hexafluoro-2-hydroxy-isopropyl) aniline.